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وزارة التعليم العالي والبحث العلمي
جامعة بابل
كلية هندسة المواد
قسم هندسة البوليمر والصناعات البتروكيمياوية

# تحضير وتشخيص البولي استر عالي التفرع المصنع والممزوج مع البولي بروبيلين للتطبيقات الصناعية

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# Preparation and Characterization of Synthesised Hyperbranched Polyester Blended with Polypropylene for Industrial Applications

A Dissertation
Submitted to the College of Materials Engineering /
University of Babylon as a Partial Fulfillment of the
Requirements for the Doctorate Degree of Philosophy in
Materials Engineering / Polymer

**By**

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2023 AD 1444 AH

بسم الله الرحمن الرحيم

قَالُواْ سُبْحَانَكَ لاَ عِلْمَ
لَنَا إِلاَّ مَا عَلَّمْتَنَا إِنَّكَ
أَنتَ الْعَلِيمُ الْحَكِيمُ

صدق الله العلي العظيم

سورة البقرة (الآية ٣٢ )

# Examination Committee Certification

We certify that we have read this thesis entitled "**Preparation and Characterization of Synthesised Hyperbranched Polyester Blended with Polypropylene for Industrial Applications**" and as an Examination Committee examined the student (**Nabeel Hasan Hameed Hussein**) on its contents and that, in our opinion, it meets the standard of a dissertation and is adequate for the award of the Degree of Doctorate of Philosophy in Materials Engineering/ Polymer.

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# List of Abbreviations

| **Abbreviation** | **Meaning** |
|---|---|
| AA’or BB’ | A Monomer have a Difference in the Activity of Functional Groups |
| ABS | Acrylonitrile Butadiene Styrene |
| AHBP<br>AHBPE | Aromatic Hyperbranched Polymers<br>Aromatic Hyperbranched Polyester |
| $A_n$ | A Monomer with n of Functional Groups |
| ASTM D | American Society for Testing Materials |
| BHBA | Beta-Hydroxybutyric Acid |
| $B_n$ | A Monomer with n of Functional Groups |
| CMM | A Method for Polymerization Using More than Two Monomers |
| DB | Degree of Branching |
| DGEBA | Diglycidyl Ether Bisphenol A |
| DMA | Dynamic Mechanical Analysis |
| DMM | A Method for Polymerization Using Two Monomers |
| DMPA | Dimethylol Propionic Acid |
| DMSO-*d6* | Dimethyl Sulfoxide-*d6* (Deuterated) |
| EHBPE | Epoxy-terminated Hyperbranched Polyseter |
| FTIR | Fourier Transfer Infrared Spectroscopy |
| GO | Graphene Oxide |
| GPC | Gel Permeation Chromatography |
| HBMs | Hyperbranched Macromolecules |
| HBPAM | Hyperbranched Poly(Acryl Amide) |
| HBPAMAM | Hyperbranched Poly(Amidoamine) |
| HBPEA | Hyperbranched Polyester Amide |
| HBPE-AD | Hyperbranched Polyester with Adipic Acid |

| | |
|---|---|
| HBPEI | Hyperbranched Poly(Ethylene Imine) |
| HBPE-MA | Hyperbranched Polyester with Maleic Acid |
| HBPEO | Hyperbranched Poly(Ether Polyols)<br>Hyperbranched Polyethylene Oxide |
| HBPE-PA | Hyperbranched Polyester with Phthalic Anhydride |
| HBPEs | Hyperbranched Polyester |
| HBPET | Hyperbranched Polyethylene Terephthalate |
| HBPE-TA | Hyperbranched Polyester with Tartaric Acid |
| HBPG | Hyperbranched Polyglycerol |
| HBPPS | Hyperbranched Poly(Phenylene Sulphide) |
| HBPs | Hyperbranched Polymers |
| HBPUs | Hyperbranched Polyurethane |
| HBUA | Hyperbranched Polyurethane Acrylate |
| HIPS | High Impact Polystyrene |
| KBr | Potassium bromide |
| LDPE-g- MA | Maleic Anhydride-Grafted-Polyethylene |
| $M_n$ | Number Average Molecular Weight |
| MW | Molecular Weight |
| $M_w$ | Weight Average Molecular Weight |
| MWCNT | Multi-wall Carbon Nanotube |
| $M_z$, $M_{z+1}$ | Size Average Molecular Weight |
| NMR | Nuclear Magnetic Resonance |
| PA | Poly(Maleic Anhydride-Alt-1-Octadecene) |
| P-COOH | Polymer has Carboxylic Group |
| PDI | Polydispersity Index |
| PHBV | Poly(Hydroxybutyrate-Co-Hydroxyvalerate) |
| P-OAc | Polymer has Acetoxy Group |
| P-OH | Polymer has Hydroxyl Group |
| PPAs | Processing Aid Additives |

| | |
|---|---|
| PP-g- MA | Maleic Anhydride-Grafted-Polypropylene |
| PUs | Polyurethane |
| PVC | Polyvinylchloride |
| rPP | Recycled Polypropylene |
| SAXS | Small Angle X-Ray Scattering |
| SEM | Scanning Electron Microscope |
| SMM | A Method for Polymerization Using One Monomer |
| TEM | Transmission Electron Microscopes |
| THF | Tetrahydrofuran |
| TPS | Thermoplastic Starch |
| VPP | Virgin Polypropylene |
| XRD | X-Ray Diffraction |

# Abstract

Most polymers suffer from certain problems during processing such as energy consumption and low flow rate. In addition, the polymeric products do not degrade easily in natural environment after being used. To overcome these problems polymeric material can be blended with other polymers that have the ability to improve the processability and biodegradation.

This study includes the preparation of four novel hyperbranched polyester polymers (HBPEs), by the preparation of the starting material B3 monomer and then mixing it with the four other types of materials as A2 monomer, using the polycondensation polymerization method for A2 + B3 type monomers. The prepared hyperbranched polyester polymers (HBPs) were added in different weight proportions (5%, 10%, and 20%) to both the virgin polypropylene (VPP) and the recycled polypropylene (rPP) polymer using a twin screw extruder. The mechanical, thermal, morphological, and rheological properties as well as the biodegradation in the soil environment of the prepared blends have been studied.

Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), and Gel permeation chromatography (GPC) were used for the characterization of the prepared hyperbranched polyester polymers (HBPEs).

In order to study the influence of hyperbranched polyester polymers (HBPEs) on the polypropylene (PP) properties, several tests were performed, such as Fourier transform infrared (FTIR), tensile strength, impact strength, hardness, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), melt flow rate (MFR), contact angle, and biodegradation in soil.

Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) results for the prepared hyperbranched polyester polymers (HBPEs) showed the presence of different functional groups in the same molecule, such as OH, C=N, and C=O. In addition, nuclear magnetic resonance (NMR) was used to predict the chemical structure of the starting material B3 monomer and the four prepared hyperbranched polyester polymers (HBPEs). Gel permeation chromatography (GPC) results show that three of the prepared HBPEs (HBPE-TA, HBPE-AD, and HBPE-PA) have narrow molecular weight and polydispersity index. While the fourth polymer (HBPE-MA) has higher molecular weight and polydispersity index.

FTIR results for the polypropylene (PP) and its blends (VPP/HBPEs, rPP/HBPEs) show that the absence of chemical interaction between the two polymers, only physical interaction with slight shifting in band values.

Tensile results show that the tensile strength, elastic modulus, and elongation at break for both virgin polypropylene (VPP) and recycled polypropylene (rPP) decreased with the increase of the four prepared hyperbranched polyester polymers (HBPEs) addition. While, impact strength has improved for the polymeric blends with the increase of hyperbranched polyester content, also it is found that the best impact strength occurs at 10% of HBPEs for all blends. While there is a slight improvement in the shore D hardness as the HBPEs added for the blends.

Scanning electron microscope (SEM) results show that there is a good dispersion of HBPs in PP at low content 5% and an agglomeration of HBPEs at higher content (10%, and 20%).

Differential scanning calorimetry (DSC) results show that the melting temperature ($T_m$) improved slightly for both VPP and rPP blends. While, the crystallization temperature ($T_c$) increases for VPP blends and decreases for rPP blends. In addition, the degree of crystallinity $X_c$ decreased for both blends. Thermogravimetric analysis (TGA) results show that two of the prepared polymers (HBPE-TA and HBPE-AD) have two stages of thermal degradation, while HBPE-MA and HBPE-PA have three stage of thermal degradation. In addition, it is found that the addition of HBPEs to PP (VPP, rPP) has improved it is thermal stability.

Melt flow rate (MFR) results show that the addition of HBPs has increased the MFR for PP (VPP and rPP) blends. Also, it is found that the MFR has the highest improvement at 10% of HBPEs. In addition, it is found that viscosity decreased for the blends and the shear rate increased. This is an indication that the HBPEs work as a processing aid additive by increasing the shear thinning behavior.

Contact angle results showed that the addition of HBPEs to PP (VPP and rPP) has improved it is hydrophilic nature by the decrease of contact angle. Also, it is found that the contact angle for rPP blends is better than VPP blends. In addition, it is found that the best contact angle results for HBPE-TA polymer addition.

The biodegradation in soil results show that the weight loss increased as the amount of HBPEs increased in PP blends (VPP/HBPEs and rPP/HBPEs). In addition, it is found that the rate of weight loss for rPP blends is higher than VPP blends; also, the higher weight loss is for HBPE-TA.

# الخلاصة

تعاني معظم البوليمرات من مشاكل عديدة أثناء عمليات التصنيع مثل استهلاك الطاقة وانخفاض معدل التدفق. بالإضافة إلى ذلك، لا تتحلل المنتجات البوليمرية بسهولة في البيئة الطبيعية بعد استخدامها. للتغلب على هذه المشاكل، يمكن مزج مادة بوليمرية مع بوليمرات آخرى لديها القدرة على تحسين قابلية التصنيع والتحلل البيولوجي.

تتضمن هذه الدراسة تحضير أربعة أنواع جديدة من بوليمر البولي استر عالي التفرع (HBPEs) باستخدام طريقة البلمرة بالتكثيف لمونومرات من نوع A2 + B3. تمت إضافة البوليمرات المحضرة (HBPEs) بنسب وزنية مختلفة (٥٪، ١٠٪، ٢٠٪) لكل من البولي بروبيلين النقي (VPP) والبولي بروبيلين المعاد تدويره (rPP) باستخدام ماكنة البثق ثنائية اللولب. تمت دراسة الخواص الميكانيكية والحرارية والمورفولوجية والانسيابية وكذلك التحلل الحيوي في بيئة التربة للخلطات المحضرة.

تم استخدام تحليل الأشعة تحت الحمراء (FTIR) والرنين النووي المغناطيسي (NMR) وقياس الوزن الجزيئي بتقنية (GPC) لتوصيف البوليمرات المحضرة (HBPEs).

من أجل دراسة تأثير بوليمرات البولي استر عالي التفرع (HBPEs) على خصائص البولي بروبلين (PP)، تم إجراء العديد من الاختبارات، كتحليل الأشعة تحت الحمراء (FTIR)، ومقاومة الشد، ومقاومة الصدمة، والصلادة، والمسح بالمجهري الإلكتروني (SEM)، التحليل الحراري التفاضلي (DSC)، والتحليل الحراري الوزني (TGA)، وقياس معدل تدفق المنصهر (MFR)، وقياس زاوية التلامس، والتحلل البيولوجي في التربة.

أظهرت نتائج تحليل الأشعة تحت الحمراء (FTIR) والرنين المغناطيسي النووي (NMR) لبوليمرات البوليستر عالية التفرع (HBPEs) وجود مجموعات وظيفية مختلفة في نفس الجزيء، مثل OH ، C = N ، و C = O. بالإضافة إلى ذلك، تم استخدام الرنين المغناطيسي النووي (NMR) للتنبؤ بالتركيب الكيميائي لمونومر المادة البادئة B3 ولبوليمرات البولي استر عالي التفرع الأربعة التي تم تحضيرها (HBPEs). أظهرت نتائج قياس الوزن الجزيئي بتقنية (GPC) أن ثلاثة من البوليمرات المحضرة HBPEs (HBPE-TA و HBEP-AD و HBPE-PA) لها وزن جزيئي ومؤشر التشتت المتعدد متقارب. في حين أن البوليمر الرابع (HBPE-MA) له وزن جزيئي ومعامل تشتت متعدد أعلى.

أظهرت نتائج تحليل الأشعة تحت الحمراء FTIR للبولي بروبيلين (PP) وخلطاته ( VPP / HBPEs، rPP / HBPEs) عدم وجود تفاعل كيميائي بين البوليمرين ، فقط تفاعل فيزيائي مع حدوث تغير إزاحة قليلة في قيم الاواصر للبولي بروبيلين PP.

أظهرت نتائج الشد أن مقاومة الشد، ومعامل المرونة، والاستطالة عند الكسر لكل من البولي بروبلين النقي (VPP) والبولي بروبيلين المعاد تدويره (rPP) قد انخفضت مع زيادة نسبة بوليمرات البوليستر الاربعة عالية التفرع (HBPEs) التي تم تحضيرها. بينما، تحسنت مقاومة الصدمة للخلطات البوليمرية مع زيادة نسبة بوليمر البوليستر عالي التفرع، وجد أيضًا أن أفضل مقاومة للصدمة كانت عند نسبة ١٠٪ من HBPEs لكل الخلائط. في حين أن هناك تحسنًا طفيفًا في الصلادة عند إضافة HBPEs للخلطات.

أظهرت نتائج الفحص بالمجهر الإلكتروني (SEM) أن هناك تشتتًا جيدًا لـ HBPEs في PPعندما تكون نسبة HBP ٥ ٪ وحدوث تكتل بسيط عندما تكون نسبة HBPs أعلى (١٠ ٪، و ٢٠ ٪).

أظهرت نتائج قياس التحليل الحراري التفاضلي (DSC) أن درجة حرارة الانصهار (Tm) تحسنت قليلاً لكل من مزيج VPP و rPP بينما زادت درجة حرارة التبلور (Tc) لخلطات VPP وانخفضت لخلطات rPP بالإضافة إلى ذلك، وجد ان درجة التبلور *Xc* لكلا الخليطين قد انخفضت. أظهرت نتائج التحليل الوزني الحراري (TGA) أن اثنين من البوليمرات التي تم تحضيرها (HBPE-TAو HBPE-AD) لهما مرحلتان من التحلل الحراري، بينما كلا من (HBPE-MAو HBPE-PA) لها ثلاث مراحل من التحلل الحراري. أيضًا، وجد أن إضافة HBPEs إلى PP (VPP وrPP) قد حسن الثباتية الحرارية للخلائط المحضرة.

أظهرت نتائج معدل تدفق المنصهر (MFR) أن إضافة HBPEs أدت إلى زيادة MFR لخلطات PP (VPP وrPP). أيضًا، وجد أن MFR كان يمتلك أعلى قيمة عند نسبة ١٠ ٪ منHBPEs. بالإضافة إلى ذلك، وجد أن اللزوجة تنخفض للخلطات ويزداد معدل القص هذا مؤشر على أن HBPs تعمل كمادة مضافة محسنة للتصنيع عن طريق زيادة سلوكshear thinning .

أظهرت نتائج قياس زاوية التلامس أن إضافة HBPEs الى PP (VPP وrPP) قد حسن طبيعته المحبة للماء عن طريق تقليل زاوية التلامس. أيضًا، وجد أن زاوية التلامس لخلطات rPP أفضل من خلطاتVPP . بالإضافة إلى ذلك، وجد أن أفضل نتائج زاوية التلامس كانت عند إضافة بوليمرHBPE-TA.

أظهرت نتائج التحلل البيولوجي في التربة أن فقدان الوزن قد زاد مع زيادة نسبة HBPEs في خلائط PP (VPP / HBPEs و rPP / HBPEs). بالإضافة إلى ذلك، وجد أن معدل فقدان الوزن لخلطات rPP كان أعلى من خلطات VPP، كما أن فقدان الوزن الأعلى كان لـ HBPE-TA.

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Firstly, all the thank and praise be to **ALLAH** in enabling me to achieve this study.

*** *** ***

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I do not know how can I reach my big respect and thank to my family for their care, patience and encouragement throughout the study period," I am really indebted to them ".

*** *** ***

Finally, I do not forget to present, big thanks to all who participated in helping and assistance me during the period of the study as well as the experimental work.

**NABEEL/2023**

# Dedication

To the One whose throne is in the sky…To the One whom we praise and thank… **Allah**

To the Messenger of Allah…**Mohammed** (peace and blessings of Allah be upon him and his progeny)

To the nymph ... **Fatima El Zahraa** (peace be upon her)

To **Ali Al Murtadha** (peace be upon him)

To the awaited **Mahdi** (calf God reappearance)

To **my parents** for their prayers, to the person who helped me to march my whole life … my brother, to my brother and sisters, thank you all for constant support and interest

# Supervisors Certification

We certify that this thesis, entitled **“Preparation and Characterization of Synthesised Hyperbranched Polyester Blended with Polypropylene for Industrial Applications"** was prepared by **"Nabeel Hasan Hameed Hussein"** under our supervision at the University of Babylon/ College of Materials Engineering/ Department of Polymer Engineering and Petrochemical Industries, in partial fulfillment of the requirements for the degree of Doctorate of Philosophy in Materials Engineering / Polymer.

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**Chapter Three: Experimental Part**

## 1.1. Introduction

In the last century, new materials have contributed immensely to industrial and technological development. The list of materials includes a large number of metals, alloys, composites ceramics and polymers. Out of these, polymers have made an important contribution to this developmental process and have established themselves as an important class of engineering materials[1]. The structure of polymers consists of a great number of repeating units and high molecular mass compounds. These days, polymer materials are very important in human life that entity of human life depends on these polymers[2].

Polymers offer a wide variety of properties that make them ideal materials for a broad range of applications, from polyethylene in garbage and sandwich bags to poly (p-phenylene terephthalamide) in bulletproof jackets [3]. Polyolefins have received significant attention recently because of their combination of flexibility, toughness, excellent barrier properties, easy manufacturing, and good chemical resistance; this has made them excellent materials for various packaging applications, especially in food packaging[4,5] such as polypropylene (PP) and polyethylene (PE) which are extensively used in commodity and packaging applications. The use of PP is continuously increasing in the plastic packaging industries due to their low cost, lightweight, high mechanical strength, water resistance, and good barrier properties [6].

Compared to today’s global plastic production, it has been predicted that the volume of plastic packaging will be increased by twofold and threefold in 2030 and 2050, respectively [7]. Until now, non-biodegradable polymers, i.e., polyethylene (PE), polypropylene (PP), ethylene vinyl alcohol, poly (ethylene terephthalate), polystyrene, expanded polystyrene, polyamides, polyurethane, and poly (vinyl chloride), have dominated in the packaging application because of their good physical and mechanical properties. These polymers are characteristically inert and resistant to microbial attacks; therefore, it remains in the environment for very long time and create huge waste management problem [8].

The food packaging plastic waste is often contaminated with food products, which becomes a limitation of recycling and therefore results in large amounts of post-consumer plastic packaging waste [9],10]. Also, the landfilling of postconsumer plastic waste continuously threatens the environment and ecological system because plastic debris has been found in rivers, lakes, marine, and coastal environments [11–16].

In order to reduce the environmental and ecological pollution by post-consumer plastic waste, environmentally friendly polymeric materials should be utilized for possible short-lifespan applications. Biodegradable polymeric materials are suitable candidates for disposable material applications such as packaging, consumer goods, and hygiene products. However, the biodegradable polymers are restricted for some applications because of their relatively high cost and insufficient mechanical and thermomechanical properties compared to certain non-biodegradable commodity polymers [17].

Therefore, developing biodegradable polymer blends with satisfactory properties can overcome these limitations. The main challenges with polymer melt blending are as follows: to improve the adhesion between the blended components, reduce the interfacial tension between the components, and to generate limited inclusion phase size [18].

Also, during the processing of polymers manufacturers specifically wish to increase the flow rate, reduce energy cost, and minimize the occurrence of extrudate irregularities. Polymer processing aids (PPAs) have long been used to efficiently eliminate the irregularities during processing that causes problems in products, thus significantly enhancing the upper limiting production rate [19]. A number of chemicals, including polymers, have been used as processing aids in an attempt to minimize surface roughness in polyolefin processing. Hyperbranched polymers (HBP) have received significant interest as PPAs, owing to their unique dendrimerlike branched structure with lack of chain entanglements and the resulting dramatically reduced melt viscosity [20].

## 1.2. Aims of the Study

This work aims to prepare and characterize the effect of a synthesized novel hyperbranched polyester polymer (HBPEs) on the biodegradation properties of polypropylene (PP) for industrial applications.

## 1.3. Thesis Objectives

The following study tasks were defined in order to accomplish the objectives, which are as follows:

1. For the synthesis of the hyperbranched polyester polymers (HBPEs), the starting material (B3) will be prepared using a mixture of urea and malonic acid in the presence of sodium and ethanol.
2. To insure that the starting material is prepared, an FTIR test is carried out.
3. For the synthesis of hyperbranched polymers, the starting material (B3 monomer) will be melt mixed with A2 monomers (tartaric acid TA, adipic acid AD, maleic acid MA, and phthalic anhydride PA) at a ratio of 1:1.5 according to the A2+B3 polycondensation methodology.
4. FTIR, $^1$H-NMR, and GPC will be employed to characterize the prepared hyperbranched polyester polymers (HBPEs).
5. The prepared hyperbranched polyester polymers will be melt blended with polypropylene (virgin polypropylene VPP and recycled polypropylene rPP) in different weight ratios (5%, 10%, and 20%) using a twin-screw extruder.
6. The effect of the prepared HBPEs on the mechanical, morphological, thermal, rheological, and biological properties of PP will be investigated.

## 2.1. Introduction

About 50 years after the introduction of the ‘macromolecular hypothesis’ by Staudinger, the entire field of polymer science could be described as consisting of only two major architectural classes: (I) linear topologies as found in thermoplastics and (II) crosslinked architectures as found in thermosets [21]. Now, at the beginning of the 21st century, four major domains can be defined and distinguished in accordance with their properties and architecture as shown by Figure (2-1):

I. linear, random coil thermoplastics such as plexiglass or nylon;
II. crosslinked thermosets such as rubbers or epoxies;
III. branched systems based on long chain branching in polyolefins such as low-density poly(ethylene) and other related branched topologies;
IV. dendritic polymers consisting of three subsets that are based on the degree of structural control, namely (a) random hyperbranched polymers; (b) dendrigraft polymers; and (c) dendrimers.

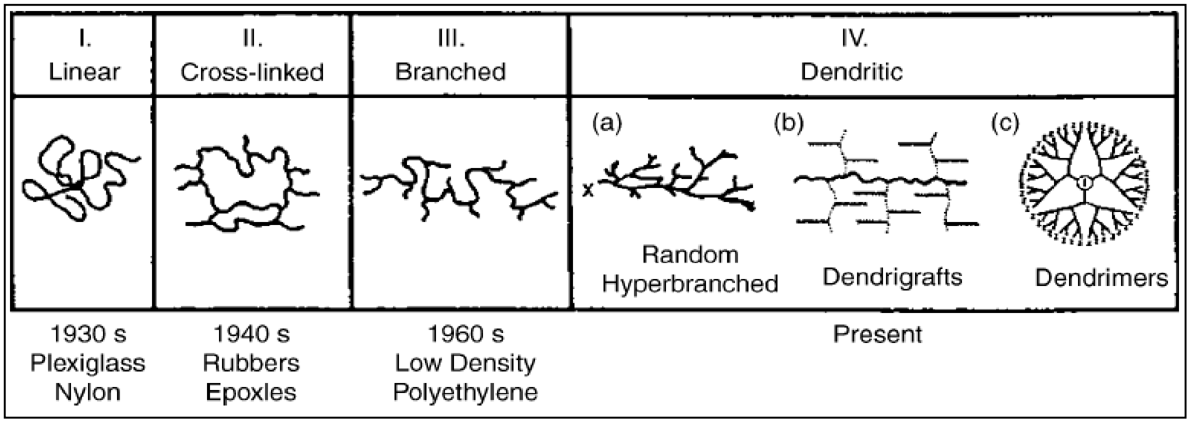


**Figure (2-1): The major classes of macromolecular architectures** [21].

Dendritic polymers refer to highly branched macromolecules with a three-dimensional architecture. Recognized as the fourth major class of polymers, after the more traditional linear, branched and cross-linked macromolecules, the family of dendritic polymers is divided as follows: (a) dendrons and dendrimers like Poly(amidoamine), (b) linear-dendritic hybrids like Poly(ethylene glycol)-Polyester for scaffold, (c) dendronized polymers like poly(phenylene acetylene), (d) dendrigrafts and dendrimer-like polymers, (e) hyperbranched polymers, (f) hyperbranched polymer brushes like poly(ethylene imine), (g) hyperbranched polymer-grafted linear macromolecules and (h) hypergrafts or hyperbranched polymer-like macromolecules, as depicted in Figure (2-2) [22].

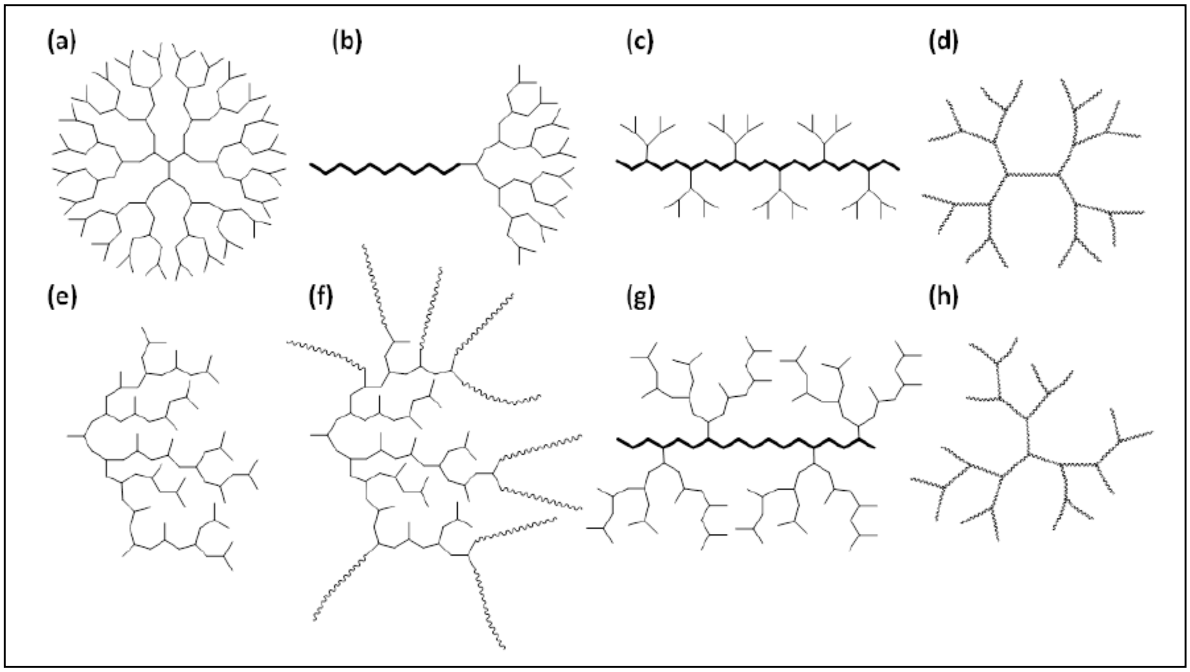


**Figure (2-2): The different structures of dendritic polymers** [22]**.**

Hyperbranched polymers (HBP) have drawn much attention and obtained intensive research activities from both industry and academia in the last three decades [23–26]. Hyperbranched polymers are highly branched macromolecules with three-dimensional dentritic structure. They have received considerable attention and have been intensively studied over last 20 years due to their unusual properties, such as low viscosity, high solubility and reactivity, and good compatibility with other materials. In addition, terminal groups of hyperbranched polymers can be modified with various functional groups to satisfy numerous possible demands. Potential applications of hyperbranched polymers in fields of coatings [27], rheological modifications [28], drug delivery [29], membranes [30], supermolecular chemistry [31] and nanomaterials [32], have been reported now. Moreover, interest in hyperbranched polymers is growing rapidly according to the increasing number of publications as seen in Figure (2-3).

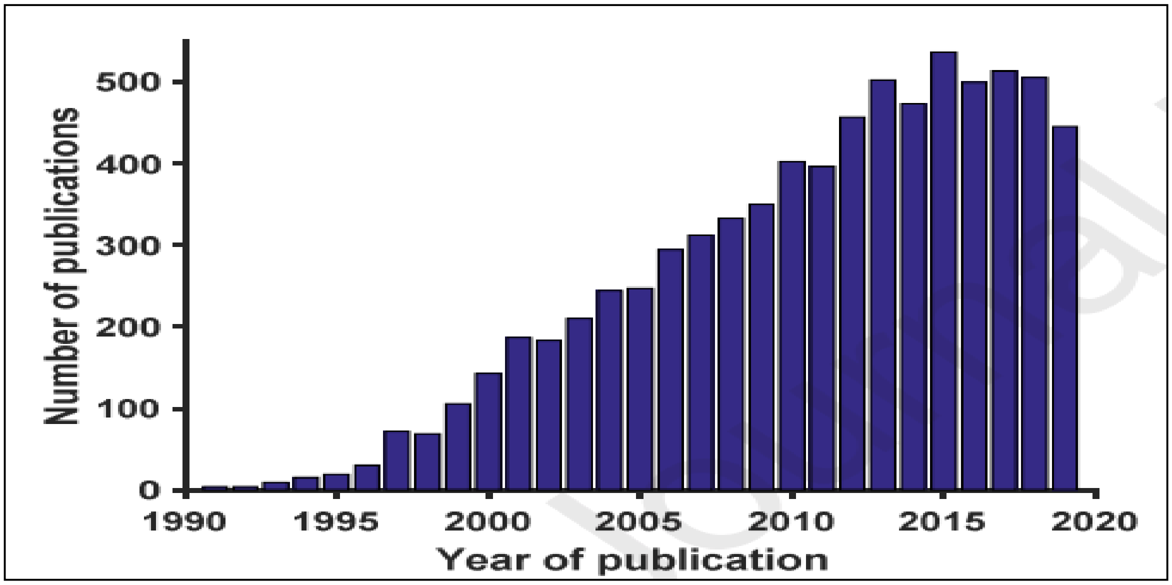


**Figure (2-3): Publication numbers during 1990 and 2020 with the topic "hyperbranched polymers" searched by ISI Web of Science**[33].

Hyperbranched polyesters (HBPEs) are an important class of hyperbranched polymers, and the availability of inexpensive raw materials has prompted many research groups to investigate HBPEs in details. The aliphatic HBPEs based on dimethylol propionic acid have been commercialized by Perstorp under the trade name Boltorn® and excessively studied. Unlike aliphatic HBPEs, aromatic HBPEs have high melt point and glass transition temperature (Tg) owing to their high aromaticity and stiffness. This fact might be one of the reasons that no product has been commercialized based on those aromatic monomers, whereas the aliphatic HBPEs have a much lower Tg and less brittleness and can be specially designed for resin and coating formulations [34]. Generally, aromatic HBPEs cannot be directly applied, but the properties of HBPEs can be easily tailored by changing the nature of end groups thus leading to many application areas. Aromatic HBPEs and their derivatives have been used in blends, coatings, sensors, non-linear optics, and other fields.

## 2.2. History of Hyperbranched Polymers

The history of hyperbranched polymers can be dated to the end of 19th century, when Berzelius reported the formation of a resin from tartaric acid ($A_2B_2$ monomer) and glycerol ($B_3$ monomer) [35]. As shown in Table 1, following the reaction between phthalic anhydride (latent $A_2$ monomer) or phthalic acid ($A_2$ monomer) and glycerol ($B_3$ monomer) reported by Smith in 1901, Kienle et al. [36] studied the reaction further, and the obtained results and conclusions are still used today. For example, Kienle et al. [37] found that the specific viscosity of samples prepared from phthalic anhydride and glycerol was lower than that of numerous synthetic linear polymers, which were given by Standinger. In 1909, Baekeland [38] obtained crosslinked phenolic polymers by the polymerization of soluble resole precursors, which were made from formaldehyde and phenol.

**Table (2-1): The history of hyperbranched polymers**[39, 40].

| Materials | Year | Author |
|---|---|---|
| Tartaric acid + glycerol | Before 1900 | Berzelius |
| Phthalic anhydride + glycerol | 1901 | Smith |
| Formaldehyde + phenolic | 1909 | Baekeland |

| | | |
|---|---|---|
| Phthalic anhydride + glycerol | 1929-1939 | Kienle |
| Molecular size distribution in theory | 1941 | Flory |
| $AB_n$ polymerization in theory | 1952 | Flory |
| $AB_2$ +AB copolymerization | 1982 | Kricheldorf |
| $AB_2$ homopolymerization | 1988 | Kim |

In the 1940s, Flory [41, 42] used statistical mechanics to calculate the molecular-weight distribution of linear polymers and extended later his calculation to three-dimensional polymers with tri- or tetrafunctional branching units in the state of gelation, and developed the ‘degree of branching’ and ‘highly branched species’ concepts. In 1952, when Flory wrote his famous book Principles of Polymer Chemistry, he theorized that highly branched polymers could be synthesized without gelation by polycondensation of multifunctional monomers, such as a monomer containing one A functional group and two or more B functional ones capable of reacting with A ($AB_n$ monomer, $n \geq 2$). However, Flory did not feel it was worthwhile pursuing this line of research at that time, because he considered these polymers would provide materials with poor mechanical strength [43].

About 30 years later, the interest in hyperbranched polymers arose again. In 1982, Kricheldorf et al. [44] obtained highly branched polyesters by copolymerization of $AB_2$ and AB type monomers. The name ‘hyperbranched polymers’ was first given to $AB_2$ polymers by Kim and Webster in 1988 [45], when they intentionally synthesized soluble hyperbranched polyphenylene. Ever since, a variety of hyperbranched polymers has been prepared and the interest in hyperbranched polymers increase extremely.

## 2.3. Synthesis Methodology of Hyperbranched Polymers

Now, the synthetic approach used to prepare hyperbranched polymers is broadened with not only the typical Flory approach of $AB_n$ monomers but also variations of some new synthetic techniques. The synthetic techniques can be divided into two groups according to the type of monomers. The first group contains techniques of the single-monomer methodology (SMM), in which hyperbranched polymers are synthesized by polymerization of an $AB_n$ or a latent $AB_n$ monomer. According to the reaction mechanism, the SMM includes four specific approaches: (1) polycondensation of $AB_n$ monomers; (2) self-condensing vinyl polymerization (SCVP) [46]; (3) self-condensing ring-opening polymerization (SCROP) [47]; (4) proton-transfer polymerization (PTP) [48]. The second group contains methods of the double monomer methodology (DMM), in which direct polymerization of two types of monomers or a monomer pair forms hyperbranched polymers. Generally, the DMM includes eight specific approaches: (1) $A_2 + B_3$ approach; (2) $A_2 + B_2 + BB_2$ 'approach; (3) $A_2 + BB_2$ 'approach; (4) $A_2 + CB_n$ approach; (5) $AB + CD_n$ approach; (6) $A^* + B_n$ approach; (7) $AA^* + B_2$ approach; (8) $A^* + CB_2$ approach. The synthesis approaches to hyperbranched polymers are listed in Table (2-2).

**Table (2-2): Synthesis techniques and methods to hyperbranched polymers** [39, 40].

| The Technique | Method | Author | year |
|---|---|---|---|
| SMM | Polycondensation of $AB_n$ | Kim/Webster | 1988 |
| | SCVP | Frechet | 1995 |
| | SCROP | Suzuki/Penczek | 1992/1999 |

| | | | |
|---|---|---|---|
| | PTP | Frechet | 1999 |
| DMM<br>$A_2 + B_3$ | Polycondensation of $A_2$+$B_3$ monomers | Jikei/Kakimoto | 1999 |
| | | Emrick/Frechet | 1999 |
| CMM | $A_2$ +$BB_2$’ | Yan/Gao | 2000 |
| | $A_2$ +$B_2$ +$BB_2$’ | Gao/Yan | 2000 |
| | $A_2$ +$CB_n$ | Gao/Yan | 2001 |
| | AB + $CD_n$ | Gao/Yan | 2001 |
| | A* + $B_n$ | Gao/Yan | 2001 |
| | AA*+$B_2$ | Gao/Yan | 2001 |
| | A* + $CB_2$ | DSM research | 2000 |
| MCM | A-A+B-B+C-C | | After 2001 |

### 2.3.1. Single Monomer Methodology (SMM)

#### 2.3.1.1. Polycondensation of $AB_2$ Monomers

The standard synthetic approach to hyperbranched polymers, based on the work of Flory [42] is polymerization of $AB_2$ (or $AB_n$) monomers possessing complementary A and B functionalities (hydroxyl and carboxylic acid groups). It is a typical feature of step growth reactions of this type that each polyfunctional oligomer present in the reaction mixture may couple with any other species in the absence of crosslinking. Polycondensation of $AB_2$ monomers permits no control over the polymerization reaction, which limits the molecular weight and polydispersity. However, it is the oldest and most widely used method for the preparation of the range of hyper branched polymers. $AB_3$, $AB_4$ and $AB_6$ monomers are also used to synthesize hyperbranched polymers while controlling the branching pattern [49]. Even though a C-C coupling reaction was used for one of the first published $AB_2$ type polymers. Two $AB_2$ monomers, 3,5-dihydroxybenzoic acid, and 5-

hydroxyisophthalic acid, have most frequently been used as starting materials to prepared aromatic HBPs. However, modifications of these are necessary because their thermal stabilities are lower than the required reaction temperature for direct esterification [50]. Many polymers could be synthesized using this methodology such as polyesters, polycarbonates, polyamides, polyethers, poly (ether ketone), polyurethanes, and polycarbosilanes [51]. Flory state that such type of polymer will have a highly branched structure and a multitude of end groups, which contains one focal group (A group), and dendritic, linear and terminal units as shown in Figure (2-4)[40].

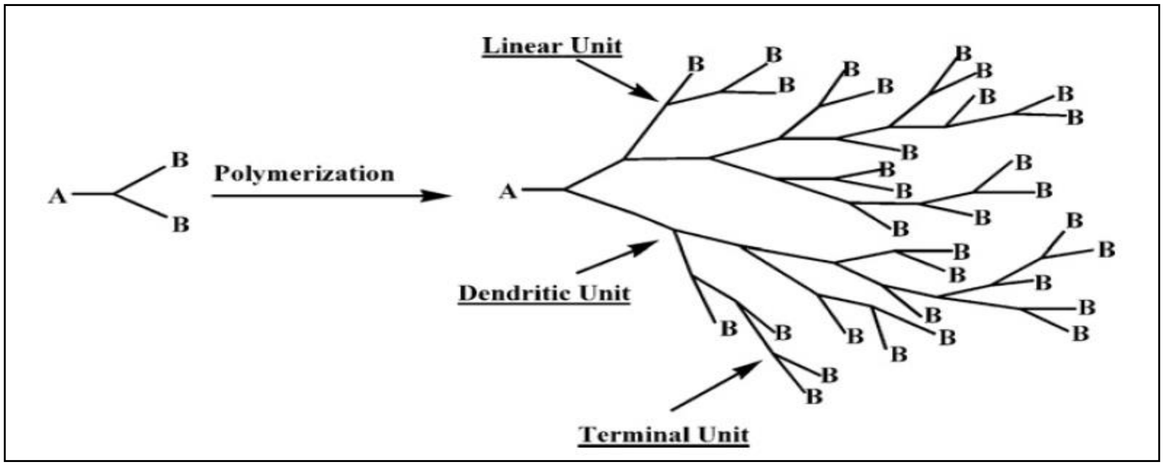


**Figure (2-4): architecture of hyperbranched polymers from AB$_2$ monomers**[40].

### 2.3.1.2. Self-Condensing Vinyl Polymerization (SCVP)

Self-condensing vinyl polymerization (SCVP) was invented as an alternative concept to AB$_2$ polycondensation, and is applied to AB vinyl monomers. Vinyl monomers allow two modes of propagation for growth: (a) polymerization of the double bond (chain growth): and b) condensation of the initiating group with the double bond (step growth) [52]. The major advantages of SCVP are faster reactions leading to lower process times in comparison with the polycondensation method. In most examples, SCVP is used in combination with the living/controlled polymerizations such as atom transfer radical polymerization (ATRP) and group transfer polymerization (GTP). As early as 1995, Fréchet et al. [53] pursued the SCVP of styrene via a 2,2,6,6-tetramethyl-piperidinyloxy (TEMPO) mediated approach. The polymerization involved the combination of both „living‟ free radical polymerization conditions and SCVP to extend the usefulness of both concepts. The reaction mechanism proceeded via thermolysis of the carbon-oxygen bond linking the TEMPO group to the vinylic monomer thereby generating a benzylic radical, which reacted subsequently with an adjacent vinyl moiety of a styrene to afford a dimer product[51]. Figure (2-5) shows the synthesis of hyperbranched poly (methyl methacrylate) using self-condensation vinyl polymerization method by Muller et al [54].

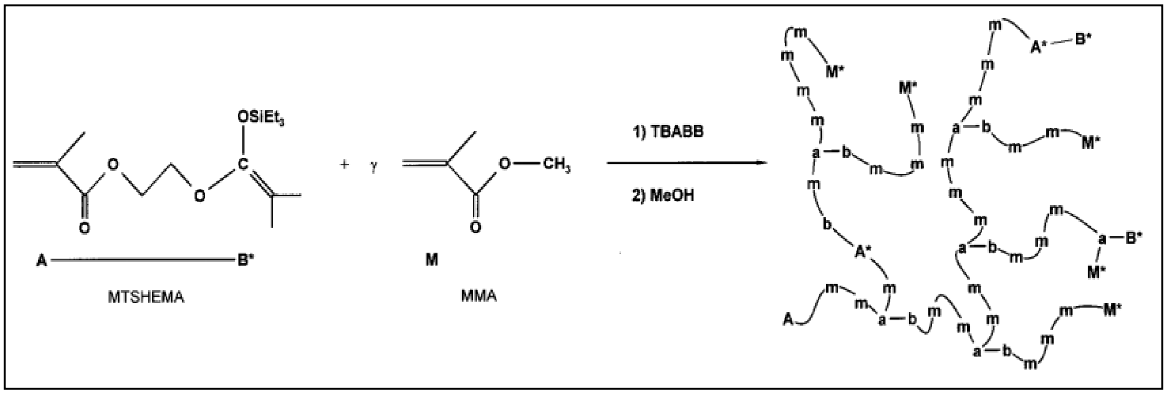


**Figure (2-5): Self-condensation vinyl copolymerization method**[54].

### 2.3.1.3. Self-Condensing Ring-Opening Polymerization (SCROP)

The SCROP method is perfectly analogous to SCVP. It is used for cyclic monomers with a heterocyclic ring having a pending functionality, which is a site for initiation. In a polymerization reaction, the first step is the ring opening from which the name of the technique is derived [39,51]. This mechanism is operative in the polymerization of caprolactones.

Hyperbranched polyamines, polyethers and polyesters have been prepared through SCROP [47]. Table (2-3) shows some of the monomers employed in SCROP and the polymerization results[55–58]. The use of SCROP has been utilized in the formation of hyperbranched polyethers. The first publication utilizing this methodology was outlined in 1999 by Frey et al. using glycidol as the latent $AB_2$ monomer. The hyperbranched polyglycerol thus produced was obtained via an anionic ring-opening polymerization approach as shown by Figure (2-6) [59]. Hedrick et al. utilized poly(ε-caprolactone) protected with bis-MPA at one end as an $AB_2$ macromonomer. The bis-MPA units acted as aliphatic branching points in the polymeric architecture [60].

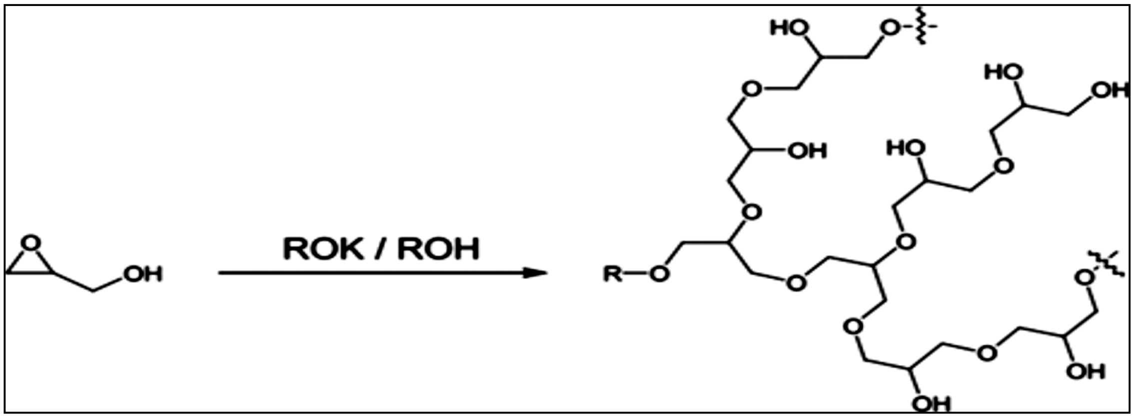
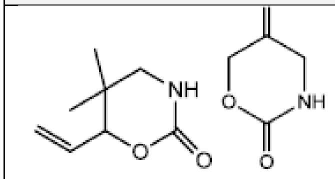
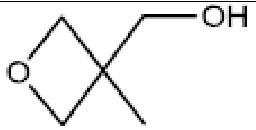
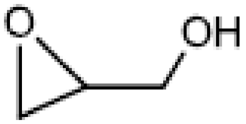
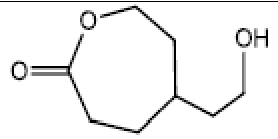


**Figure (2-6): Hyperbranched polyglycerol synthesis via SCROP**[60]**.**

**Table (2-3): Some types of monomers used in SCROP**

| Monomer | Condition | Mn(g/mol) | PDI | DB |
|---|---|---|---|---|
|  | Pd(0),25 °C for 48 h in THF | 1800 | 1.5 | 0.61 |
|  | $BF_3{\cdot}OEt_2$, -10 to 4 °C for 48 h | 1780 | 1.28 | 0.33 |

| | | | | |
|---|---|---|---|---|
|  | $CH_3OK$, 95 °C for 12 h | 6310 | 1.47 | 0.59 |
|  | $Sn(Oct)_2$, 110°C in bulk | 20300-26500 | 3.2 | 0.5 |

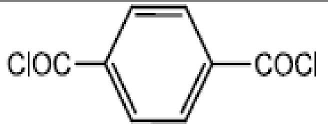
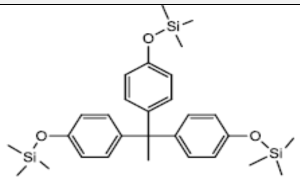
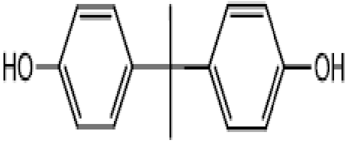
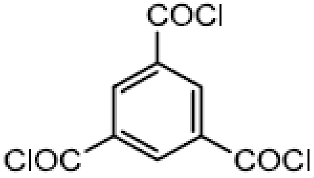
### 2.3.2. Double Monomer Methodology (DMM)

#### 2.3.2.1. $A_2 + B_3$ Method

In $A_2 + B_3$ methodology, two monomers are used; one with two and the other with three functional groups and the method is based on three assumptions. (1) an equal reactivity of all A or B groups at any given stage of the reaction with no side reactions; (2) the reaction is restricted to the condensation of A and B groups; (3) there is no intramolecular cyclisation and chain termination in the process [61]. The advantages of these methods are facile synthesis and the availability of the range of reactants or monomers. The success of this approach is dependent upon many factors, including the ratio of functionalities, solvent and reagent purity and the reaction time and temperature. There have been three main polymer architectures studied to date polyamides, polycarbonates and polyureas [62, 63]. The first intentional preparation of HBPs using the $A_2 + B_3$ approach was reported by Fréchet et al. although the method had been explored to prepare crosslinked polymeric materials more than a century before. The reaction involved the direct polycondensation of the $A_2$ monomer with the $B_3$ monomer in the presence of condensation agents such as triphenyl phosphate and pyridine. The polymerization was carried out at 80 °C in the polar solvent and afford hyperbranched polyamides that were soluble in polar media with degrees of branching of approximately 0.5. Also, aromatic

HBPEs prepared via the $A_2 + B_3$ approach have been reported by Komber et al. focusing on melt polycondensation[64, 65].

**Table (2-4): Some types of monomers used in $A_2$+$B_3$ method** [51].

| $A_2$ | $B_3$ | Polymerization method |
|---|---|---|
|  |  | Melt |
|  |  | Solution |

### 2.3.3. Couple-Monomer Methodology (CMM)

Couple monomer methodology offers a process for the formation of hyperbranched polymers with the advantages of the commercial availability of monomers and lack of gelation. The methodology invented by Gao and Yan is based on the non-equal reactivity of functional groups in specific monomer pairs. Here, two types of monomers would preferentially generate one type of $AB_n$ intermediate in-situ that polymerizes to produce hyperbranched polymers, and hence the name, couple monomer methodology (CMM). Choosing a suitable pair of monomers is the most important step for the molecular design of a hyperbranched polymer using CMM. Based on the type of functional groups A, A' and B, B' in monomers, and the corresponding initiated radical, different approaches can be considered for CMM. The basic principle of CMM is shown in Figure (2-7). In monomer A, A', if A is identical to A', and B is equal to B', CMM degenerates into the ‘$A_2 + B_3$’ polymerization. It is anticipated that crosslinking will not occur if an asymmetric monomer AA' or B'$B_2$ is used. If A' has a higher reactivity that A, CMM affords 'AA' + $B_3$' polymerization; and if B' is more active than B, CMM presents '$A_2$ + B'$B_2$' and '$A_2$ + $CB_2$' polymerization systems [66, 67].

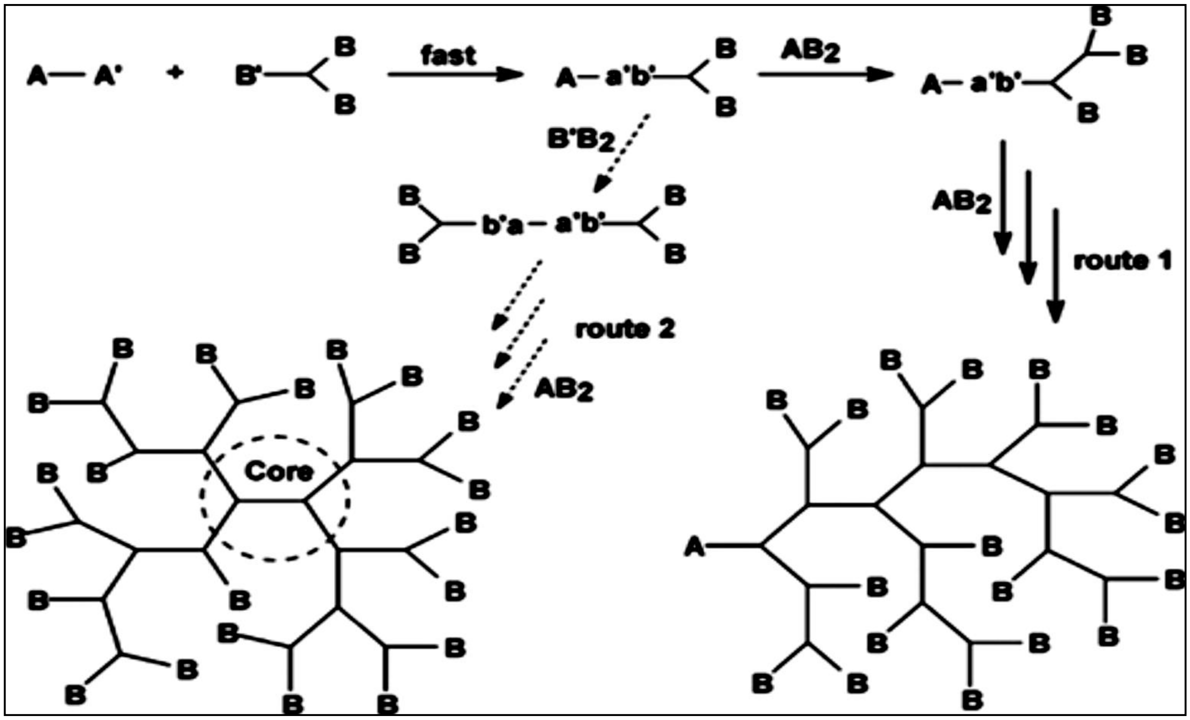


**Figure (2-7): A typical example for the principles of CMM** [51].

### 2.3.4. Multicomponent Methodology (MCM)

When three or more monomers are involved in the synthesis of HBPs, the strategy is called multi-component methodology (MCM). This approach is the most recently reported methodology. It still proceeds in one-pot following a step-growth mechanism, but relies on a sequence-controlled pathway. For instance, in Figure (2-8), the reaction between A and C leads to the formation of D function. This intermediate group is the only one capable of reacting with B affording HBPs with rather 'controlled' architecture [22]. In this context, isocyanate-based multi-component routes such as Passerini and Ugi reactions have been successfully applied to the preparation of HBPs [68] also biodegradable HBPs have been prepared using this method [69].

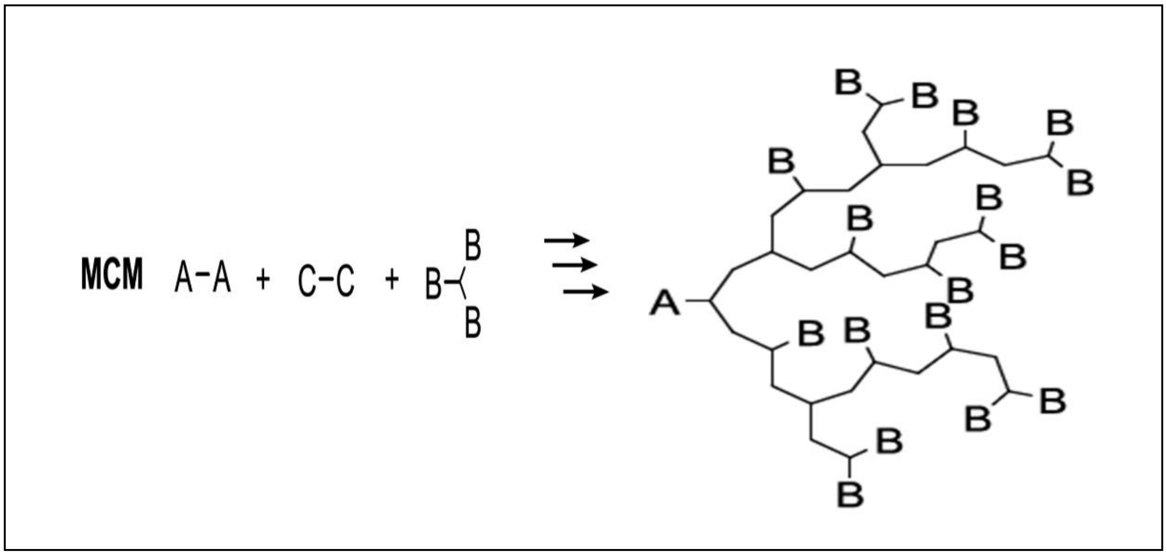


**Figure (2-8): A typical example of MCM polymerization**[22]**.**

## 2.4. The General Properties of Hyperbranched Polymers

### 2.4.1. Solution Properties

The high solubility of HBPs induced by a branched backbone is one of the important properties that differ from those of the linear analogs. Kim and Webster reported that hyperbranched polyphenylenes had very good solubilities in various solvents as compared with linear polyphenylenes [70]. Not only the solubility but also the solution behavior of HBPs differs from linear polymers. It is well known that the solution viscosity of dendritic macromolecules is lower than that of conventional linear polymers. Such a low viscosity indicates that dendritic macromolecules are less entangled because of their spherical shape [71]. The relationship between intrinsic viscosity and molecular weight (MW) is shown in Figure (2-9).

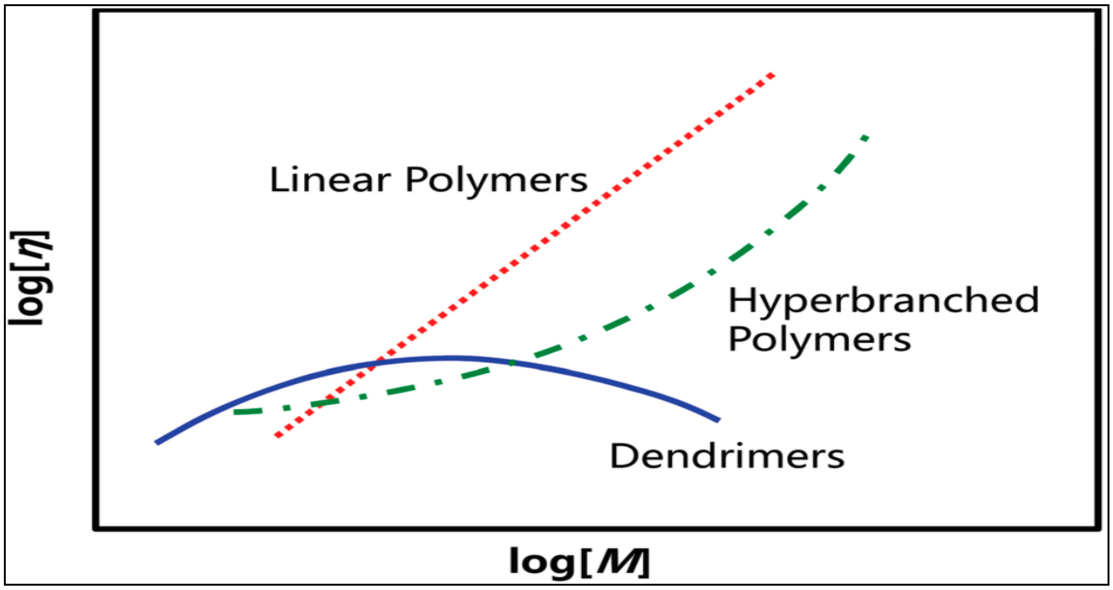


**Figure (2-9): A plots for the relationship between log M and log [η] for different macromolecules**[72]**.**

Dendrimers display a bell-shaped relationship resulting from their regular globular structures. On the other hand, the intrinsic viscosity of HBPs increases with their increasing MW, although the slope of the plots is lower than that of linear polymers. In general, the α-values in the Mark–Houwink–Sakurada equation range from 0.5 to 1.0 for randomly coiled linear polymers. On the other hand, many kinds of HBPs possess α-values < 0.5, suggesting a spherical shape of the molecules in a solution. Moreover, in size exclusion chromatography (SEC) measurements, the retention volume for HBPs tends to be greater than that of linear polymers having the same MWs. This also suggests a more compact formation of HBPs in a solution compared with linear polymers[71].

### 2.4.2. Thermal Properties

Hyperbranched polymers are almost exclusively amorphous materials, although some exceptional examples have been reported in which the polymers have been modified to induce liquid crystallinity or crystallinity.

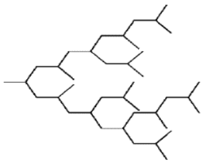
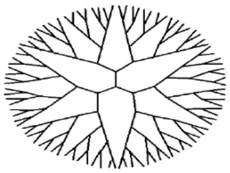
The lower glass transition temperature of HBPs than that of the linear counterparts is one of the most important features. The glass transition behavior is related to the relatively large segmental motions within the polymer chains, and the role of the end groups can be discarded above a certain MW of the linear polymer. However, for HBPs, the segmental motions are strongly affected by the branching points and the presence of numerous end groups. Therefore, the glass transition for HBPs is strongly affected by the translational movement of the entire molecule instead of a segmental movement. The chemical natures also affect the $T_g$ values; for example, an aliphatic polyester generally has a much lower $T_g$ value than the aromatic polyester[71].

### 2.4.3. Mechanical and Rheological Properties

The rheological properties of HBPs are characterized by a Newtonian behavior in the melt state; that is, no shear thinning or thickening is observed, indicating the lack of entanglements for these polymers. The non-entangled state imposes rather poor mechanical properties, sometimes resulting in brittle polymers. These features of HBPs have limited their use in thermoplastics in which mechanical strength is of importance[71]. However, HBMs can be used as additives for modification of viscosity to enhance the processability of thermoplastics[73]. The stress–strain behavior of hyperbranched polymers can be similar to that of ductile metals as observed by Rogunova et al. for hyperbranched polyesters. Like ductile metals, hyperbranched polyesters do not strain harden. This is due to their globular structure, which does not permit the process of chain extension and orientation (the usual mechanisms of strain hardening). However, intermolecular associations, such as hydrogen bonding and possibly intermolecular crystallization of a few linear segments, provide connections between the hyperbranched macromolecules[74].

Dendritic macromolecules have attracted considerable attention during recent decades, because of their unusual properties, such as low viscosity, high solubility, and high functionality. These properties stem from their globular and spherical molecular architectures. Table (2-5) shows the differences between linear polymers, hyperbranched and dendrimers.

**Table (2-5): Comparison of hyperbranched polymers with linear polymers and dendrimers**[73, 75].

| **Polymer** | **Linear** | **Hyperbranched** | **Dendrimer** |
|---|---|---|---|
| **Structure** |  |  |  |
| **Topology** | 1D linear | 2D irregular | 2D regular |
| **Synthesis** | One step, easy | One step, relatively easy | Multi step, hard |
| **Mw** | Discrepant | Discrepant | Identical |
| **PDI** | >1.1 | >1.1 | 1.0 (<1.05) |
| **DB** | 0 | 0.4-0.6 | 1 |
| **Entanglement** | Strong | Weak | Very weak or no |
| **Viscosity** | High | Low | Very low |
| **Solubility** | Low | High | High |
| **Functional group** | At two ends | At linear and terminal units | On terminal units |
| **Reactivity** | Low | High | High |
| **Strength** | High | Low | Very low |

## 2.5. Hyperbranched Polyester

Polyesters are an important class of hyperbranched polymers. Their relative ease of synthesis and the availability of suitable raw materials have indeed prompted the research in this field. Early works were related to the synthesis of hyperbranched copolyesters while considerable research in the 1990s addressed aliphatic, aliphatic-aromatic and aromatic hyperbranched polyesters (HBPEs)[22,76].

As an important class of hyperbranched polymers, aliphatic, aromatic and aliphatic-aromatic hyperbranched polyesters have attracted increased interest and are intensively studied because of their excellent thermal stability, chemical resistance, and mechanical properties[77]. The field of aliphatic HBPEs is mainly focused on the use of 2,2-bis(methylol)propionic acid (bis-MPA) as $AB_2$-type building block, the base monomer of the Boltorn® range that has been commercialized by Perstorp. Low molar mass aliphatic HBPEs have found applications in coatings and resins, fields where the combination of their high functionality, low viscosity and improved miscibility was of high interest. Aromatic HBPEs have also been extensively studied in the literature, but in contrast to their aliphatic analogues, their high melting points and glass transition temperatures have restricted their uses to blends, sensors or non-linear optics[22].

## 2.6. Types of Hyperbranched Polyester

### 2.6.1. Aromatic Hyperbranched Polyester

Two $AB_2$ monomers, 3,5-dihydroxybenzoic acid (DHBA) and 5-hydroxyisophthalic acid (HIPA), have most frequently been used as starting materials to prepare aromatic HBPEs. However, modifications of these are necessary because their thermal stabilities are lower than the required reaction temperature for direct esterification Perhaps, among those, the hyperbranched polyesters that have been most extensively studied are the fully aromatic hyperbranched systems based on a 3,5-dioxybenzoyl building block [22, 76, 77]. Figure (2-10) shows the common types of monomers that used to prepare aromatic hyperbranched polyester.

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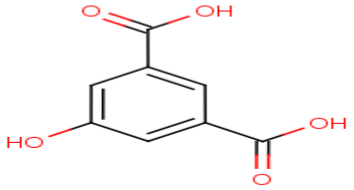
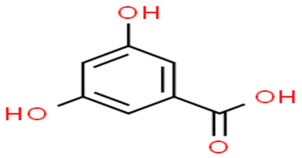
|  |  |
| **HIPA** | **DHBA** |

**Figure (2-10): some monomers for synthesis of Aromatic HBPEs**[22].

As early as in 1982, Kricheldorf et al. reported on the synthesis of a branched polyester based on $AB_2$ and AB type monomers, 3,5-(bis trimethylsiloxy) benzoyl chloride and 3- (trimethylsiloxy)benzoyl chloride. Following that, a systematic investigation of HBPEs derived from 3,5-bis(trimethylsiloxy)benzoyl chloride was conducted by Fréchet et al.[78, 79]

### 2.6.2. Aromatic-Aliphatic Hyperbranched Polyester

The other widely used $AB_2$ monomer for hyperbranched polyester formation is 4,4'bis(4-hydroxyphenyl) pentanoic acid (BHPPA). This monomer is commercially available and can be used in melt polycondensation without any activation or transformation of the acid in the ester [77]. The introduction of alkyl chains in the backbone of precursors of aromatic HBPEs leads to a decrease in the glass transition temperature (Tg) of the resulting polymers enabling to perform their melt polycondensations at lower temperatures [22]. Actually, no difference can be found in the reaction when the functionalities are varied. The resulting hyperbranched polyester is amorphous, with a Tg around 100–110°C, a value that can be further varied by the addition of a core molecule during polycondensation. It is not as brittle as the fully aromatic structures and thus it is easier to handle. Compared with DMPA and BHBA, the reactive functionalities are far apart and located at different phenyl rings[76],[77].

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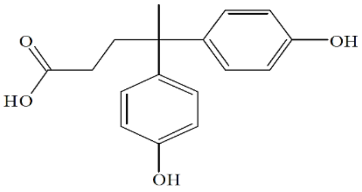
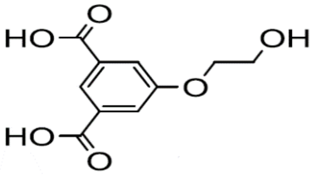
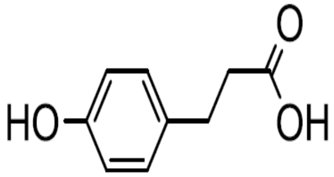
|  |  |  |
| **BHPPA** | **DMPA** | **BHBA** |

**Figure (2-11): Some monomers for synthesis of aromatic-aliphatic HBPEs** [76,77]**.**

### 2.6.3. Aliphatic Hyperbranched Polyester

The field of aliphatic HBPEs is focused around 2,2-bis(methylol)propionic acid (bis-MPA), one easily available $AB_2$-type monomer bearing one carboxylic acid and two hydroxyl functional groups. There is also the possibility of using 2,2-bis (hydroxymethyl) propionic acid[80]. The first preparation of HBPEs derived from bis-MPA dated back to the 1990s. Since then, this system and its derivatives have been the subject of numerous investigations regarding their synthesis, properties, characterization, theory, modifications and applications[22, 76, 77].

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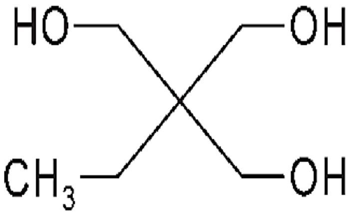
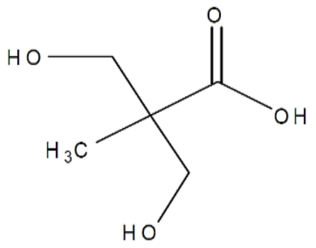
|  |  |
| bis-MPA | bis-HMPA |

**Figure (2-12): the most widely used monomers for synthesis of aliphatic HBPEs.**

## 2.7. Application of Hyperbranched Polymers

The novel physical properties of hyperbranched macromolecules render these polymers ideal candidates for use in a wide range of applications. A schematic diagram of the most common applications in which hyperbranched polymers have been used is shown in Figure (2-13)[81].

Aromatic HBPEs and their derivatives are potentially useful in the areas of polymer blends, sensors, coatings, additives, optical and electronic materials, and so forth. Because the properties of aromatic HBPEs such as good solubility, polarity, rheology, and thermal properties can be tailored, it can be expected that more and more fascinating materials and devices based on aromatic HBPEs will be successfully developed and fabricated[77].

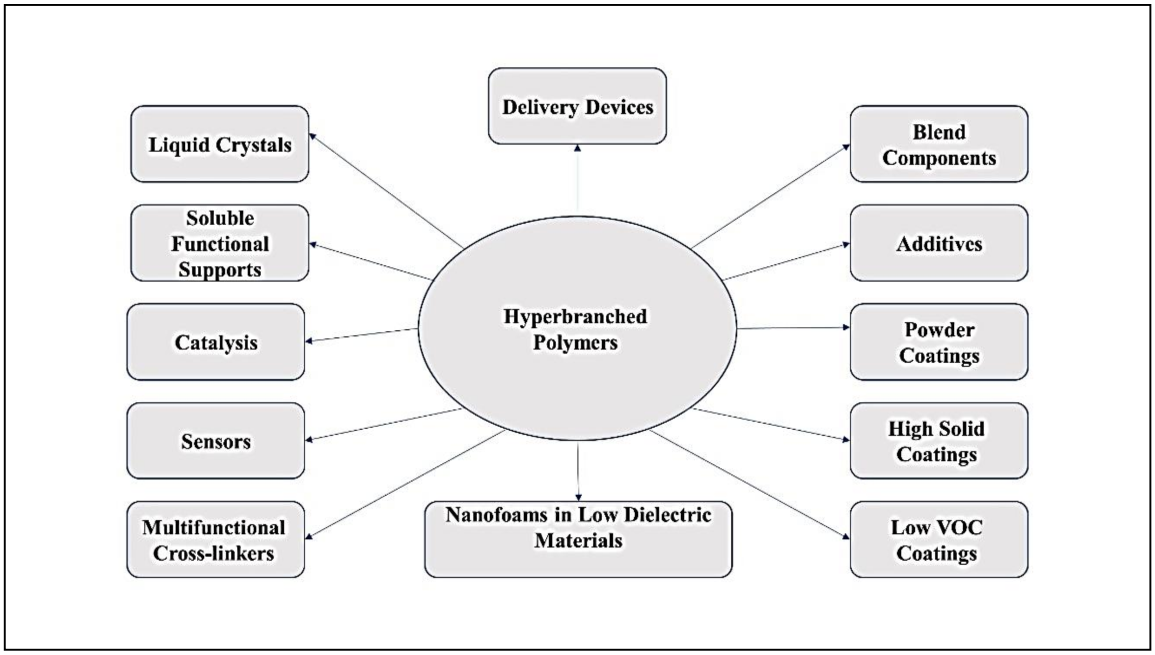


**Figure (2-13): Application of Hyperbranched polymers**[81].

### 2.7.1. Blends

At present, polymer blends have become a major tool for designing and improving polymeric materials. Virtually almost all classes of commercial polymers have been blended with other polymers to improve physical and chemical properties, such as modulus, toughness, processability, barrier properties, and chemical resistance. The aromatic structures endow HBPEs with high Tg values, and are expected to result in high moduli. Blending, in the melt state, aromatic HBPEs with linear polymers may be a route to novel materials having improved moduli and heat-distortion temperatures. Table (2-6) lists some application of HBPEs in blends[40].

The use of hyperbranched polymers blended with linear polymers has resulted in new polymeric materials for example, Kim and Webster blended hyperbranched polyphenylenes with polystyrene. The addition of the hyperbranched polyphenylene to the polystyrene improved the thermal stability and melt viscosity of the polystyrene as a consequence of thermal chain transfer. Another effect that was observed was the change in the mechanical properties of the polystyrene on blending the initial modulus improved which was attributed to the weak cross-linking of the polystyrene through aryl–aryl interactions[70].

According to Shi et al., it should be mentioned that the HBUA could also serve as an effective toughener for thermoplastic polypropylene (PP). The addition of 5 wt% HBUA greatly improved the notched impact strength of PP matrix with a slight improvement in the tensile strength and without obvious decline in breaking elongation. They thought that the cured HBUA particles in the PP/HBUA blends acted as heterogeneous nucleation agent for PP, therefore, the presence of HBUA could increase the crystallization temperature and decrease the melting temperature of PP matrix, which resulted in the decrease of spherulite size with less perfection of PP crystals, and thus improvement of the toughness of PP matrix [82].

**Table (2-6): HBPEs used as modifiers and additives in blends**[40]**.**

| Blended compound | The aim of blend | function | year |
|---|---|---|---|
| PC, PE, PA | Investigating the phase behavior of the blends | Molecular reinforcing agent | 1995 |
| i-PP, HBPE | Investigating the effect of HBPEs in blend with polyolefins | Dye carrier | 1999 |
| PP | Improving the impact performance of PP | Toughener | 2004 |
| PA | Exploring the potential application of HBPEs for modifying PA | Processing aid | 2009 |

### 2.7.2. Coatings

The most prominent use of HBPEs is as polyols or reactive multifunctional components in coatings and resin formulations. The features of HBPEs are also very favorable in coating applications; the large number of end groups offers versatile crosslinking possibilities, the approximate globular structure of HBPEs enables very low viscosity even at high molecular weights. The application of aromatic HBPEs in coatings is mainly involving UV-curable coatings and hybrid coatings [23,81,83, 84].

#### 2.7.2.1. UV-Curable Coatings

UV-curable coatings represent a class of coatings with no or low volatile organic compounds, offering many advantages such as fast drying, broad formulating range, reduced energy consumption, and low space and capital requirement for curing equipment. Aromatic HBPEs with acrylate, vinyl ether, or epoxy functions have been used as a multifunctional crosslinker in coatings with UV curing methods. Coatings containing aromatic HBPEs exhibit very rapid cure rate and lower shrinkage, and the UV-cured films have excellent hardness, high chemical resistance, and good scratch resistance[23, 26, 75, 85].

### 2.7.2.2. Hybrid Coatings

In the last few years, hybrid organic/inorganic nanocomposites have been broadly studied because they combine both the advantageous properties of an organic polymer (flexibility, good impact resistance and good processability) and inorganic materials (high mechanical strength, good chemical resistance, thermal stability and optical properties) [26,77,86]. Sangermano et al. prepared advanced scratch resistant and tough nanocomposite epoxy coatings, a high loading silica hybrid coating, based on phenolic-terminated HBPE synthesized from a melt polycondensation of 4,4-bis(4-hydroxyphenyl) valeric acid, and an epoxy functionalized alkoxysilane additive [87].

### 2.7.3. Stabilizers for Nanocrystals

Nanocrystals (NCs) include insulator, semiconductor and metal crystals. They exhibit unique size-dependent physical or chemical properties. Spontaneous aggregation among NC particles leads to performance degradation. To restrain this, HBPs are often used as a stabilizer in the preparation of NCs because of their specific three-dimensional structure, good solubility, and plenty of intramolecular cavities. The influence of the HBP architecture on the synthesis of NCs mainly shows through in the following three aspects: (a) their unique 3D structure can provide sufficient hindrance and can efficiently suppress the tendency for the NCs to aggregate; (b) plenty of cavities in the HBP templates confine the free diffusion of NCs' precursors, and hence are useful for controlling the size of the NCs; and (c) the terminal groups endow the HBPs with enough functionalized flexibility to facilitate the synthesis and the size control of NCs [73, 75]. Three methods have been reported for the synthesis of NCs: (a) HBMs first (HBMs use as stabilizers to directly prepare NCs); (b) ligand exchange (NCs-coated surfactants or linear polymers as ligands are exchanged into an appropriate HBMs); and (c) NCs first (the grafting or in situ growth of HBMs occurs on the surface of NCs), as shown in Figure (2-14) [73, 75]. Up to now, six major kinds of HBPs were employed to prepare NCs, namely HBPAMAM, HBPEI, HBPG, HBPE, HBPAM and HBPEO [73,75].

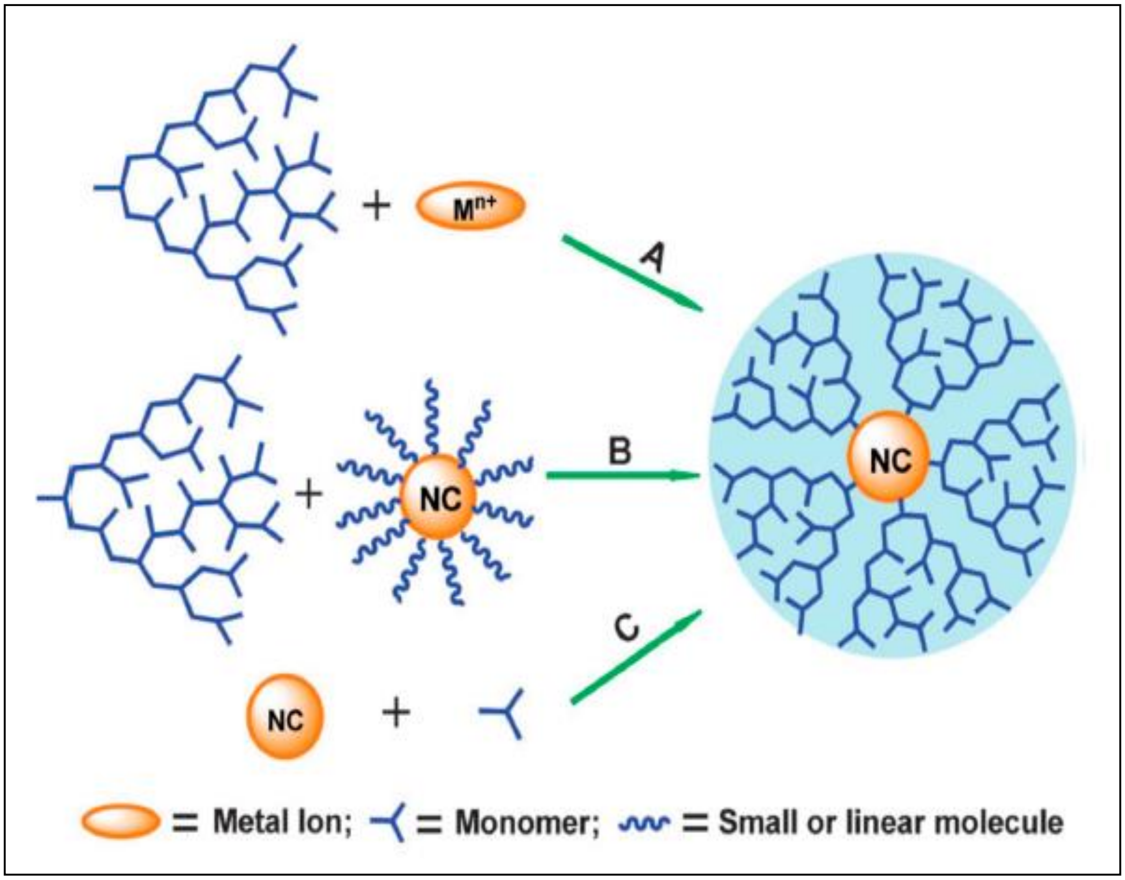


**Figure (2-14): The stabilization methods of nanocrystals with HBP**[75,73]**.**

### 2.7.4. Bio-Application

Similar to the amphiphilic linear block copolymers, amphiphilic HBMs can be self-assembled into various supramolecular structures in solution or through interfacial self-assembly. Supramolecular structures have potential applications in biomedical areas, because of their biocompatibility and adjustable molecular architectures. Hyperbranched polyethers, polyesters, polyphosphates, and polysaccharides could be candidates for biomedical uses in areas including cytomimetic chemistry, drug delivery, gene transfection, antimicrobial material, and bio-imaging fields [88, 89].

HBMs have also been widely used as antibacterial/antifouling materials. Due to their good biocompatibility and chemical stability, HPGs are promising antifouling materials that can be employed to prevent the attachment of proteins[90].

### 2.7.5. Sensors

Aromatic HBPEs have proved to be interesting materials for chemical sensors, which allowed the calibration and discrimination of series of alcohols and different halogenated hydrocarbons. Three aromatic HBPEs with different end groups (P–OH, P–COOH and P–OAc) were prepared by melt polycondensation of the $AB_2$ monomers 3,5-trimethylsiloxyl benzoyl chloride, 3,5-diacetoxy benzoic acid, and 5-acetoxyphthalic acid, respectively. The surface properties of thin films of the HBPEs were investigated using contact angle measurements and showed differences in hydrophilic/hydrophobic properties because of the different end groups, predicting different behavior in sensoric applications. Therefore, these sensitive layers demonstrated different behavior in interaction with the homologous series of alcohols from methanol to pentanol and freons [91].

### 2.7.6. Shape Memory Materials

Shape memory polymers (SMPs) are those materials that can maintain deformation in a temporary state and can recover their primal shapes as they are subjected to specific external stimuli. This deformation and recovery process correspond to the reversible storage and release of entropy energy. PCL-based HPUs, HPU–MWCNTs and HPU–GO have served as advanced thermo-responsive SMPs[75].

### 2.7.7. Adhesives

Adhesives serve as the important media to link up two or more objects. Good wettability, strong interfacial interaction and high mechanical performances are essential features of an adhesive. Hyperbranched poly(triazole)s were used as adhesives and have shown high adhesive strength at ambient temperature and at 200 °C due to their abundant rigid aromatic and triazole rings. Moreover, their strong polar triazole groups give rise to large binding energy between the HP-based adhesive and metal substrates[92].

### 2.7.8. Elastomers

Generally, elastomers have low Tg, ultrahigh molecular weights, and a suitable degree of cross-linking. A low Tg endows the elastomer with a large deformability and the modest degree of cross-linking makes its deformation restorable. PUs have been widely used as elastomers. Introducing hydroxyl functional HBPs into PU elastomers gives the products better mechanical properties than those of their linear counterparts [93].

## 2.8. Polypropylene PP

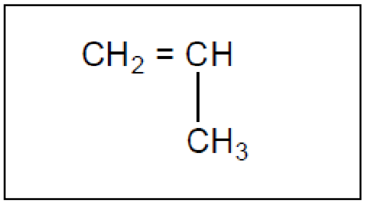
Polypropylene is a type of thermoplastic polymer; it is a part of both the average household and is in commercial and industrial applications. The chemical designation is $C_3H_6$, PP is widely used in variety of applications including packaging, textiles (e.g., ropes, thermal underwear and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, and automotive components. An addition polymer made from the monomer propylene, it is rugged and unusually resistant to many chemical solvents, bases and acids. Most commercial PP is isotactic and it has an intermediate level of crystallinity between that of low-density polyethylene (LDPE) and high-density polyethylene (HDPE)[94,95].

Polypropylene is the second-most widely produced commodity plastic (after polyethylene). In 2019, the global market for polypropylene was worth \$126.03 billion. Revenues are expected to exceed US\$145 billion by 2019. The sales of this material are forecast to grow at a rate of 5.8% per year until 2021[96].

Polypropylene is a semicrystalline polymer containing both crystalline and amorphous phases. The relative amount of each phase depends on structural and stereo chemical characteristics of the polymer chains and the conditions under which the resin is converted to final products such as fibers, films, and various other geometric shapes during fabrication by extrusion, thermoforming, or molding[97]. The properties of polypropylene depend on the molecular weight and molecular weight distribution, crystallinity, type and proportion of comonomer (if used) and the iso-tacticity[98].

Polypropylene is a versatile thermoplastic material, compatible with many processing techniques and used in many different commercial applications. The moderate cost and favorable properties of polypropylene contribute to its strong growth rate. It is one of the lightest of all thermoplastics (0.9 g/cm$^3$), so that fewer pounds are required for finished parts. Due to its high strength-to-weight ratio, it is more rigid than other polyolefins. It has the highest melting temperature (160–170°C) of all commodity thermoplastics and better heat resistance than other low-cost thermoplastics; unmodified polypropylene, however, it becomes brittle at ambient temperatures. Polypropylene is available in a wide variety of melt flow rates, ranging from 0.3 to over 1000 g/10 min., and it is easily recycled[94]. Typical crystallinity of PP is between 40-60%[98].

Polypropylene (PP) was first produced by G. Natta, following the work of K. Ziegler, by the polymerization of propylene monomer in 1954 as shown in Figure (2-15). The macromolecule of PP contains 10,000 to 20,000 monomer units. The steric arrangement of the methyl groups attached to every second carbon atom in the chain may vary. If all the methyl groups are on the same side of the winding spiral chain molecule, the product is referred to as isotactic PP. A PP structure where pendant methylene groups are attached to the polymer backbone chain in an alternating manner is known as syndiotactic PP. The structure where pendant groups are located in a random manner on the polymer backbone that is the atactic form[98].



$$CH_2 = \underset{\displaystyle CH_3}{\underset{|}{CH}}$$

**Figure (2-15): Polypropylene monomer**[98]**.**

Polypropylene properties are affected by stereoregularity. The factors which determine the stereo arrangement of polypropylene are (1) the degree of branching (linear or branched), (2) regiospecificity (head-to-tail, or head-to-head or tail-to-tail), and (3) stereospecificity (right or left hand). Hence, polypropylene can be produced with different isotactic, syndiotactic, and atactic tacticities. The different tacticities in PP are shown in Figure (2-16)[99,100].

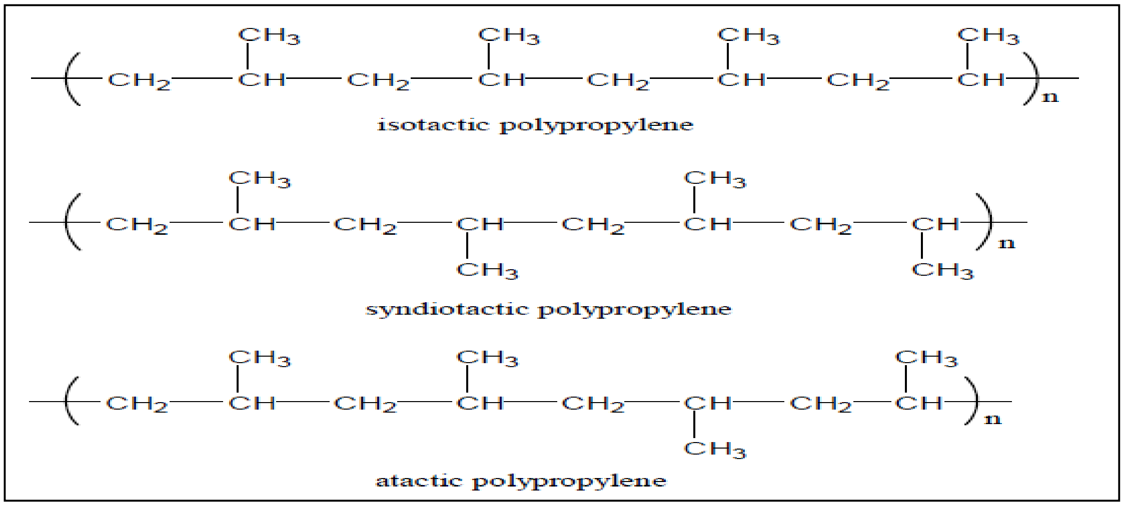


**Figure (2-16): The different forms of polypropylene molecule**[98,99]**.**

The major disadvantages of unmodified PP compared with other competitive thermoplastics are that PP has significantly higher mould shrinkage, higher thermal expansion and lower impact strength, particularly at sub-ambient temperatures, than HIPS, PVC and ABS. However, PP has lower mould shrinkage and thermal expansion coefficient than HDPE and LDPE. Poor UV resistance and poor oxidative resistance in the presence of certain metals such as copper are other disadvantages of PP. As any semi-crystalline material, PP also suffers from high creep under sustained load in comparison to an amorphous plastic such as ABS or PVC[101].

However, most of these disadvantages could be overcome, either completely or to a certain degree, by adding other materials. The materials added at a high concentration to PP compound are called modifiers. Polypropylene modifiers include organic polymer (blending with other polymers)[102], minerals filler and reinforcing fibers[103].

## 2.9. Plastic Waste and Reusing

Plastics are considered extremely effective materials to recycle for two primary reasons. Firstly, there is a demand to use more and more plastics in our everyday life. Therefore, the demand for raw materials will increase and recycled plastics will serve as a necessary source. Secondly, the recovery processes comply with the environment guidelines that promote the reduction of waste arising at the source and the recycling of materials. The possibility of using recycled materials to manufacture relatively good article depends on the rheological and mechanical behavior of the recycled polymers. Therefore, it is essential to understand these fundamental concepts in order to make the acceptable product[104].

Reusing of plastic materials is strategically very important for the environmental policy of industry. This is especially true for high consumption plastics as polypropylene (PP). The key factor to the success of PP is its versatility, which is due to the fact that the structure and properties of PP can be tailored to requirements. Fracture toughness, as a material parameter that indicates of stiffness, strength and strain to failure, is of basic importance for application fields in which recycled plastics are subjected to impact and severe safety requirements have to be fulfilled by the designer[105].

The recycling process could change mechanical, physical, and chemical properties of plastic materials. This perception of change in properties results in recycled plastics having a low value and the tendency of industries to avoid recycled materials because they can possibility affect product performance. At recycled materials were grinded and molded more than one time, this process causes that chain length decrease and mechanical properties such as ultimate tensile strength and modulus of elasticity, decrease too[106].

Material recycling is a term used to describe processes in which the macromolecular structure is kept basically intact, and the material is reformed into a new product. Recycling of plastics is an important industrial application due to its damage to the environment. The aim of recycling is to decrease the amount of waste by recirculation of raw materials and to improve the material utilization[107].

Recycled polypropylene is of great interest, particularly for the automotive industry. One problem with recycled resins is that mechanical properties usually decrease during recycling and restoration requires additives, so several methods have been used to overcome this problem by blending with other polymers or reinforcing the polymer with nanomaterials[108].

## 2.10. Polymer Blends

A polymer blend is defined as the combination of two or more dissimilar polymers by physical mixing with/without chemical interaction between them. Polymer blends have potential technological significance, which can be proven by their global presence in consumer products. In comparison to copolymerization, polymer blends can provide desired properties at a low cost by simple physical processes rather than chemical approaches. There are several methods for polymer blend preparation (melt blending, mill mixing and fine powder mixing technique, solution casting method, freeze drying, latex blending, mechanochemical blending, and Interpenetrating Polymer network technology). Generally, the melt blending is an economic and convenient way to create new materials with modified performances, and is the preferred method by industries. The pursuit of further understanding the physical and mechanical properties of polymer blends has developed new principles and revealed new opportunities for research that can address a number of practical issues. There are three major factors, morphology, miscibility, and compatibility, which mainly decide the performance of the polymer blends [109–112].

## 2.11. Types of polymer blends [113, 114]

1. **Homogeneous blend**: A mixture of two homologous polymers, usually narrow molecular weight distribution fractions of the same polymer. In this blend, both blend components lose part of their identity and the final properties usually are the arithmetical average of both blend components.
2. **Heterogeneous blend**: The properties of all blend components are present. Weakness of one polymer can, to a certain extent, be camouflaged by strength of the others.
3. **Miscible polymer blend**: Polymer blends which are homogeneous down to the molecular level are associated with the negative value of free energy of mixing: $\Delta G_{mix} \approx \Delta H_{mix} \leq 0$.
4. **Immiscible polymer blend**: Any polymer blends whose $\Delta G_{mix} \approx \Delta H_{mix} > 0$.
5. **Compatible polymer blend**: A term indicating a commercially attractive polymer mixture with enhanced physical properties over the constituent polymers.
6. **Polymer alloy**: An immiscible polymer blend having a modified interface and/or morphology.

## 2.12. Literature Review

In the recent years, several studies have been conducted for studying the effect of the addition of hyperbranched polymers to different types of polymers. In this section of this chapter, the studies conducted by many researchers will be briefly explained as follow:

**Huizhi Yan and Yanmo Chen 2010** [115] had been synthesized hyperbranched poly(phenylene sulphide (HPPS) and studied its effect on polypropylene for the development of dryable fibers. Twin-screw extruder was used for blend preparation with two different weight percentage of HPPS 1% and 3%. Results showed that the mechanical properties are slightly affected by the incorporation HPPS. DSC thermograms show that the crystallinity ($\chi c$) of HPPS/PP fibres is lower than that of the neat PP fibre. DMA tests show that HPPS/PP blends consist of single-phase amorphous regions. The SEM micrographs show that the size of the HPPS domains is in sub-micrometer order and they have good interfacial compatibility with PP phases.

**Alireza Javadi et al. 2011** [116] had been explored the effect of adding hyperbranched polymers (HBPs) and various nanoclays on the mechanical, morphological, and thermal characteristics of solid and microcellular polyhydroxybutyrate-co-hydroxyvalerate (PHBV). The addition of HBP+poly(maleic anhydride-alt-1-octadecene) (PA), nanoclay reduced the average cell size and increased the cell density of the microcellular components. The addition of (HBP+PA), nanoclays increases the degree of crystallinity for both solid and microcellular components in comparison with neat PHBV. In addition, with the addition of 12% (HBP+PA), toughness, and strain-at-break of the PHBV–HBP nanocomposite increased significantly for both solid and microcellular specimens, whereas the storage modulus, Young’s modulus, and tensile strength decreased. The addition of 2% nanoclays into the PHBV–HBP nanocomposites improved the storage modulus, Young’s modulus, and tensile strength of the PHBV–HBP–nanoclay.

**Keqing Han et al. 2011**[117] had been studied the enhancement of Mechanical Properties and Melt Flow Ability of PA6 by Blending with a Hyperbranched Polymer (polyester). The blends were prepared with different HBPE contents varied between 0.1 and 2.0 wt%. The blends were melt blended with twin screw extruder. The results showed that the melt flow index of the blends was greatly improved by a small amount of HBPE. The yield strength, tensile modulus, Izod impact strength, and flexural strength of samples were simultaneously enhanced. The PA6/HBPE blends showed the higher content of α-form crystal and a higher degree of crystallinity than those of pure PA6.

**Qingchun Fan et al. 2012** [118] had been examined the isothermal crystallization kinetics of PP/hyperbranched polyester (HBPE) blends. Various HBP contents have been added (1%, 2%, 5% and 10%). An injection molding machine was used to extrude the granules of PP/HBPE blend. The findings reveal that HBPE works as a nucleating agent for PP and that the hyperbranched polyester can significantly reduce the half-crystallization time (t1/2) and boost the crystallization rate of PP. The nucleation mechanism of the PP is not changed by HBPE, and the crystallization nucleation is heterogeneous.

**A. M. Tomuta et al. 2013** [119] had been investigated the effect of aliphatic-aromatic hyperbranched polyester with different end groups on the epoxy thermosets. The percentage of HBPE added were 5 and 10% w/w. The findings revealed in the case of vinyl terminated HBPE, these investigations imply that HBPE slow down the curing rate of epoxy/AH, whereas OH terminated HBPE speeds up the first stages but slows down the final. The thermosets produced improved in microhardness and impact strength without lowering the Tg or other thermal parameters. When undecenoyl HBPE derivatives or a 10% allyl HBPE derivative was used in the formulation, microparticle phase separation was observed.

**Morteza Ganjaee Sari et al. 2014**[120] had been studied the effect of adding two types of hyperbranched polyester amide polymer on the characteristics of polypropylene. The blends were prepared via Brabender Plasticorder internal mixer. 5% of each hyperbranched polymer was added separately with and without maleic anhydride. The morphological studies showed that the blends with maleic anhydride form a more homogeneous morphology. It was concluded from the rheological data that the expected grafting reaction occurs and the flowability of the modified samples is enhanced. SAXS studies demonstrated that the nanocrystalline structure of PP can be affected in the presence of hyperbranched polymers.

**Haroon A.M. Saeed et al. 2014** [121] had been studied the properties of recycled poly (ethylene terephthalate) (PET)/hyperbranched polyester (HBPET) for composite fiber preparation. HBPET contents were 0.5% and 1 wt%. The blends were melt blended in co-rotating twin-screw extruder then melt spun using a melt spinning process. Results showed that mechanical properties of the fibers were improved. Moreover, the crystallinity of composites fibers was also increased with an increasing of HBPET content. The improvement in mechanical properties may be due to the increase of orientation of fiber molecules along the fiber axis. Moreover, addition of HBPET serves as lubricant within recycled PET matrix which increased its mechanical properties.

**Pyus D. Tatiya et al. 2014** [122] had been studied the effect of blending hyperbranched polyester on the melt processing and characterization of PP/$Na^+$ MMT nanocomposite. 5 phr of MMT nanoclay and the hyperbranched polyester content was 5, 10 and 15 phr. Maleic anhydride was used as compatibilizer for PP/MMT and compare its result with the blends that have HBP. The blends with nanocomposite were fabricated by direct melt compounding on a Brabender torque rheometer. The XRD and TEM results reveal that addition of HBPE in PP/clay composites causes better clay dispersion compared with PP/clay composites compatibilized with PP-g- MA. The surface aspect of processed composite blend with HBPE reveals smoother surface morphology than PP-g-MA. The HBP in the composite acted as nucleation sites for PP crystallization, and showed a higher crystallization rate than the composite compatibilized with PP-g-MA.

**Qingchun Fan et al. 2015**[123] had been investigated the non-isothermal crystallization of PP/ HBPE polyester blend. The contents of HBPE were 1%, 2%, 5% and 10%. The blends of PP/HBPE blends were extruded under an injection molding machine. Crystallization rate increases with the addition of HBPE. The crystallization rate reaches a maximum when the content of HBPE is 5%. The HBPE acts as nucleating agent during the crystallization of the blends.

**Manuel Guzmán and Edwin A. Murillo 2015** [124] had been investigated the structural, thermal, rheological, morphological, and mechanical properties of the blends by preparation thermoplastic starch TPS from starch and 40 wt% of HBPE and then grafted maleic anhydride on LDPE and blend it with TPS. Thermo Scientific torque rheometer was used for blend preparation. The blends exhibited a reduction in the A-type crystallinity and a pseudoplastic rheological behavior. Scanning electronic microscophy provided an evidence for the presence of starch granules in all the blends and for low interaction degree between LDPE-g-MA and TPS.

Young's modulus and tensile strength of the LDPEg- MA/TPS blends decreased with the decreasing LDPE-g- MA/TPS ratio.

**Ming-ji Wang et al. 2015** [125] had been investigated the influences of hyperbranched polyethylenimine (HBPEI) on the blending properties of polycarbonate (PC) and amorphous polyamide (aPA). Blend samples were prepared in a Haake miniCTW laboratory mixer. Results show that the compatibility in PC/aPA blends can be significantly improved by adding a small amount of HPEI, mainly due to the interchange reactions between the polymers leading to the formation of block copolymers, cross-linked polymers and molecules with other constitutions. The augmented double cantilever beam experiments showed that the reactive process drastically reinforced the interfacial adhesion between planar layers of PC and aPA. However, degradation takes place during annealing at 180 $^{o}$C, which was responsible for the production of small molar mass species of PC.

**Asım Davulcu 2015** [126] had been investigated the effect of hyperbranched poly(ester amide) (HBPEA) on the dyeability of polypropylene wilth natural dyes. The HBPEA content in samples was 1wt% and 3wt%. The samples were prepared by twin screw microextruder coupled with winding unit. Results showed that the polar structure of HBPEA enhanced interaction with the functional groups in natural dye sources. It is observed from the SEM images that the HBPEA uniformly dispersed into the PP matrix. The incorporation of HBPEA causes acceptable reduction at both stress at break values (σ) and elongation at break values (ε). The $T_m$ and $X_c$ values of modified fiber samples are almost close to those of the unmodified PP fiber.

**Mina Ahani et al. 2016** [127] had been studied the Preparation and characterization of poly(ethylene terephthalate)/hyperbranched polymer nanocomposites. The HBPE contents used in the nanocomposite were 0.5, 1, 2, and 3 wt %. PET/HBPE samples were melt blended by using an internal mixer. Results showed that the hyperbranched polymer works as a modifier decreased the complex viscosity and enhanced liquid-like behavior. This happened more significantly by increasing the content of hyperbranched polymer. The DSC analysis results revealed that crystallinity and glass transition temperature decreased by adding the amount of hyperbranched polymer.

**Ricardo Mesias and Edwin Murillo 2018** [128] had been concentrated to evaluate the compatibilizer effect of hyperbranched polyester polyol of the second generation (HBPE2) modified with polylactic acid (HBPE2-g-PLA) in a TPS/PLA blend (50/50 wt%). The blend was prepared using torque rheometer Thermo Science. The torque value of the TPS/PLA blends with HBPE2-g-PLA was lower than that of the control sample, while thermal stability and crystallinity followed opposite behavior. The glass transition temperature (Tg) and degree of crystallinity of the TPS/PLA blends with HBPE2-g-PLA decreased with increasing mass fraction of HBPE2-g-PLA. SEM images show that the morphology of the TPS/PLA blends with HBPE2-g-PLA was more homogeneous than that of the control sample, confirming that HBPE2-g-PLA acted as a compatibilizer and plasticizing agent to the TPS/PLA blends.

**Haroon AM Saeed et al. 2018** [129] had been studied rheological and thermal properties of recycled poly (ethylene terephthalate)/hyperbranched polyester (HBPET) composites. Different amounts of hyperbranched polyesters (HBPET), 3 wt% and 5 wt % were added to the RPET. RPET and HBPET, which were melts-blended in co-rotating twin-screw extruder. RPET-3 and RPET-5 composites were improved rheological characteristics and enhanced the thermal stability. Decrease in the complex viscosity (η) of the blends was observed with increasing content of HBPET.

**Manuel Guzmán and Edwin A. Murillo 2018** [130] had been evaluated the effect of the proportion of a hyperbranched polyester (HBPE) on the structural, thermal, rheological, morphological and mechanical properties of tapioca starch/HBPE blends. The starch/HBPE ratio was 30/70, 40/60 and 50/50. The torque rheometer Thermo scientific was used for blend preparation. FTIR analysis showed that the presence of HBPE produced a displacement at the absorptions of the C-OH, C-O and C-O-C bonds of the TPS. The XRD analysis showed that the starch crystallinity is A and B type, which increased with the HBPE amount. The glass transition temperature (Tg) increased with the HBPE content, but the thermal stability and viscosity presented an opposite behavior. SEM revealed that the granular structure of the starch was not completely destructed.

**Jingru Liu et al. 2018** [131] had been investigated the effect of phenyl-terminated hyperbranched polyester (HBPE) with different generation as a special β-nucleating agent on the toughness of isotactic polypropylene (iPP). The proportions of HBP in iPP/HBPE blends were 0.3, 0.7, 1, 2, and 4% by weight. iPP/HBPE blends were prepared by using an internal mixer. The results show that the β nucleating activity of HBPE significantly depends on its concentration and molecular structure. The Kβ values of iPP/HBPE-G1-1% and iPP/HBPE-G4-1% blends are 26.52% and 20.80%, respectively facilitating the π–π interaction between phenyl terminated groups and the helix chains of iPP crystallize on it, and therefore relatively good dispersibility, high β nucleating activity and excellent toughening effect are obtained. The impact strength of iPP was dramatically improved, especially with addition of 1 wt% HBPE-G1.

**Zengheng Hao et al. 2019** [132] had been evaluated the influence of Hyperbranched Polyester on the Isotactic Polypropylene/Graphene Oxide Composites. The GO and GO-H202 percentage was 1% and 5% wt.%. The composites of iPP/GO and iPP/GO-H202 were prepared by using twin-extruder. Results showed that the addition of GO enhanced the nucleation rate and crystallizability of the composites; while GO-H202 exhibited a higher crystallization acceleration effect compared to neat GO. Results of isothermal crystallization showed that both the overall crystallization rate and crystal growth rate increase after the addition of GO and GO-H202, but the crystallization speed of GO-H202 stronger compared to GO.

**Yujuan Jin et al. 2019** [133] had been studied the reinforcing and toughening of poly(propylene carbonate) PPC by epoxy-terminated hyperbranched polymer (EHBPE). The amount of EHBPE in the blend was 0, 0.2, 1, 3 and 5g. The blends were prepared by melt blending method using Internal Mixer. The results indicate that when the content of EHBPE is 0.5 wt%, the tensile strength increased by 73.8%; elongation at break increased by 131.7%; the impact strength increased by 88.4%. The glass transition temperature increased upon addition of EHBPE. It indicates that upon addition of EHBPE, both physical hydrogen bonding and chemical bonding occurred.

**Aldobenedetto Zotti et al. 2020** [134] had been studied the effect of the addition of an aromatic hyperbranched polyester (AHBPE) on mechanical, thermal, and fracture toughness properties of a thermosetting resin system. Bulk poly-condensation reaction was used for the synthesized of AHBPE filler. Three different weight percentages were used to manufacture the AHBPE/epoxy samples 0.1, 1, and 5 wt.%. Results showed that the fracture toughness was improved by adding 5 wt% of AHBPE compared to the neat epoxy matrix. Tg reduced by about 4 °C at 5 wt% of filler content. Static and dynamic compression tests covering strain rates ranging from 0.0008 to 1000 $s^{-1}$ revealed a pronounced strain rate sensitivity for all AHBPE/epoxy systems. The AHBPE composites all showed an increase of the true peak yield compressive strength with the best improvement associated with the sample with 0.1 wt% of AHBPE.

**R Mesias and E A Murillo 2020** [135] had been studied the properties of the thermoplastic starch/polylactic acid blends compatibilized by hyperbranched polyester. One weight ratio 50/50% of starch/polylactic acid was used. HBPE compatibilizer content used were 5 wt%, 10 wt% 15 wt%, and 20 wt%. The blends were prepared in a torque rheometer. Results showed that Torque value decreased with the proportion of compatibilizing. Therefore, the HBPE acted as plasticizer. FTIR analysis showed that the increasing on the compatibilizing content enhanced the intensity of the signals corresponding to OH and C=O groups. XRD and DSC analysis observed a reduction of the crystallinity of the blends obtained with compatibilizing. Rheological analysis was evidenced the formation of a microstructure, which is able to elastically deform.

## 2.13. Conclusions and Remarks

The previous paragraphs covered some of the previous work of many researchers who prepared different types of HBPs and studied their effect on different polymer properties. The researchers' conclusion can be summarized as follows:

1- Several studies focused on the preparation of HBPs using different molar ratios such as 1:1, 1:2, and 1:2.5.

2- Studies focused on the addition of HBPs to polar polymers (PA, PVC, PC, and PET) and nonpolar polymers (PP, LDPE, and HDPE) with different percentages 0.5% to 20%.
3- Some studies focused on the effect of HBPs on the properties of composites such as PP/clay, and PP/nano-GO and other on the properties of blends such as LDPE/TPS, PLA/TPS as compatibilizers.
4- Studies focused on the effect of HBPs on the mechanical, morphological, thermal, and rheological properties. Different results were achieved when the HBPs were added.

In the present study, four novel HBPEs will be prepared using A2+B3 melt polycondensation polymerization, and the effect of the prepared HBPEs on the physical, thermal, and biological properties of PP (VPP, and rPP) will be studied to be used for packaging applications.

## 3.1. Introduction

In this chapter, a detailed description of the experimental methodology is presented, which includes, materials selection, preparation of HBPE polymer, sample preparation methods of blends and detailed description of test instruments used. The flow chart (3 -1) and (3-2) show the experimental part steps for the synthesis of HBPEs and PP/HBPEs blends:

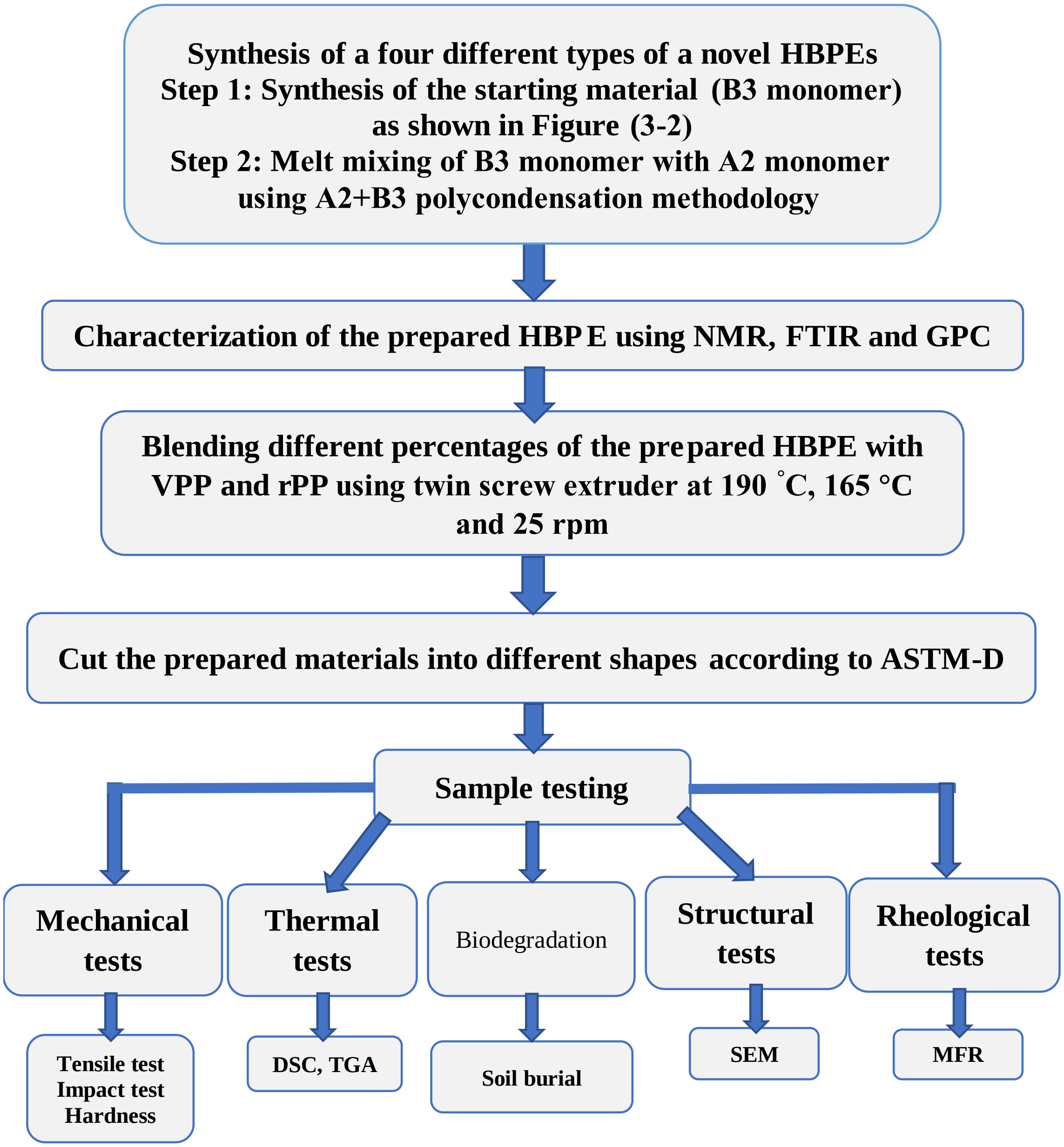


**Figure (3-1): Flow chart of experimental part steps.**

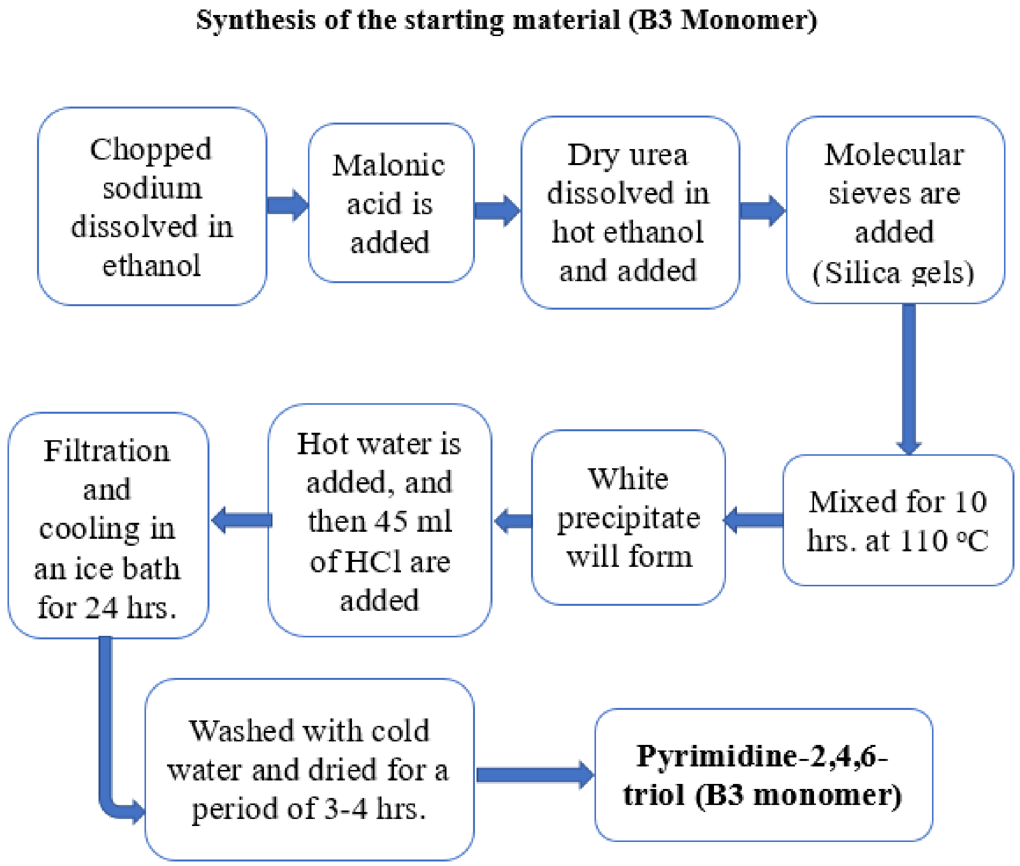


**Figure (3-2): Flow chart for the steps of the synthesis of HBPEs.**

## 3.2. The Materials Used in this Study

Several materials were used in this study, this section include the materials that used for the preparation of the starting material and the materials used for the preparation of hyperbranched polyesters as the minor phase (All the materials used in the synthesizing of Hyperbranched Polyester polymer HBPEs used without purification). All the materials that used for the preparation of the starting material and the HBPE were used in molar ratio and converted into grams by multiplying it is number of moles by molecular weight of each material. In addition, it include the main materials that used for the preparation of polymeric blends as the major phase.

### 3.2.1. The Materials Used for the Synthesis of the Starting Material

#### 3.2.1.1. Ethanol

Ethanol, which is an organic compound with the chemical formula $C_2H_6O$, it is used as solvent in the preparation of the starting material. It is properties and chemical structure are shown in table (3-1).

**Table (3-1): the properties of Ethanol.**

| Property | Value |
|---|---|
| Molar mass | 43.044 (g/mol) |
| Density | 0.78945 (g/cm$^3$) |
| Chemical formula | $C_2H_6O$ |

#### 3.2.1.2. Sodium (Na)

Sodium is a chemical element; it was supplied from the college of science/department of chemistry/University of Babylon. It is used as a catalyst in the synthesis of the starting material B3 monomer. It is properties are shown in table (3-2).

**Table (3-2): The properties of Sodium.**

| Property | Value |
|---|---|
| Appearance | silvery white metallic |
| Density | 0.968 (g/cm$^3$) |
| Melting Point | 97.794 (°C) |

#### 3.2.1.3. Malonic Acid

Malonic acid is a dicarboxylic acid with structure $CH_2(COOH)_2$. It was supplied from the college of science/department of chemistry/University of Babylon. It is used as the first main material in the synthesis of the starting material B3 monomer. It is properties are shown in table (3-3).

**Table (3-3): The properties of Malonic acid.**

| Property | Value |
|---|---|
| Molar mass | 104.061 (g/mol) |
| Density | 1.619 (g/cm$^3$) |
| Melting Point | 135 (°C) |

### 3.2.1.4. Urea

Urea is an organic compound with chemical formula $CO(NH_2)_2$. It was supplied from the college of science/department of chemistry/University of Babylon. It is used as the second main material in the synthesis of the starting material B3 monomer. It is properties are shown in table (3-4).

**Table (3-4): The properties of Urea.**

| Property | Value |
|---|---|
| Molar mass | 60.06 (g/mol) |
| Density | 1.32 (g/cm$^3$) |
| Chemical formula | 133 (°C) |

## 3.2.2. The Materials Used for the Preparation of Hyperbranched Polyester Polymers

### 3.2.2.1. Tartaric Acid

Tartaric acid is a white, crystalline organic compound with the chemical formula $C_4H_6O_6$. It is supplied from Aldrich and Lancaster and used as the A2 monomer for the synthesis of HBPE-TA. The properties and chemical structure are in table (3-5).

### 3.2.2.2. Adipic Acid

Adipic acid is an organic compound with the formula $(CH_2)_4(COOH)_2$. It is supplied from Aldrich and Lancaster and used as the A2 monomer for the synthesis of HBPE-AD. The properties and chemical structure are in table (3-5).

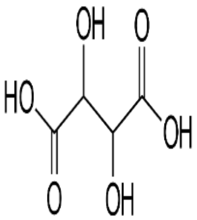
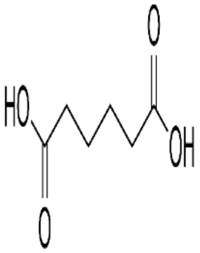
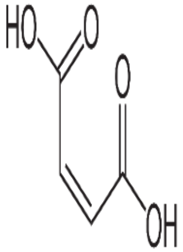
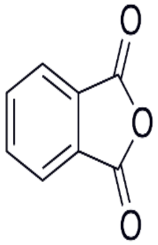
### 3.2.2.3. Maleic Acid

Maleic acid is an organic compound that is a dicarboxylic acid. It is chemical formula is $HO_2CCH=CHCO_2H$. It is supplied from Aldrich and Lancaster and used as the A2 monomer for the synthesis of HBPE-MA. The properties and chemical structure are in table (3-5).

### 3.2.2.4. Phthalic Anhydride

Phthalic anhydride is an organic compound with the formula $C_6H_4(CO)_2O$. It is supplied from Aldrich and Lancaster and used as the A2 monomer for the synthesis of HBPE-PA. The properties and chemical structure are in table (3-5).

**Table (3-5): The properties of materials used for the synthesis of HBPEs.**

| Material / Property | Tartaric acid | Adipic acid | Maleic acid | Phthalic anhydride |
|---|---|---|---|---|
| **Mw (g/mol)** | 150.087 | 146.142 | 116.072 | 148.1 |
| **Density (g/cm$^3$)** | 1.79 | 1.36 | 1.59 | 1.53 |
| **Melting point °C** | 148 | 152.1 | 135 | 131.6 |
| **Chemical formula & structure** | $C_4H_6O_6$<br> | $C_6H_{10}O_4$<br> | $C_4H_4O_4$<br> | $C_8H_4O_3$<br> |

### 3.2.3. The Materials Used for Blend Preparation

#### 3.2.3.1. Virgin Polypropylene (VPP)

Polypropylene used as major phase material in the preparation of polymer blend provided from Saudi Basic Industries Corporation (Subic). The physical and mechanical properties of VPP are shown in Table (3-6).

**Table (3-6): The physical and mechanical properties of VPP.**

| Property | Test method | Data | Unit |
|---|---|---|---|
| **Tensile Strength** | ASTM D-638 | 35-37 | MPa |
| **Elastic Modulus** | ASTM D-638 | 0.12-0.13 | GPa |
| **Density** | ASTM D-1505 | 0.89-0.90 | Kg/m$^3$ |
| **MFR** | ASTM D-1238 | 9 | g/10 min |

#### 3.2.3.2. Waste Polypropylene (rPP)

The waste polypropylene is provided from the recycling of food containers from houses and shops. The physical and mechanical properties of this polymer are shown in Table (3-7).

**Table (3-7): The physical and mechanical properties of rPP.**

| Property | Test method | Data | Unit |
|---|---|---|---|
| **Tensile Strength** | ASTM D-638 | 20-30 | MPa |
| **Elastic Modulus** | ASTM D-638 | 0.12-0.13 | GPa |
| **Density** | ASTM D-1505 | 0.87 | Kg/m$^3$ |
| **MFR** | ASTM D-1238 | 25 | g/10 min |

## 3.3. The Synthesis of the Starting Material (Pyrimidine-2,4,6-triol B3 monomer) (Equation 1)

For the synthesis of the starting material, 11.5 g of chopped sodium was dissolved in 250 ml of ethanol using an Erlenmeyer flask with a glass condenser protected by a calcium chloride tube. Then a 0.5 mol (52.03) g of malonic acid was added to the mixture followed by a 0.5 mol (30.03) g of dry urea dissolved in 250 ml of hot ethanol. A 20 g of molecular sieves was added then to the mixture. Subsequently, the ingredients were mixed for 10 hours at a temperature of 110 °C and after completion, a white precipitate was formed. Then a 500 ml of hot water at 50 °C was added followed by a 45 ml of HCl. The mixture was cooled in an ice bath for 24 hrs. then filtered and washed with 50 ml of cold water and dried at a temperature of between 105-110 °C for a period of 3-4 hrs [136, 137]. The final product (Pyrimidine-2,4,6-triol) was used as a raw material for the polymerization process. Figure (3-3) shows a sketch for the synthesis of the starting material.

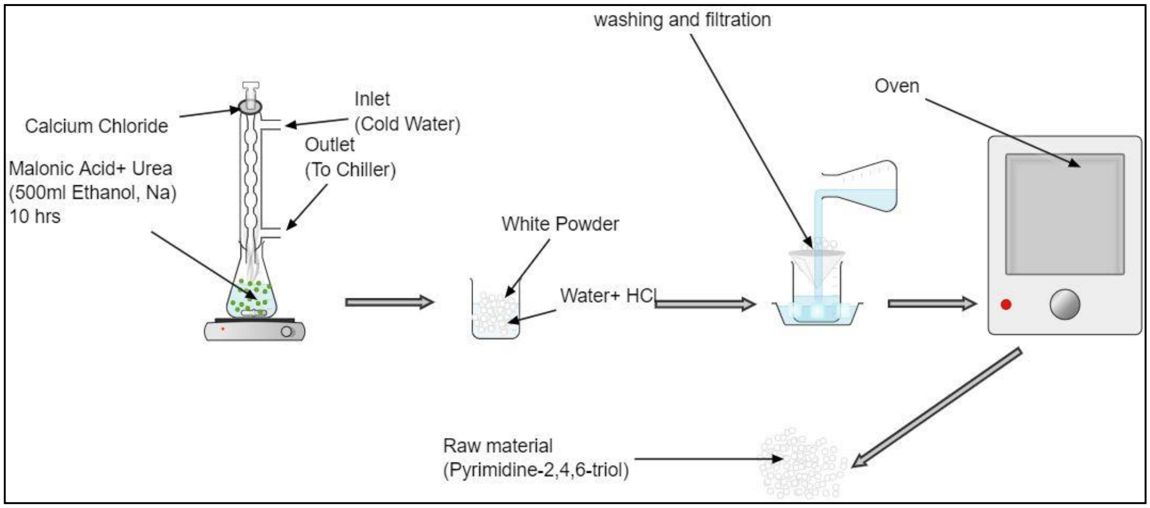
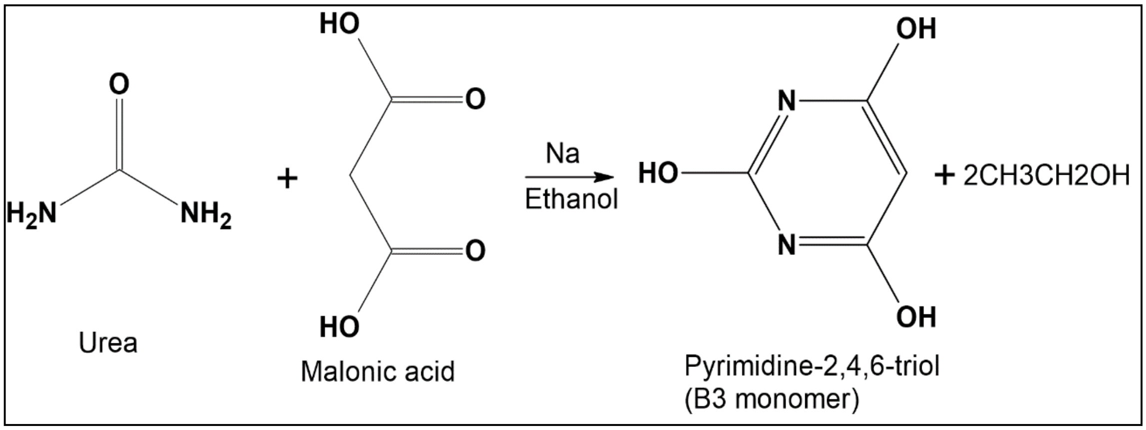


**Figure (3-3): the steps for the synthesis of the starting material.**



**Equation 1: The synthesis of pyrimidine-2,4,6-triol.**

## 3.4. The Synthesis of Hyperbranched Polyester Polymer HBPEs (Equation 2-5)

For the synthesis of HBPE, A2+B3 methodology melt polycondensation used. 0.2 mol (25.6g) of the white precipitate (pyrimidine-2,4,6-triol compound) was mixed with 0.3 mol (45 g) tartaric acid TA in a round bottom flask set over an oil bath. The bath temperature was steadily increased to 170°C and then held at 160 °C for 4 hours. A continuous mixing was used until the reactants were fully melted producing a pale brown material (Hyperbranched Polyester Polymer HBPE-TA) equation 2 as shown by Figure (3-5).

The same procedure was used for the preparation of the other three hyperbranched polymers with some difference in the amount of materials and the temperature depending on the melting temperature and molecular weight of these materials as shown in the table (3-8). The structure and reaction between the starting material (pyrimidine-2,4,6-triol) B3 monomer compound and the other four A2 monomers (tartaric acid TA, adipic acid AD, maleic acid MA, and phthalic anhydride PA) are shown by equation 3 to equation 5 and Figure (3-5). Figure (3-4) show a sketch for the synthesis of all HBPEs polymers.

**Table (3-8): The conditions and amount of materials used for the synthesis of HBPEs.**

| Material | Starting material B3 monomer (g) | A2 monomer (g) | Temperature (°C) | Color |
|---|---|---|---|---|
| **HBPE-TA** | 25.6 | 45 | 160 | Pale brown |
| **HBPE-AD** | 25.6 | 44.8 | 170 | Pale brown |
| **HBPE-MA** | 25.6 | 35.8 | 150 | Pale yellow |
| **HBPE-PA** | 25.6 | 45 | 150 | Pale yellow |

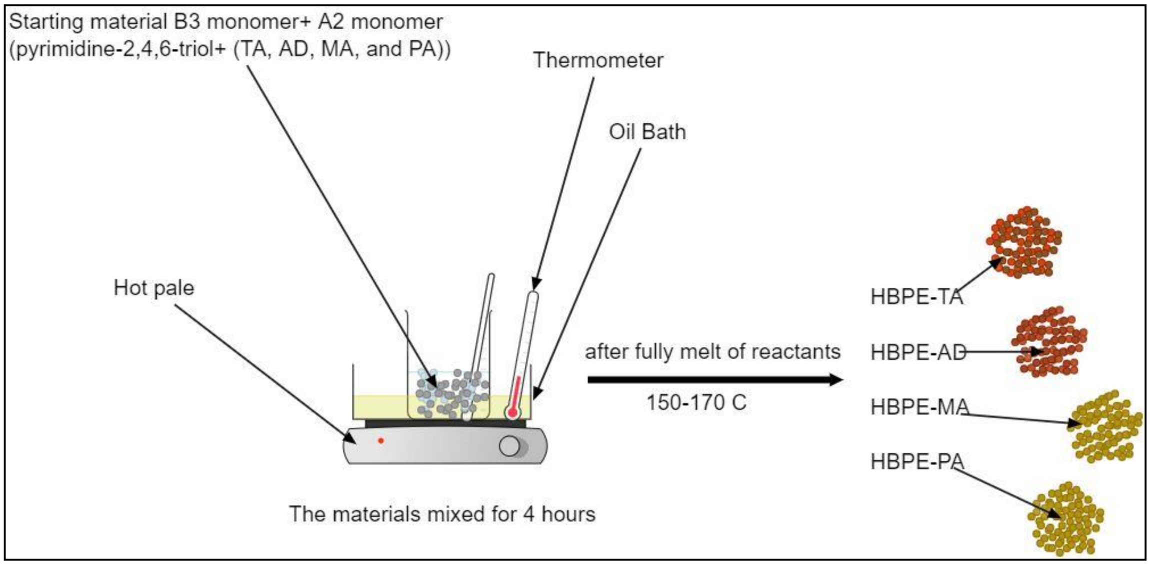
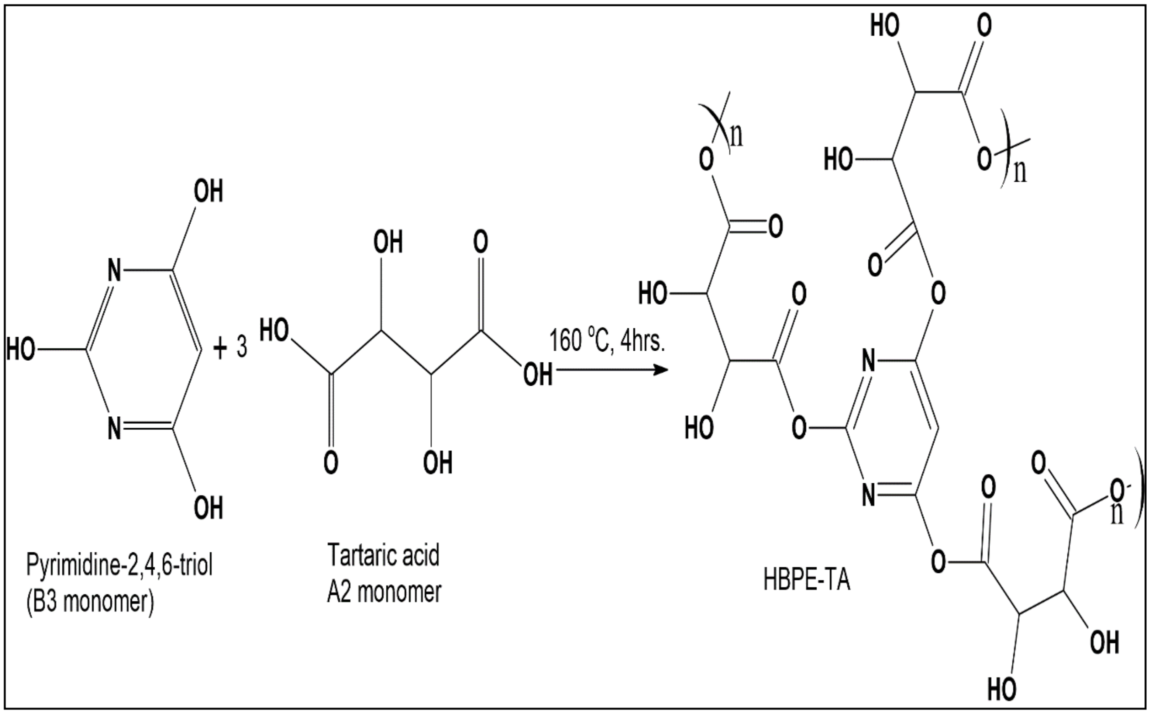
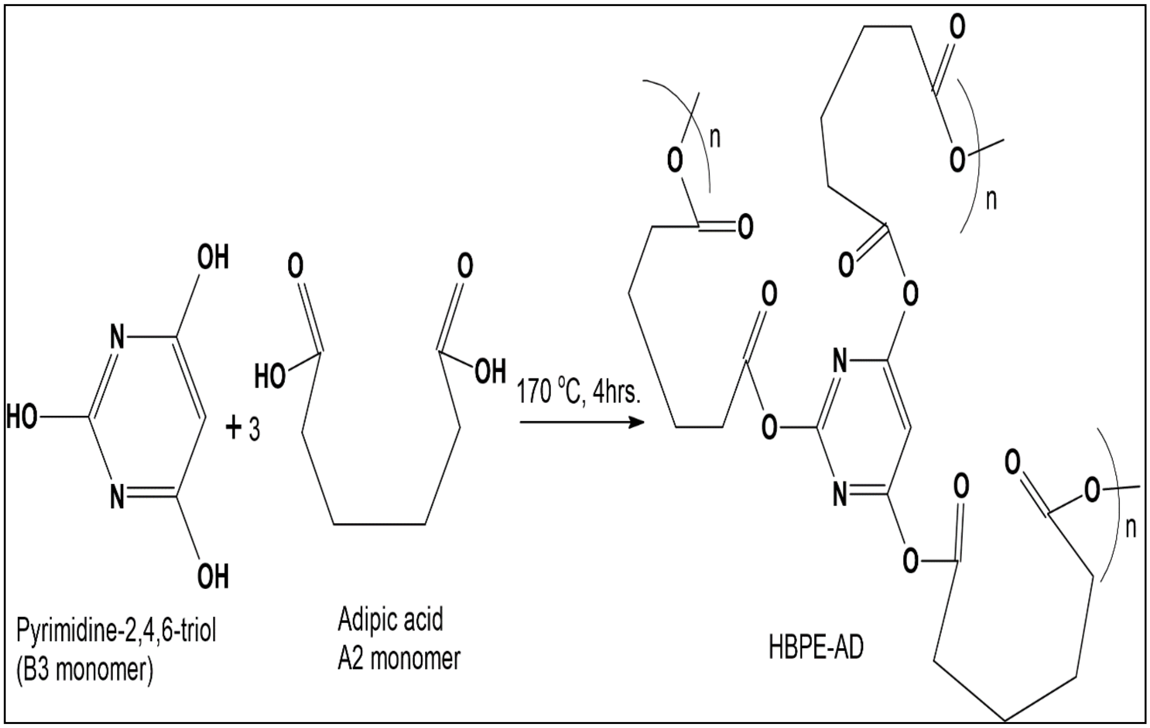


Figure (3-4): the synthesis of HBPEs.

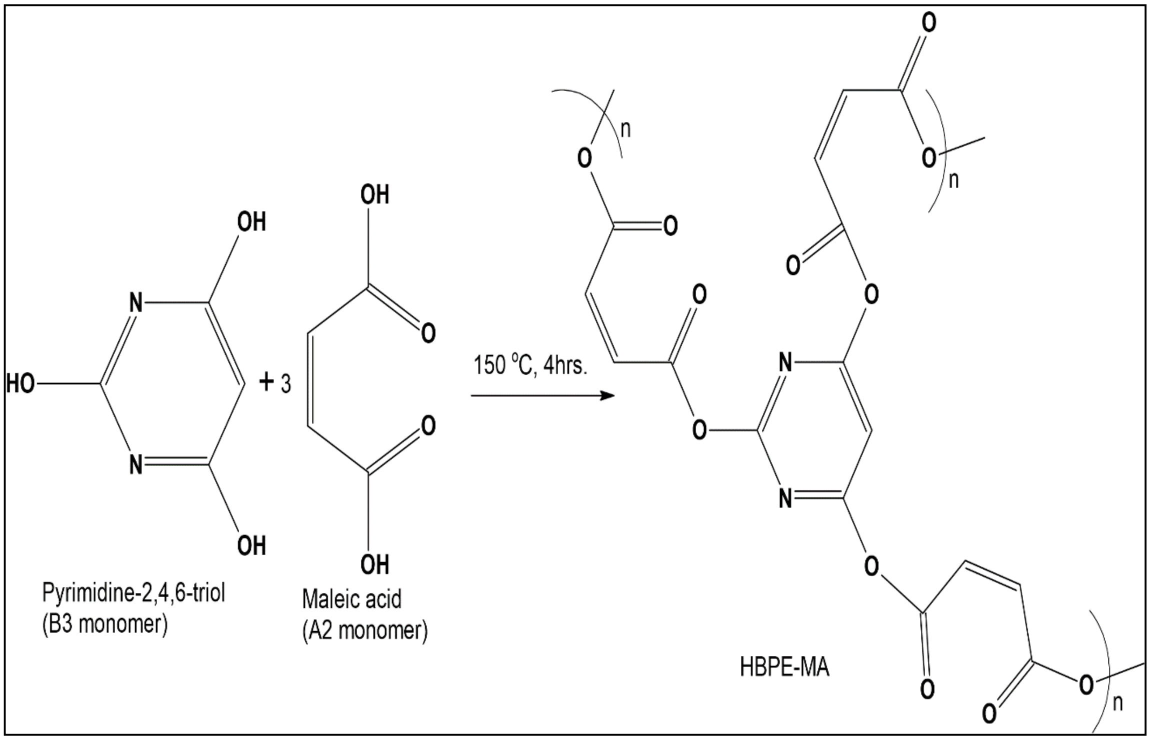
Figure (3-5): The prepared Hyperbranched polymers.



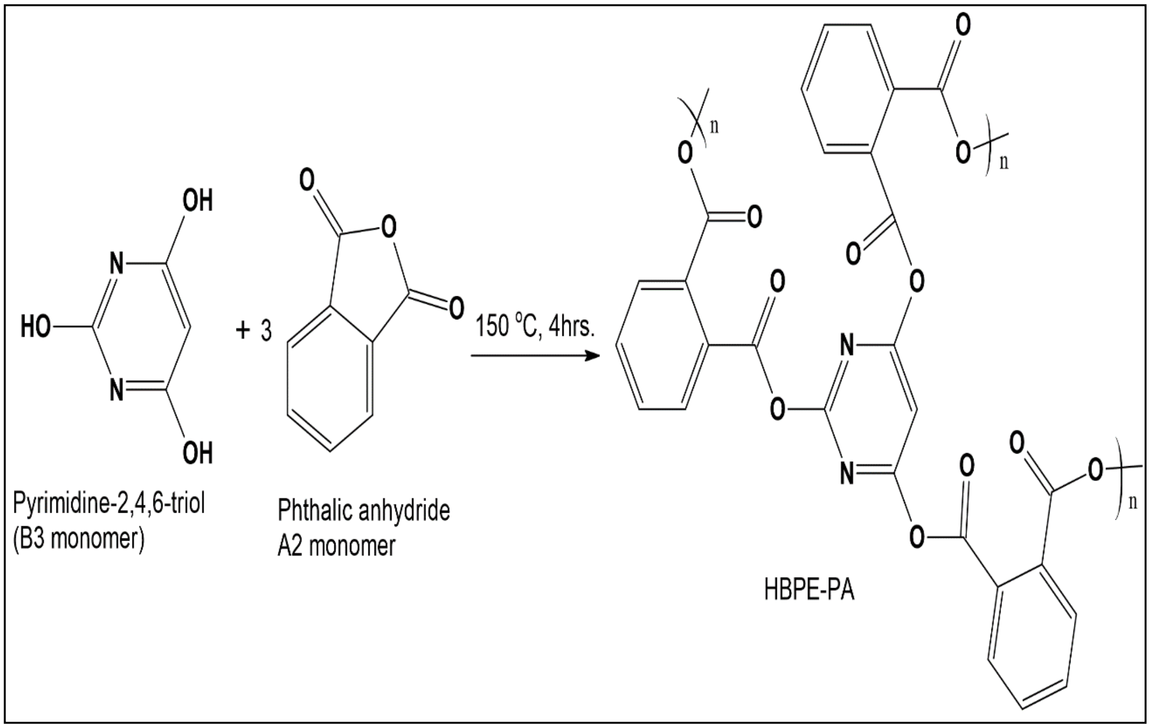
Equation 2: The synthesis of Hyperbranched polyester polymer (HBPE-TA).



Equation 3: The synthesis of Hyperbranched polyester polymer (HBPE-AD).



**Equation 4: The synthesis of Hyperbranched polyester polymer (HBPE-MA).**



**Equation 5: The synthesis of Hyperbranched polyester polymer (HBPE-PA).**

## 3.5. Preparation of Polymer Blends

### 3.5.1. Weighting

VPP, rPP material pellets and the four kinds of the prepared HBPEs were weighted according to the selected ratios shown in table (3-8) to prepare the batches for Extrusion.

### 3.5.2. Mixing

For optimum distribution, VPP, rPP material and HBPEs mixed according to the ratios that shown in table (3-9) in dry condition at room temperature by using a mechanical stirrer.

### 3.5.3. Extrusion

Forming process was carried out using a twin-screw extruder model (SLJ-30A) which is available in laboratory of Materials Engineering college /University of Babylon. The mixed materials were fed from a hopper on the screw. The materials then conveyed along the barrel where it is heated by conduction from the barrel heaters and shear due to its movement along the screw flight. The depth of the twin-screw channel is reduced along the length of the screw so as to compact the material. At the end of the extrusion, the melt passes through a die in the form of sheet. The extruder operation conditions were 25 rpm in the beginning then increased to 50 of screw speed. The temperatures used for zones 1 and 2 were 190-180˚C for preparing VPP/HBPEs blends and 165- 155 ˚C for preparing rPP/HBPEs blends respectively. Figure (3-6) shows a cross section of twin-screw extruder and Table (3-10) shows the specifications of twin-screw extruder used for blend preparation.

**Table (3-9): Polymeric blends percentages.**

| VPP | | | | |
|---|---|---|---|---|
| **PP (wt.%)** | **HBPE-TA (wt.%)** | **HBPE-AD (wt.%)** | **HBPE-MA (wt.%)** | **HBPE-PA (wt.%)** |
| 100 | - | - | - | - |
| 95 | 5 | 5 | 5 | 5 |
| 90 | 10 | 10 | 10 | 10 |
| 80 | 20 | 20 | 20 | 20 |
| **rPP (wt.%)** | | | | |
| 100 | - | - | - | - |
| 95 | 5 | 5 | 5 | 5 |
| 90 | 10 | 10 | 10 | 10 |
| 80 | 20 | 20 | 20 | 20 |

### 3.5.4. Rolling and cutting

After the material melts and out from the extruder, it passes through two co-rotating rollers that pressurize the material to give high molecular orientation and eliminate from any voids.

The samples are cut according to required shapes by using laser CNC machine Chinese device at Al-Warith Furniture Company, Karbala. Cutting was done according to international standard specifications (ASTM) for tensile and impact test as shown in Table (3-11).

**Table (3-10): Twin-screw extruder specifications.**

| Specifications of the twin-screw extruder | Data |
|---|---|
| Model | SLJ – 30 A |
| Diameter of screw | 30mm |
| Speed of screw | 0 to 320 rpm |
| Output | 20 Kg / h |
| Weight | 450 Kg |
| Screw length | 16D |
| Screw design | Double screw |
| Place of origin | Shandong - China |
| Certification | ISO9001 |

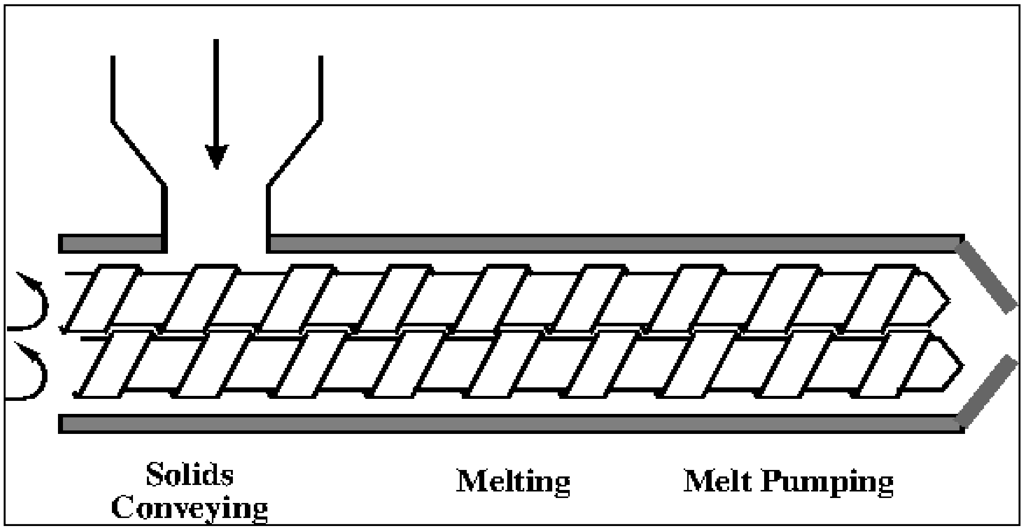
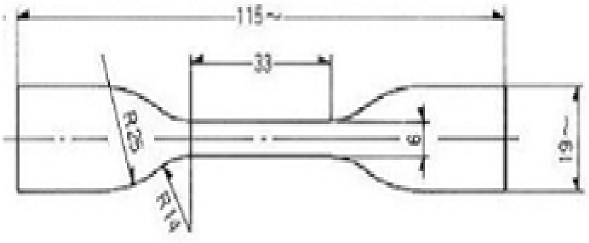
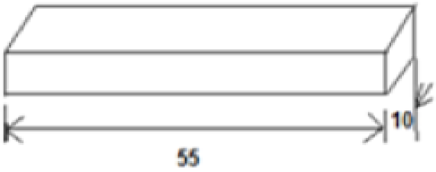


**Figure (3-6): Co-rotating twin-screw extruder diagram**[138].

**Table (3-11): The standard sample dimensions.**

| **Property** | **Sample** | **ASTM** |
|---|---|---|
| **Tensile** |  | **D 638** |
| **Impact** |  | **D 256-87** |

## 3.6. Characterization of Hyperbranched Polyester Polymers (HBPEs)

### 3.6.1. Nuclear Magnetic Resonance ($^1$H-NMR)

The $^1$H-NMR analysis was carried out on a Bruker DRX-300Hz at the Ferdowsi University/Iran spectrometer operating at 300 MHz for $^1$H measurements. 5 mg of sample was dissolved in DMSO-*d6*. Chemical shifts were referenced to DMSO-*d6* at 2.5 ppm for the $^1$H-NMR spectra.

### 3.6.2. Fourier Transform spectroscopy (FTIR)

Fourier transform infrared spectra technique is used for the characterization of the prepared samples. Instrument, type IR Affinity-1 (made in Japan), which is available in laboratory of Materials Engineering college /University of Babylon, was used for this purpose. In order to measure a sample, calibrate the device using the KBr, and then prepare powder of the sample to be examined, and mixed with KBr (mixing ratio 99% KBr). The mixing process achieved thoroughly then pressed as tablet-shaped semi-transparent to the possibility of penetrating radiation.

### 3.6.3. Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC; Shimadzu, Japan) with a refractive index detector which is available in Iran was used to characterize the molecular weight of the prepared hyperbranched polyester polymers. Samples were prepared in THF solvent at a 5 mg/mL concentration. The flow rate of the mobile phase was kept at 1.0 mL/min. The instrument was calibrated with polystyrene standards.

## 3.7. Characterization of Polymer Blends (PP/HBPEs)

### 3.7.1. Tensile Test

The machine used for the testing of tensile properties is micro computer controlled electronic universal testing machine model (WDW-5E) China, located in the laboratory of Materials Engineering college/University of Babylon, according ASTM-D 638. Three samples are tested and the mean values were considered. The test was conducted at applied load (5KN) and speed value (10 mm/min) for all the samples at room temperature. Tensile stress was applied until the failure of the sample and stress-strain curve was obtained. All the results for tensile strength, elastic modulus and elongation at break were achieved from the device.

### 3.7.2. Charpy Impact Test

Charpy impact strength was determined using tester Model WP 400 German, Gunt (HAMBURG) Company, located in the laboratory of Materials Engineering college/University of Babylon according to ASTM D-256 as shown in table (3-11). The testing method of this instrument includes lifting of the pendulum to its maximum height and fixing it firmly .The specimen is fixed in its pertaining place, and then the energy gauge is initialized (on zero position) after that, the pendulum is freed where its potential energy would be changed to kinetic energy, three sample are tested and then take the average of these values. Impact strength (I.S.) is calculated by applying the relationship as shown in equation (3.1) [139].

$$\mathbf{I.S = U_C/A} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(3.1)}$$

**Where:-**

**I.S:** impact resistance of the material (J/m$^2$).

**U$_C$:** impact energy (J).

**A:** cross-sectional area of the sample (m$^2$).

### 3.7.3. Shore D Hardness

Shore D hardness device model (TH 210 FJ) made in Germany, which is available in laboratory of Materials Engineering College /University of Babylon. Cylindrical samples were prepared according to the ASTM D 2240. Shore instrument is similar to compass containing needle placed in a position perpendicular to the sample and it takes waiting 10-15 sec to read the value and to have some accuracy an average of three readings have to be taken in different locations and at different points for each sample.

### 3.7.4. Differential Scanning Calorimetry (DSC)

The thermal characteristics of blend samples were evaluated using a differential scanning calorimetry DSC type TA-60 WS instrument (Shimadzu, Japan) which is available in laboratory of Materials Engineering College /University of Babylon. The samples with an average weight of (8-10±0.5) mg were mounted in aluminum pans and heated at a heating rate of 10 °C/min from 30 to 250 °C, then cooled down at the same rate from 250 to 30 °C under an inert gas. Equation (3.2) was used to estimate the degree of crystallinity ($X_c$) of the blends [140].

$$X_c = (\Delta H_m / \Delta H_o * W_f) * 100\ \% \quad \text{..............................} (3.2)$$

**Where:-**

**$\Delta H_m$**: melting enthalpy as determined by DSC, **$\Delta H_o$**: melting enthalpy, which is (209 J/g) of fully crystalline PP[141], and **$W_f$**: weight fraction percentage of PP in the blend.

### 3.7.5. Thermogravimetric Analysis (TGA)

The thermal stability of the blends was studied using Thermogravimetric analysis TGA model Pyris 1 instrument (Perkin Elmer, USA) which is available in Amirkabir University of Technology (Tehran Polytechnic ). The samples were heated at a heating rate of 10 °C/min from 30 to 800 °C under nitrogen atmosphere with an average weight of (5-10±0.5) mg.

### 3.7.6. Field Emission Scanning Electron Microscopy (FESEM)

The Field Emission Scanning electron microscope (FESEM) model (ZEISS) which found in Amirkabir University of Technology (Tehran Polytechnic) used to examine the morphology of polymer blends and to identify the distribution of HBPE polymer within PP matrix. The fractured samples from tensile test were tested using SEM. To obtain good electric conductivity, all samples were first coated with thin layer of gold, which has been made from the surface along the edge using sputtering device.

### 3.7.7. Melt Flow Rate (MFR)

Melt index device (SHI JIA ZHUANG ZHONG SHI TESTING MACHINE CO., LTD) based on International Standard (ISO 1133:2005) is used to measure the melt flow rate (MFR) of pure polymers and their blends through capillary die with diameter of 2.095mm and length 8mm. The melt flow rate has been tested at 230 ºC temperature and 2.16 Kg load. 4 grams of each sample has been taken and inserted in the device and preheated for 6 min and then the load is applied. The extruded material then cut into three pieces during specific intervals (10 sec), and then the average of these pieces has been taken and inserted into the device to give the melt flow rate MFR using the following equation (3.3):

$$MFR=t_{ref}*w/t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.3)$$

**Where:-**

$t_{ref}$ =600 sec, **t**= time (sec), **w**= average weight of of sample (g).

In addition, the viscosity and shear rate can be calculated using the below equations:

$$\eta=4.98*10^4*\rho*L/MFR \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.4)$$

$$\dot{\gamma}_w= (1840/\rho) * MFR \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.5)$$

**Where: -** $\dot{\gamma}_w$= Shear rate at the wall ($s^{-1}$), **ρ**= Density ($kg/m^3$) [142].

### 3.7.8. Contact Angle

The wettability of PP (VPP, rPP) and its blends with HBPE at different wt. % percentages have been investigated using the device, SL 200C - Optical Dynamic I Static Interfacial Tensiometer & Contact Angle Meter, which using circle fitting method of water on samples surface. The tested data have been collected at two intervals after 3 sec and 60 sec. The aim of this test is to study the effect of the HBPE on the wettability of polypropylene PP.

### 3.7.9. Biodegradation (Soil burial) test

The effect of burial in the soil on the biodegradation behavior of VPP, rPP, and VPP/HBPE, rPP/HBPE blends were examined according to ASTM-D 5988, soil burial test was carried out on a laboratory scale. The degradation phenomenon was evaluated through weight loss.

The samples were cut into specific sizes and placed in an oven at 80 °C for 24 hours before being buried in the soil. Then the samples were buried in the soil with pH 7.56 at a distance of 10 cm from the surface for 90 days and thus undergo to the action of microorganisms in which soil is their major resident, where the samples were taken out every 10 days and washed with distilled water and dried for 24 hours at a temperature of 80 °C before being weighed.

The weight loss was determined every 10 days from the starting day, and was calculated using the below equation [143]:

$$\% \text{ weight loss} = [W_b - W_a)/W_b] * 100 \ldots\ldots\ldots\ldots\ldots (3.6)$$

Where $W_b$ and $W_a$ are initial mass before and after degradation in the soil respectively.

## 4.1. Introduction

This chapter includes all the experimental results that are obtained from the mechanical and physical tests for the prepared HBPE polymer and its blends under investigation. It includes the description of the effect of HBPE polymer on the mechanical, thermal, rheological and morphological behavior of virgin and waste PP.

The results of the prepared HBPE polymer including (FTIR, NMR, and GPC) have been presented. Moreover, the results of the blends system were also investigated. The mechanical properties such as (tensile strength, modulus, and elongation at break, Impact strength, and hardness). In addition, the structural and thermal properties results including (Fourier transforms spectroscopy FTIR, differential scanning calorimeter DSC and thermo-gravimetric analysis TGA). The rheological properties using MFR and the most important the morphology for polymer blend were performed by scanning electron microscopy SEM. In addition, the water contact angle and the biodegradation of blends in soil burial were also investigated.

In this chapter, the results of all samples that have been selected for polymer blend systems are presented:

- **VPP/ HBPE-TA, rPP/ HBPE-TA.**
- **VPP/ HBPE-AD, rPP/ HBPE-AD.**
- **VPP/ HBPE-MA, rPP/ HBPE-MA.**
- **VPP/ HBPE-PA, rPP/ HBPE-PA.**

In the current chapter, the results that have been obtained from the tests mentioned in chapter three are discussed.

## 4.2. Characterization of Hyperbranched Polyester Polymers HBPEs

### 4.2.1. FTIR Analysis

Figure (4-1) to Figure (4-5) show the FTIR spectrums of the pyrimidine-2,4,6-triol (raw materials) and the four types of the prepared HBPE. Figure (4-1) shows the FTIR of raw materials (pyrimidine-2,4,6-triol). It is shown from Figure (4-1) that the bands values at 3332.99 cm$^{-1}$ and 3209.55 cm$^{-1}$ are for OH group. The band at 1651.07 cm$^{-1}$ is for C=N and the band at 1419.81 cm$^{-1}$ is for Ar(C-C), and the bands at 1249.87 cm$^{-1}$ is for C-O stretch, the band at 1157.87 cm$^{-1}$ is for CH wagging,  and the band at 1095.57 cm$^{-1}$ is for C-O stretch (R2CHOH). The band at 995.27 cm$^{-1}$ is for (=CH) out of plane. The bands at 740.67 and 702.09 are for (N-H) and (C-H) out of plane.

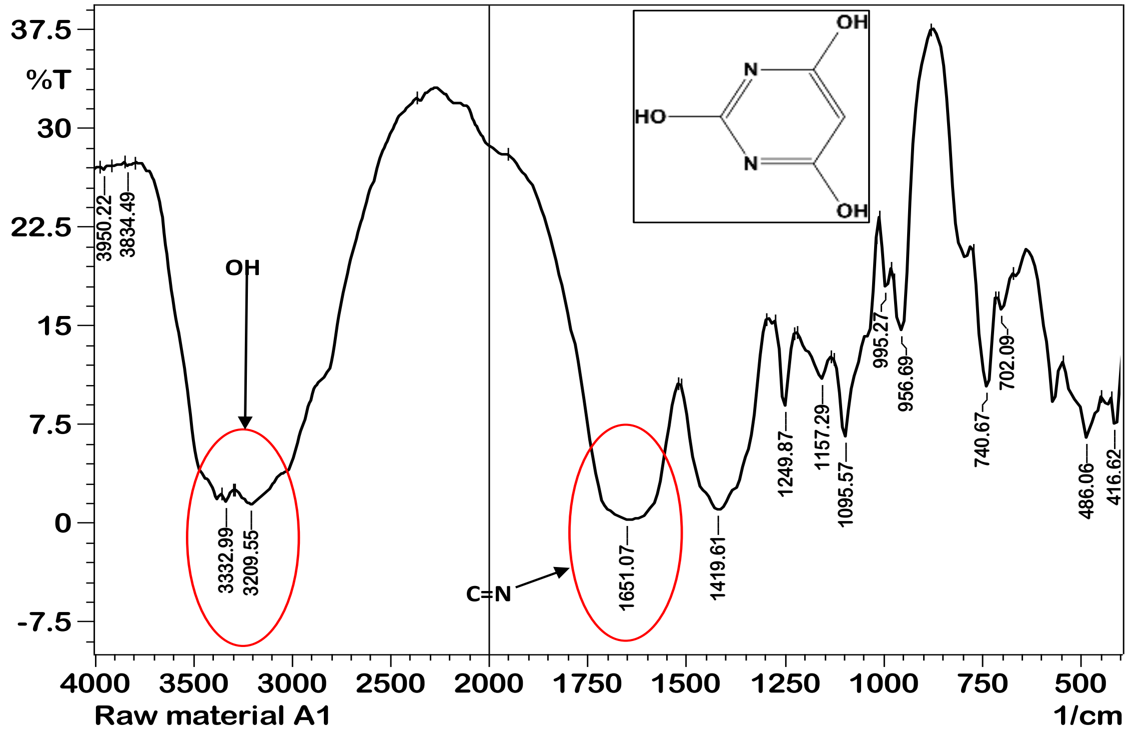


Figure (4-1): FTIR of pyrimidine-2,4,6-triol (raw material).

Figure (4-2) shows the FTIR spectrum of HBPE-TA. It is shown from Figure (4-2) that the band values at 3410.15 cm$^{-1}$ and 3224.98 cm$^{-1}$ for O-H stretch, the band at 3101.54 cm$^{-1}$ for OH dimer. The band at 2877.79 cm$^{-1}$ is for aliphatic CH stretch, and the band at 1712.79 cm$^{-1}$ is for dimer C=O, while the band at 1419.61 is for Ar (C-C) stretch. Also, the band at 1365.60 cm$^{-1}$ and 1350.17 cm$^{-1}$ is for C-H rocking. While the band at 1249.87 cm$^{-1}$ is for C-O stretch esters (RCOOR'), and the band at 1195.87 cm$^{-1}$ is for C-O stretch phenol Ar(OH). The bands at 1134.14 cm$^{-1}$ is for C-O-C stretch, the band at 1087.85 cm$^{-1}$ is for C-O stretch, and the band at 1033 cm$^{-1}$ is for C-O stretch (R2NH), while the bands at 802.39 cm$^{-1}$ and 771.53 cm$^{-1}$ are for CH out of plane (Ar tri-sub.) and the band at 732.95 cm-1 is for C-H out of plane(Ar mono-sub.), and the bands at 663.51 cm-1 and 632.65 cm-1 are for C-H bend.

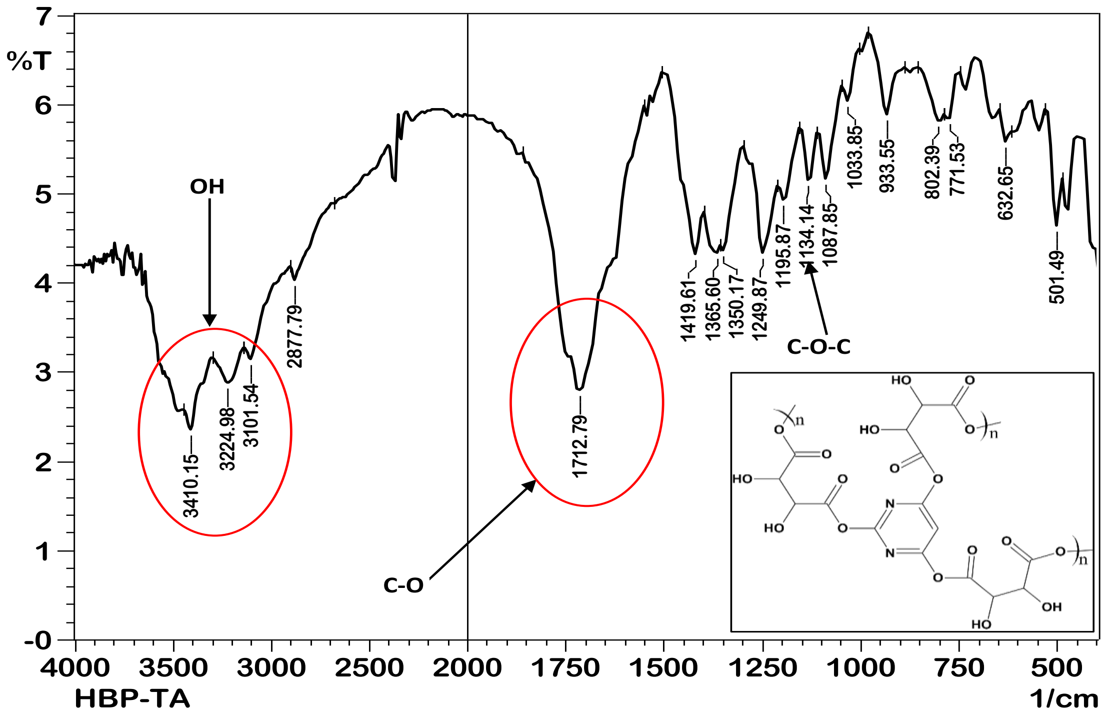


**Figure (4-2): FTIR of Hyperbranched Polyester Polymer with Tartaric acid HBPE-TA.**

Figure (4-3) shows the FTIR spectrum of HBPE-AD. It is shown from Figure (4-3) that the band at 3479.58 cm$^{-1}$ is for OH stretch, and the bands at 3186.4 cm$^{-1}$ and 3101.54 cm$^{-1}$ are for OH dimer. While the band at 2962.66 cm$^{-1}$ is for $CH_2$ stretch and the band at 2877.79 cm$^{-1}$ is for aliphatic CH stretch. The band at 1697.36 cm$^{-1}$ is for C=O stretch and the band at 1419.61 cm$^{-1}$ is for Ar(C-C) stretch. In addition, the band at 1350.17 cm$^{-1}$ is for C-H rocking, and the bands at 1280.73 cm$^{-1}$ is for C-N stretch, 1195.87 cm$^{-1}$ is for C-O stretch, and 1033.85 cm$^{-1}$ are for C-O stretch. The other band at 925.83 cm$^{-1}$ is for O-H bend (RCOOH), and the bands at 771.53 cm$^{-1}$ is for is for C-H out of plane (Ar tri-sub.) and at 732.95 cm$^{-1}$ is for C-H out of plane (Ar mono-sub.), the band at 686.66 cm$^{-1}$ is for =CH out of plane, and the band at 632.65 cm$^{-1}$ is for C-H bend.

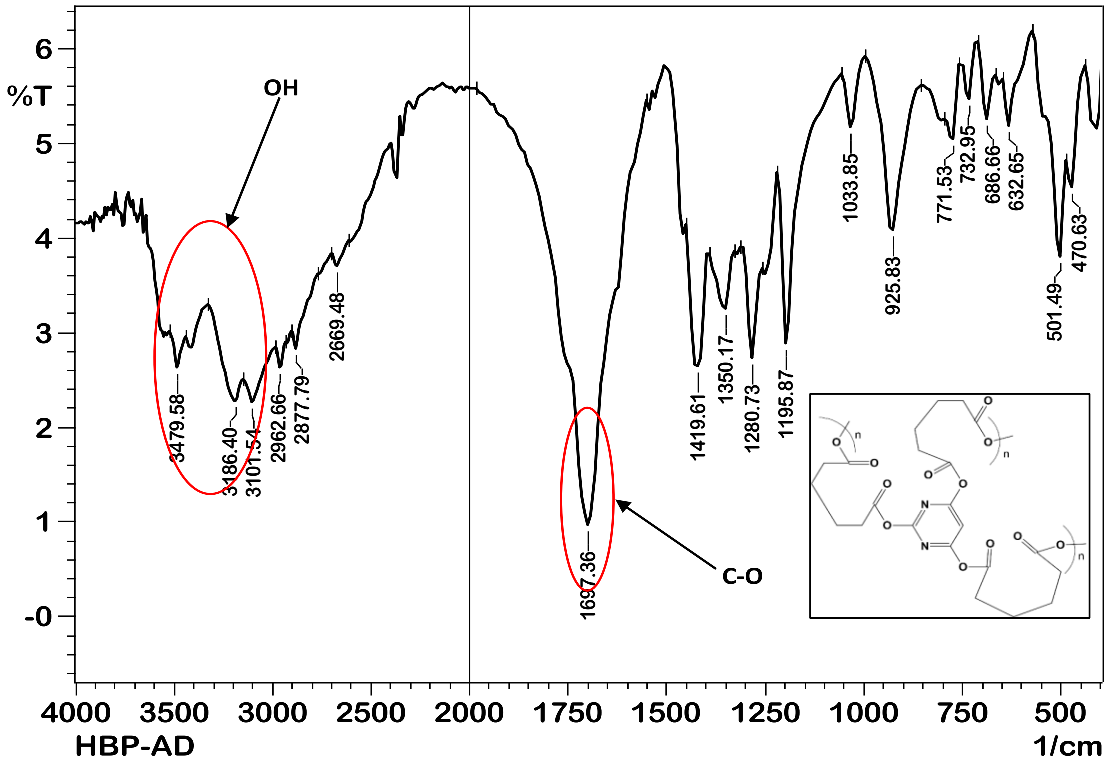


**Figure (4-3): FTIR of Hyperbranched Polyester Polymer with Adipic acid HBPE-AD.**

Figure (4-4) shows the FTIR spectrum of HBPE-MA. It is shown from Figure (4-4) that the bands at 3479.58 cm$^{-1}$ and 3417.89 cm$^{-1}$ are for OH stretch, and the bands at 3201.83 cm$^{-1}$ and 3062.96 cm$^{-1}$ are for OH dimer bonded. While the band at 2877.79 cm$^{-1}$ is for aliphatic CH stretch, and the band at 1705.07 cm$^{-1}$ is for C=O stretch. The band at 1635.64 cm$^{-1}$ is for N-H bend out of plane. The bands at 1589.34 cm$^{-1}$ and at 1427.32 cm$^{-1}$ are for Ar.(C-C) stretch. In addition, the band at 1373.32 cm$^{-1}$ for $CH_2$, and the bands at 1257.59 cm$^{-1}$ is for C-N stretch and at 1033.85 cm$^{-1}$ is for C-O stretch for esters, while the band at 933.11 is for OH bend of (RCOOH). The other bands at 864.11 cm$^{-1}$ and 779.24 cm$^{-1}$ are for Ar. C-H out of plane, and bands at 632.65 cm$^{-1}$ and 609.51 cm$^{-1}$ are for C-H bend.

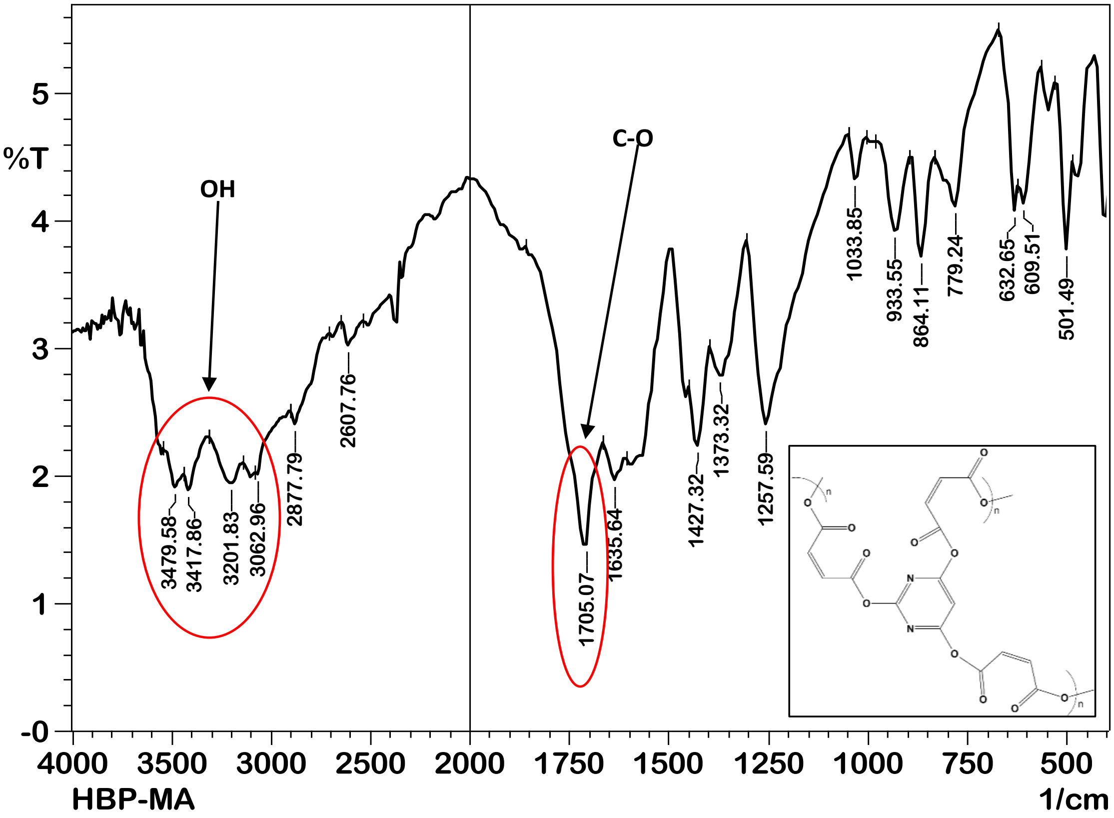


**Figure (4-4): FTIR of Hyperbranched Polyester Polymer with Maleic acid HBPE-MA.**

Figure (4-5) shows the FTIR spectrum of HBPE-PA. It is shown from Figure (4-5) that the band at 3479.58 cm$^{-1}$ is for O-H stretch, and the band at 3194.12 cm$^{-1}$ and at 3101.54 cm$^{-1}$ are for OH dimer. While the band at 2877.79 cm$^{-1}$ is for aliphatic CH stretch, and the band at 1759.08 cm$^{-1}$ is for C=O stretch symmetric (anhydrides RCO-O-COR'). In addition, the band at 1697.36 cm$^{-1}$ is for C=N, and the band at 1411.89 cm$^{-1}$ is for Ar(C-C) stretch, while the band at 1350.17 cm$^{-1}$ is for C-H rocking. Also the band at 1257.59 cm$^{-1}$ is for esters C-O stretch (RCOOR'), and the band at 1111.89 cm$^{-1}$ is for C-O-C stretch, and the bands at 1072.42 cm$^{-1}$ , and 1033 cm$^{-1}$ are for C-O stretch. The other bands at 910.40 cm$^{-1}$ and 794.67 cm$^{-1}$ are for =CH out of plane, and the bands at 740.67 cm$^{-1}$ and 709.80 cm$^{-1}$ are for Ar (C-H) out of plane, while the bands at 671.23 cm$^{-1}$ and 632.65 cm$^{-1}$ are for C-H bend.

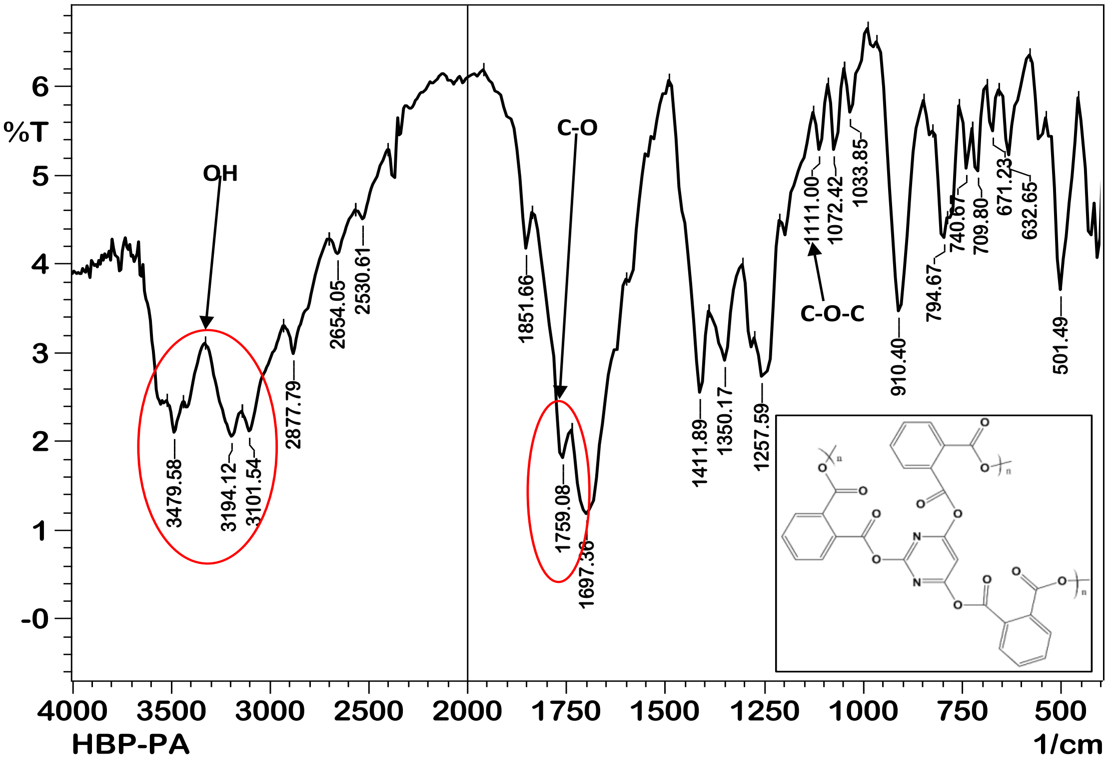


**Figure (4-5): FTIR of Hyperbranched Polyester Polymer with Phthalic anhydride HBPE-PA.**

### 4.2.2. $^1$H-NMR Analysis

In order to further confirm the chemical structure of the starting material (pyrimidine-2,4,6-triol) and the four types of prepared HBPEs (HBPE-TA, HBPE-AD, HBPE-MA and HBPE-PA), the $^1$H-NMR measurements were performed. The data of $^1$H-NMR confirmed the structure of the raw material (pyrimidine-2,4,6-triol) and HBPE polymers.

Figure (4-6) shows the $^1$H-NMR of pyrimidine-2,4,6-triol, it is shown that DMSO-*d*6 signal was seen at 2.4 ppm. The signals at 4.162-4.315 ppm attributed to (S, 1H, imidic OH), signal at 8.499 ppm (S, 1H, CH pyrimidine), and the signal at 10.165 ppm related to (S, 1H, phenolic OH). The disappearance of this signal (10.165 ppm) from the $^1$H-NMR is an indication that there is a chemical interaction occur between the starting material (B3 monomer) and the other materials TA, AD, MA, and PA (A2 monomer).

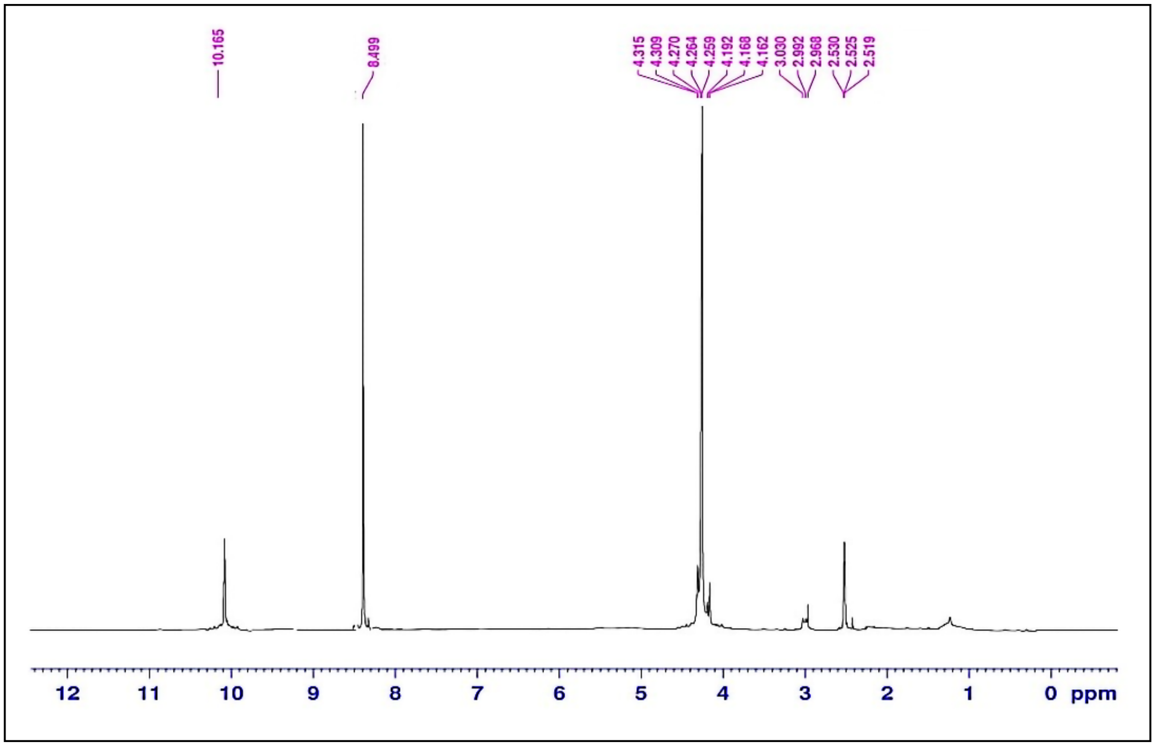


Figure (4-6): $^1$H-NMR of pyrimidine-2,4,6-triol (starting material).

Figure (4-7) shows the $^1$H-NMR of Hyperbranched polyester polymer with tartaric acid (HBPE-TA), it is found that the signal at 4.082 ppm related to (3OH), the signals at 3.062-3.082 ppm related to (d, 6H, OH tartaric group), and the signal at 5.153 ppm attributed to (d, 6H, CH tartaric group).

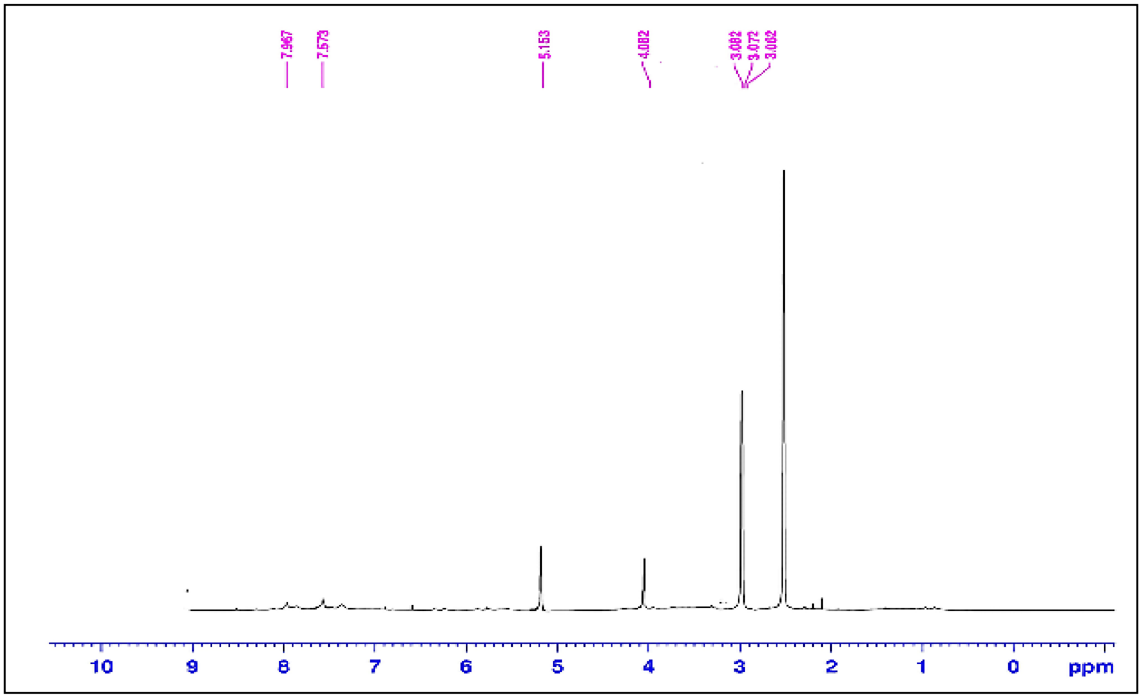


**Figure (4-7): $^1$H-NMR of Hyperbranched Polyester Polymer with Tartaric acid HBPE-TA.**

Figure (4-8) shows the $^1$H-NMR of Hyperbranched polyester polymer with adipic acid (HBPE-AD), it is found that the signals at 3.965-4.091 ppm are for (3OH), the signals at 1.649-1.689 ppm related to (t, 12H, $CH_2$ adipic group) the signals at 2.016-2.033 ppm are for (t, 12H, $CH_2$ adipic group).

Figure (4-9) shows the $^1$H-NMR of Hyperbranched polyester polymer with Maleic acid (HBPE-MA), it is found that the signal at 4.052 ppm is for (3OH), the signals from 6.504-6.514 ppm are for (d, 3H, malic acid (trans)), and the signals from 6.661-6.663 ppm are for (d, 6H, malic acid (cis)).

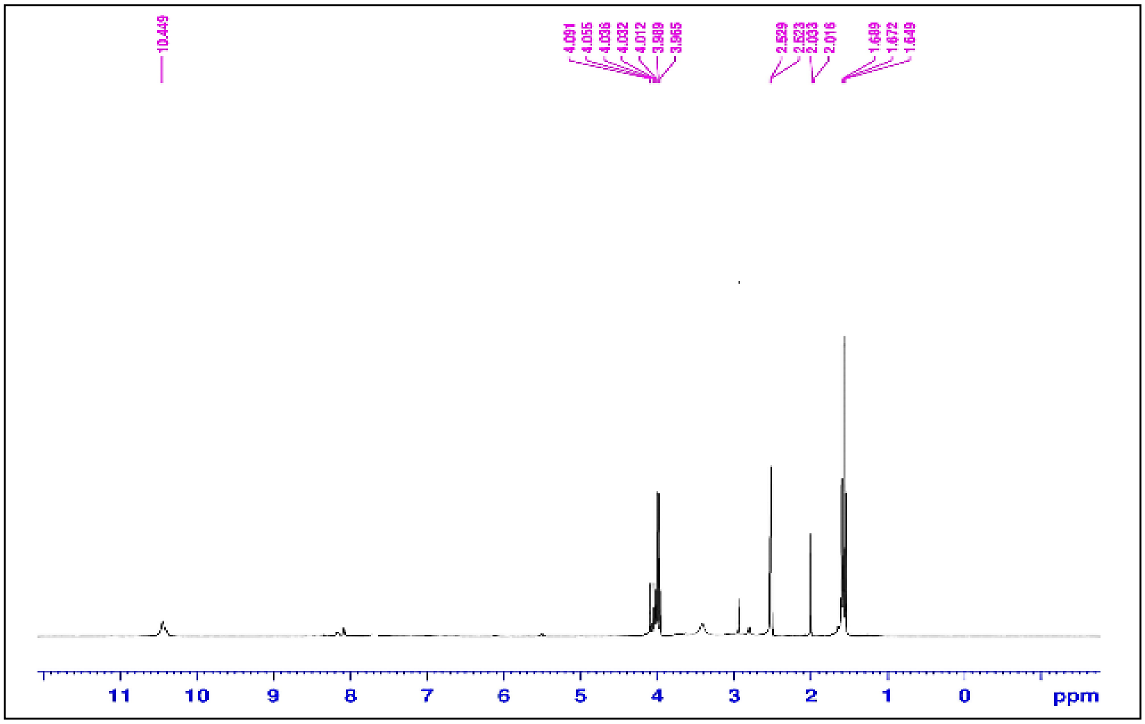


**Figure (4-8): $^{1}$H-NMR of Hyperbranched Polyester Polymer with Adipic acid HBPE-AD.**

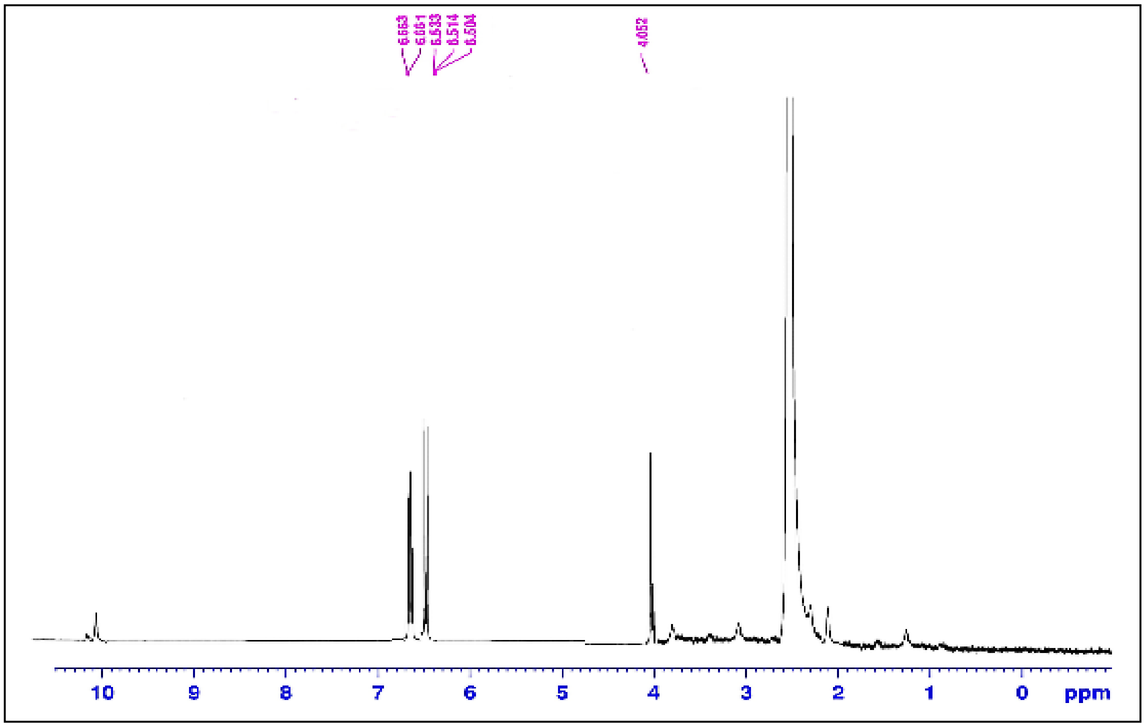


**Figure (4-9): $^{1}$H-NMR of Hyperbranched Polyester Polymer with Maleic acid HBPE-MA.**

Figure (4-10) shows the $^1$H-NMR of Hyperbranched polyester polymer with Phthalic anhydride (HBPE-PA), the signal at 4.015 ppm related to (3OH) the signals from 6.506-6.734 ppm attributed to (6H, Ar-ring) and signals from 6.956-7.145 ppm related to (6H, Ar-ring).

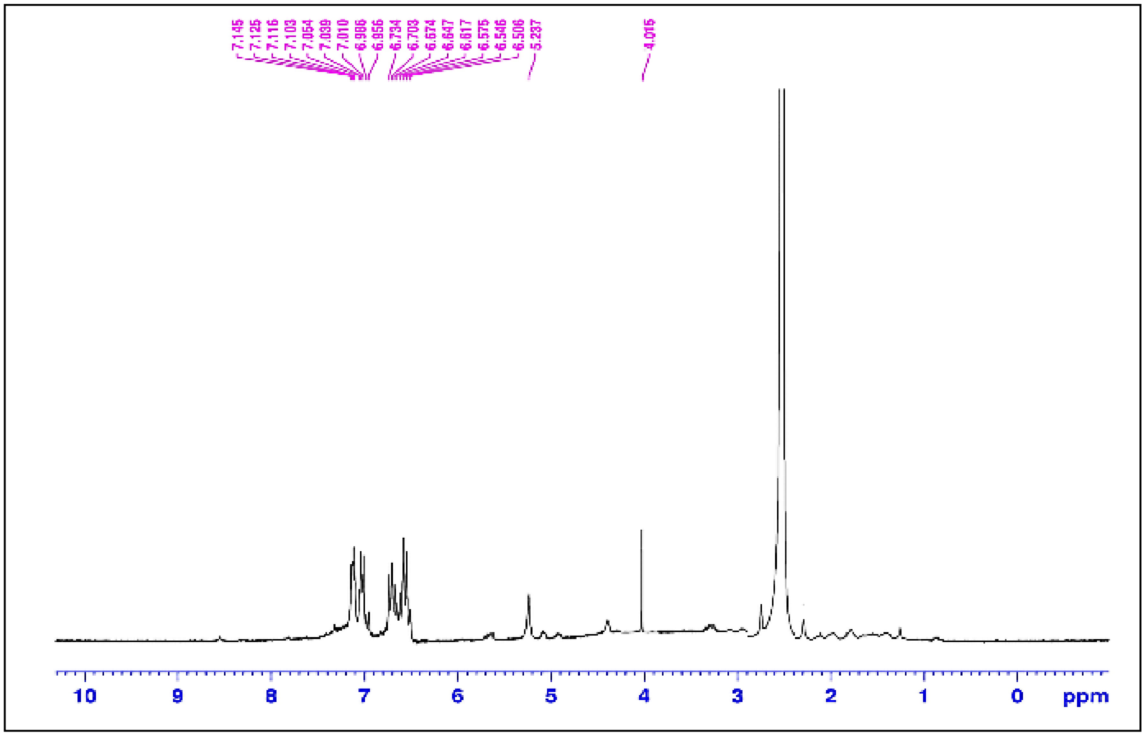


**Figure (4-10): $^1$H-NMR of Hyperbranched Polyester Polymer with Phthalic anhydride HBPE-PA.**

### 4.2.3. GPC Analysis

The molecular weights of the four types of polymers that were prepared have been determined by GPC using THF as the solvent and compered with polystyrene as the reference material. The weight average molecular weight $M_w$, the number average molecular weight $M_n$ and polydispersity index PDI ($M_w/M_n$) have been obtained from the GPC curves.

Figure (4-11) shows the molecular weight distribution curve of HBPE-TA, it is shown that the Mw of the polymer is 1140 g/mol, Mn is 870 g/mol and the midpoint molecular weight (Mp) is 1130 g/mol. The polydispersity PDI is 1.30.

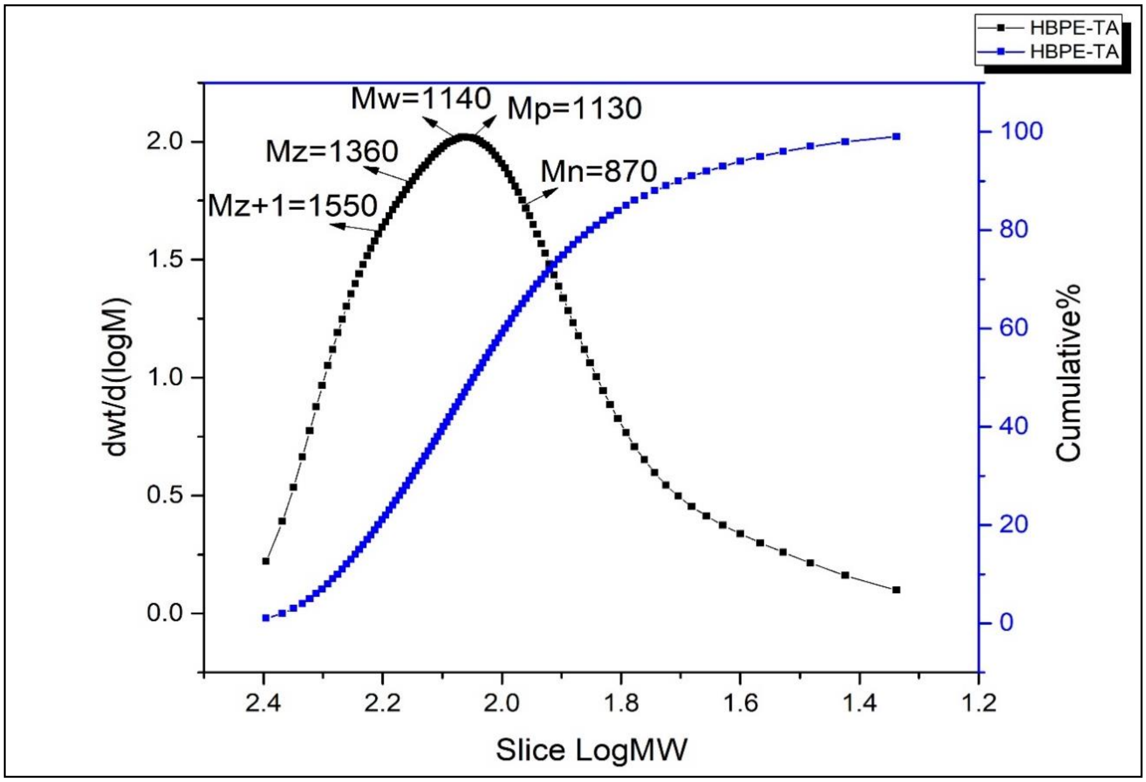


**Figure (4-11): GPC curve of HBPE-TA polymer.**

Figure (4-12) shows the molecular weight distribution curve of HBPE-AD; it is shown that the Mw of the polymer is 1120 g/mol, Mn is 890 g/mol and the midpoint molecular weight (Mp) is1040 g/mol. The polydispersity index PDI is 1.26.

Figure (4-13) shows the molecular weight distribution curve of HBPE-MA. It is shown that the polymer has a molecular weight Mw of 1880 g/mol, a Mn of 1705 g/mol with a midpoint Mp of 1875 g/mol and a polydispersity index PDI of 1.185.

Figure (4-14) shows the molecular weight distribution curve of HBPE-PA, it is found that the polymer has a molecular weight Mw 910 g/mol and

Mn 820 g/mol and a midpoint Mp of 950 g/mol with polydispersity index PDI 1.11.

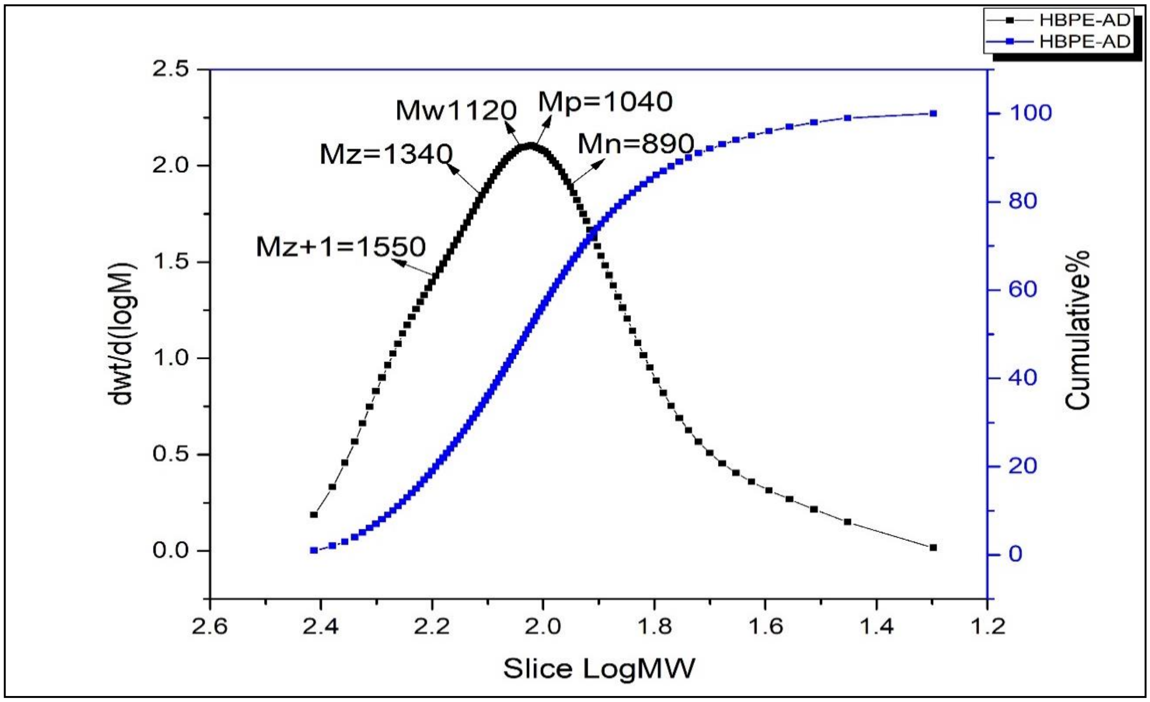


Figure (4-12): GPC curve of HBPE-AD polymer.

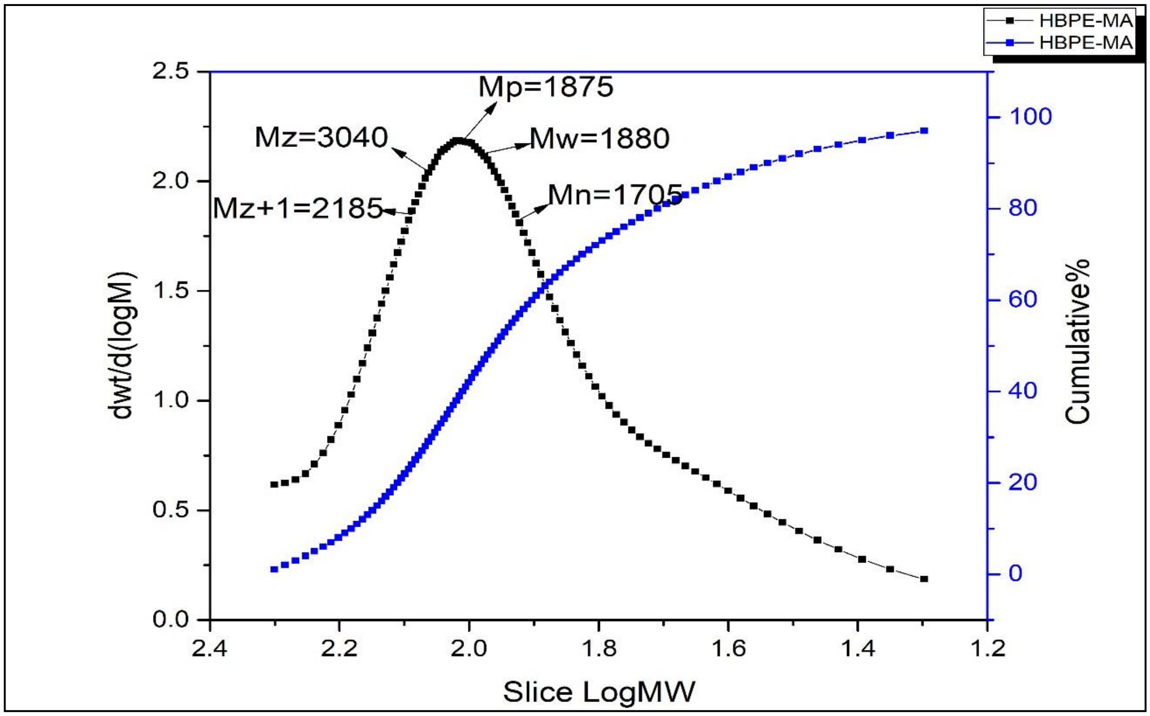


Figure (4-13): GPC curve of HBPE-MA polymer.

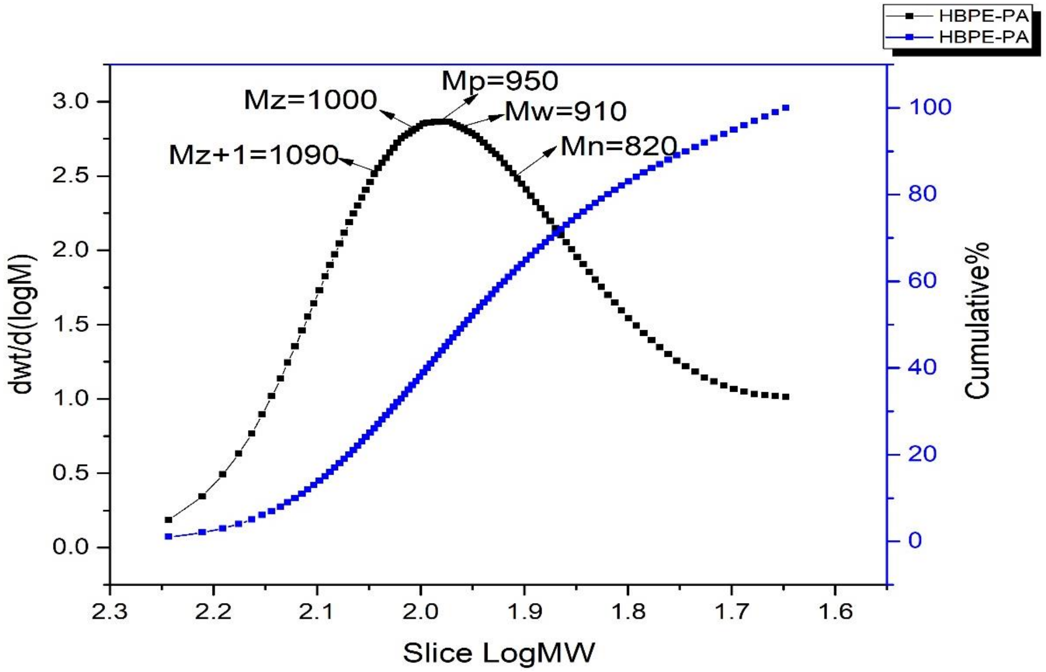


**Figure (4-14): GPC curve of HBPE-PA polymer.**

From the above results, it is found that all the prepared HBPE polymers (HBPE-TA, HBPE-AD, and HBPE-PA) have low molecular weight and narrow molecular weight distribution, except HBPE-MA, which shows the highest molecular weight when compared with the other polymers. These results could be attributed to the chemical structure of the components (TA, AD, MA, and PA) that used for polymerization, PA has an aromatic ring that could restrict the polymerization process, while the other components (MA, AD, and TA) have simpler structure that not affect the polymerization process and reflected on the molecular weight. In addition, it is found that the HBPE-TA has the highest PDI while the other polymers have lower PDI, this is an improvement that HBPE-TA has broad chain lengths compared to the other polymers (as the PDI increase the broadness increase). Also it is found that the size average molecular weight Mz has the same results as the Mw and Mn for the same reasons. The overall results that were obtained from GPC are listed in Table (4-1) as shown below.

**Table (4-1): The GPC data for the prepared polymers.**

| Material | Mn | Mw | Mp | Mz | Mz+1 | PDI |
|---|---|---|---|---|---|---|
| **HBPE-TA** | 870 | 1140 | 1130 | 1360 | 1550 | 1.302874 |
| **HBPE-AD** | 890 | 1120 | 1040 | 1340 | 1550 | 1.257632 |
| **HBPE-MA** | 1705 | 1880 | 1875 | 3040 | 2185 | 1.184764 |
| **HBPE-PA** | 820 | 910 | 950 | 1000 | 1090 | 1.108942 |

**All the data are in (g/mol) except PDI has no units.**

## 4.3. Characterization of PP and PP/HBPE Blends

### 4.3.1. FTIR Analysis Result

FTIR spectroscopy was used to analyze the effect of the prepared HBPE addition on the chemical structure of VPP and rPP. Figure (4-15) and (4-16) show the bands values and the changes in these values with the addition of HBPE. Table (4-2) and (4-3) list the most important bands of PP and its blends with HBPE as derived from Figure 4-15 and 4-16 and compare them with the bands mentioned in [144, 145]. The following bands were identified for vPP and rPP: 2954.95 $cm^{-1}$ and 2885.51 $cm^{-1}$ for $–CH_3$ asymmetric stretching vibration and $–CH_3$ symmetrical stretching vibration, bands at 995.27 $cm^{-1}$, 972.12 $cm^{-1}$ and 1165 $cm^{-1}$ related to $–CH_3$ rocking vibration. The peaks at 1458.18 $cm^{-1}$, 2839.22 $cm^{-1}$ and 2924.09 $cm^{-1}$ are related to $–CH_2$ symmetric bending, $–CH_2$ symmetric stretching and $–CH_2$ asymmetric stretching. The peak at 1373.32 $cm^{-1}$ is attributed to $–CH_3$ symmetric bending vibration mode. The peak at 840.96 $cm^{-1}$ for $C–CH_3$ stretching vibration and peak at 810.10 $cm^{-1}$ is for $CH_2$ rock, C–C stretch, C–CH stretch. The addition of the prepared HBPE to vPP and rPP had some shifting on the bands of PP; also, the bands of HBPE appears in the IR spectrum. From these results, it can be concluded that the interaction between the two polymers, PP and HBPE, are physical and not chemical.

### Table (4-2): IR transmission bands for VPP and its blends.

| Bond type | PP[144], [145]standard | vPP | PP/HBPE-TA | PP/HBPE-AD | PP/HBPE-MA | PP/HBPE-PA |
|---|---|---|---|---|---|---|
| C-C stretch | 808 | 810.1 | 802.39 | 802.39 | 802.39 | 802.39 |
| C-H rocking | 840 | 840.96 | 848.68 | 840.96 | 843.55 | 840.96 |
| $CH_3$ rocking<br>C-C stretch | 973 | 972.12 | 972.12 | 972.12 | 972.12 | 972.12 |
| $CH_3$ rocking<br>C-C stretch | 996 | 995.27 | 996.07 | 995.27 | = | 995.27 |
| CH wagging<br>$CH_2$ rocking | 1166 | 1165 | 1165 | 1165 | 1141.86 | 1165 |
| $CH_3$ sym.bend | 1376<br>1456 | 1373.32<br>1458.18 | 1381.03<br>1458.18 | 1381.03<br>1458.18 | 1404.18<br>1458.18 | 1373.32<br>1458.18 |
| $CH_3$ stretch | 2870 | 2885.51 | 2877.19 | 2885.51 | 2877.19 | 2877.79 |
| $CH_3$ asym.stretch | 2920 | 2924.09 | 2924.09 | 2931.8 | 2931.8 | 2924.09 |
| $CH_3$ asym.stretch | 2950 | 2954.95 | 2962.66 | 2954.95 | 2962.66 | 2954.95 |

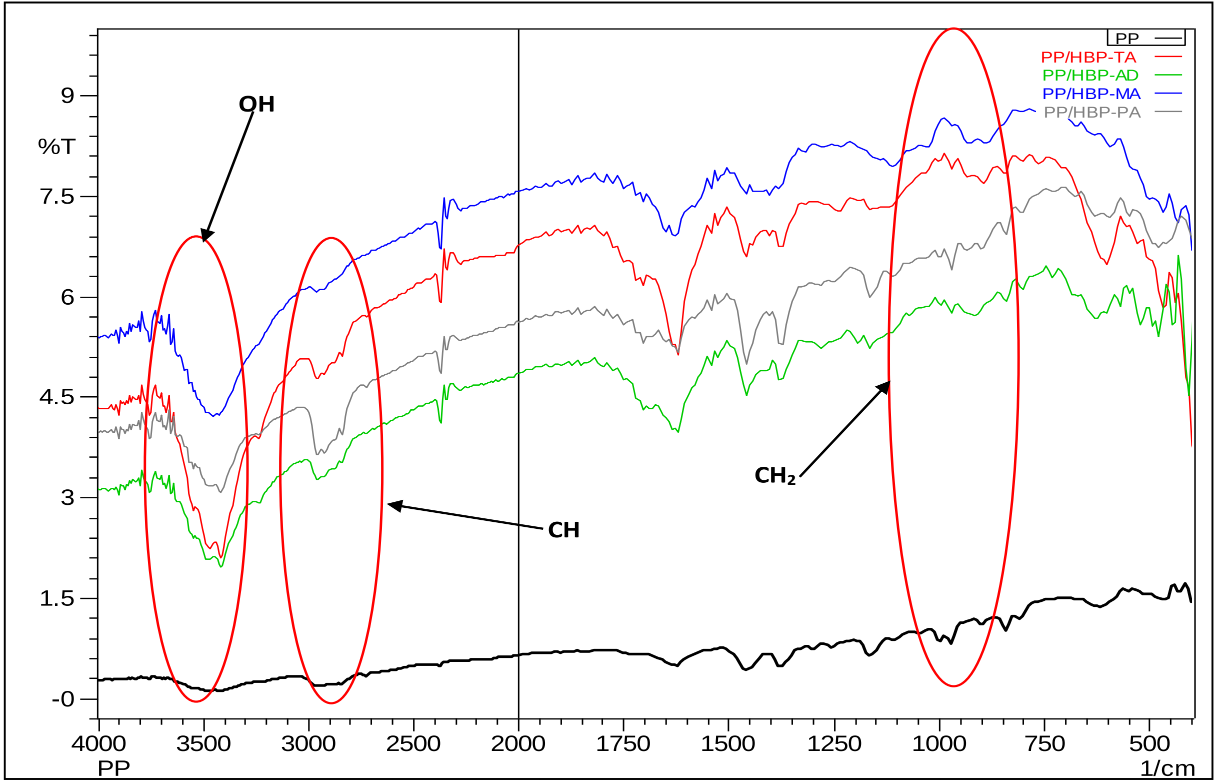


Figure (4-15): IR spectrum for VPP and PP/HBPE.

**Table (4-3): IR transmission bands for rPP and its blends.**

| Bond type | PP[144], [145]standard | rPP | PP/HBPE-TA | PP/HBPE-AD | PP/HBPE-MA | PP/HBPE-PA |
|---|---|---|---|---|---|---|
| C-C stretch | 808 | 810.1 | 810.1 | 802.39 | 802.39 | 802.39 |
| C-H rocking | 840 | 840.96 | 840.96 | | | |
| $CH_3$ rocking<br>C-C stretch | 973 | 972.12 | 972.12 | 972.12 | 972.12 | 972.12 |
| $CH_3$ rocking<br>C-C stretch | 996 | 995.27 | = | = | = | = |
| CH wagging<br>$CH_2$ rocking | 1166 | 1165 | 1165 | 1149.57 | 1188.15 | 1149.57 |
| $CH_3$ sym.bend | 1376<br>1456 | 1373.32<br>1458.18 | 1381.03<br>1458.18 | 1381.03<br>1458.18 | 1381.03<br>1458.18 | 1381.03<br>1458.18 |
| $CH_3$ stretch | 2870 | 2877.79 | 2877.79 | 2877.79 | 2883.11 | 2889.37 |
| $CH_3$ asym.stretch | 2920 | 2924.09 | 2931.8 | 2924.09 | 2931.8 | 2924.09 |
| $CH_3$ asym.stretch | 2950 | 2954.95 | 2962.66 | 2962.66 | 2962.66 | 2962.66 |

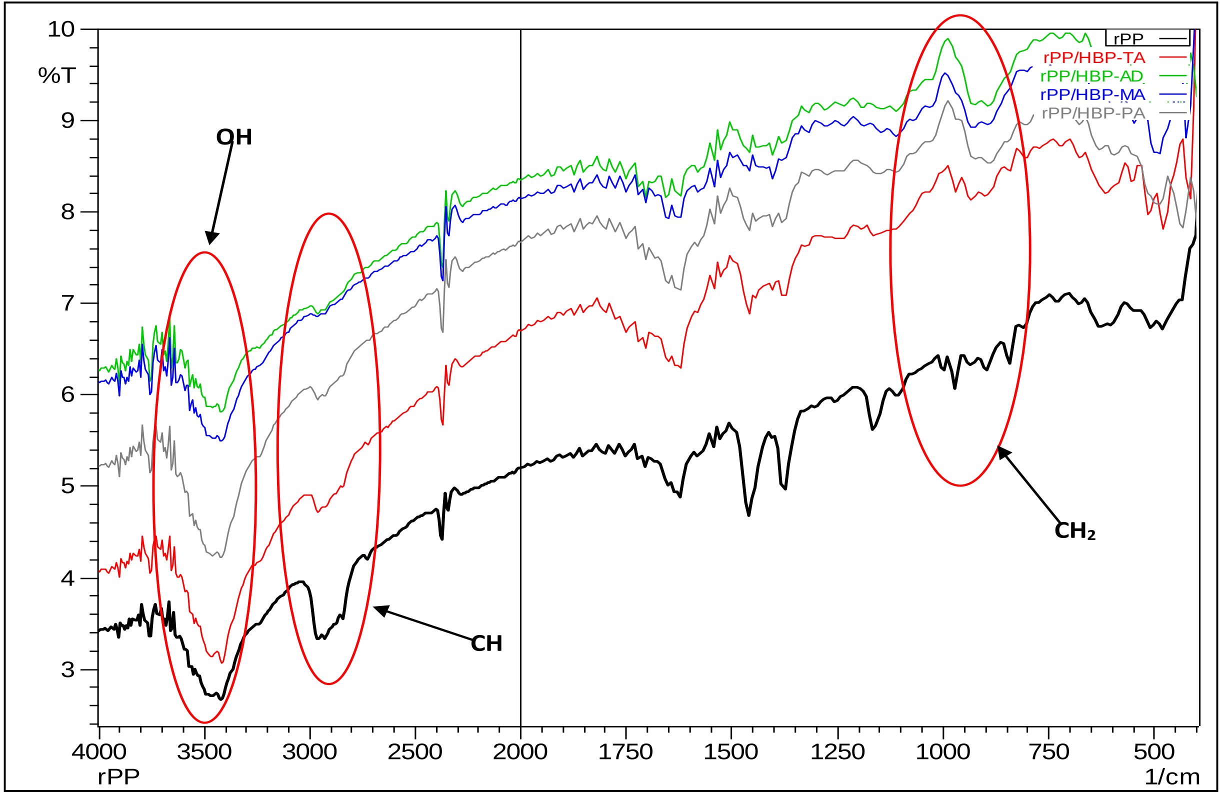


Figure (4-16): IR spectrum of rPP and rPP/HBPE.

### 4.3.2. Tensile Test Results

The tensile properties of VPP and rPP blended with the four prepared types of HBPE are shown by Figure (4-17) to Figure (4-22). Figure (4-17) shows the influence of HBPE content on the tensile strength of VPP/HBPE blends. The results showed that the tensile strength for all blends dropped when the prepared HBPE blended with VPP. It is shown that the tensile strength was reduced by 2.27 MPa, 2.96 MPa and 2.38 MPa for the 5%, 10% and 20% of HBPE-TA samples, and reduced by 3.17 MPa, 1.86 MPa and 3.6 MPa for the 5%, 10% and 20% of HBPE-AD samples. While it was reduced by 4.3 MPa, 3.28 MPa and 3.3 MPa for the 5%, 10% and 20% of HBPE-MA samples, and for HBPE-PA it was reduced by 1.03 MPa, 5.4 MPa and 5.8 MPa for the 5%, 10% and 20% samples, respectively.

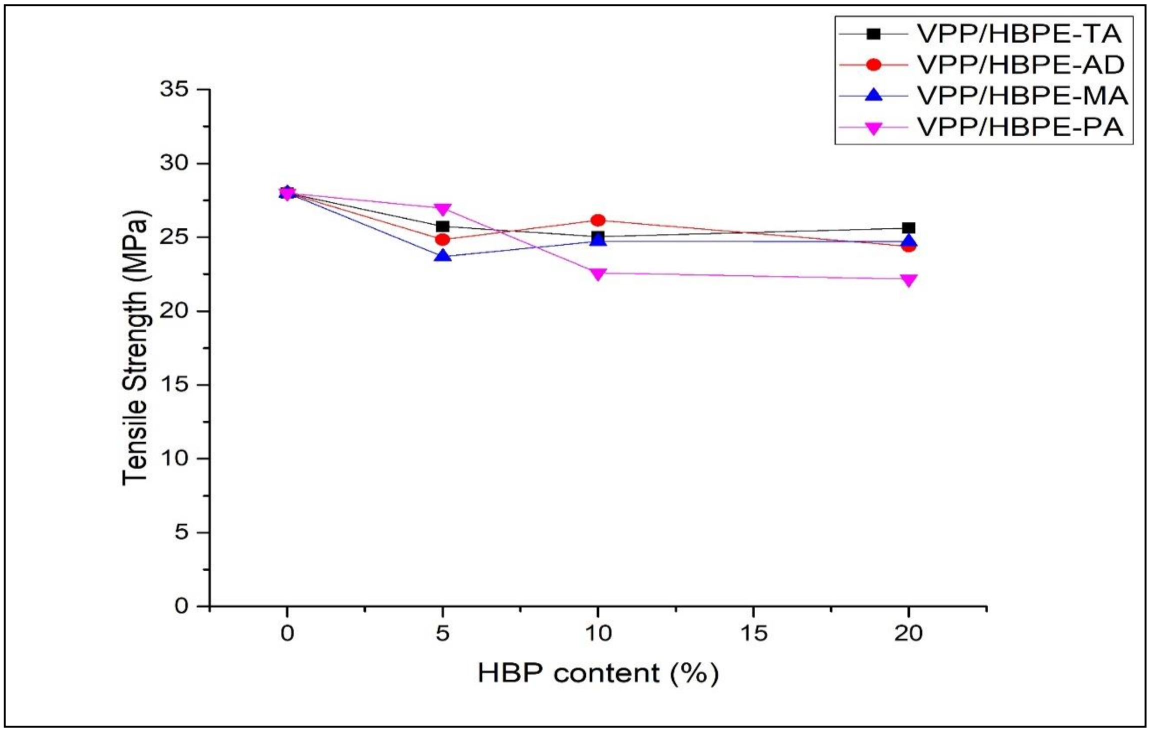


**Figure (4-17): Tensile strength of VPP/HBPE vs. HBPE content.**

In addition, it is found that tensile strength of rPP/HBPE blends decreased when the content of prepared HBPE increased as shown in Figure

(4-18). It is shown that the tensile strength was dropped by 1.7 MPa, 3.01 MPa and 4.4 MPa for the 5%, 10% and 20% of HBPE-TA samples, dropped by 2.2 MPa, 2.5 MPa and 2 MPa for the 5%, 10% and 20% of HBPE-AD samples. While it was dropped by 2.5 MPa, 4.4 MPa and 3.7 MPa for the 5%, 10% and 20% of HBPE-MA samples, and dropped by 3.1 MPa, 5.2 MPa and 5.4 for the 5%, 10% and 20% of the HBPE-PA samples, respectively.

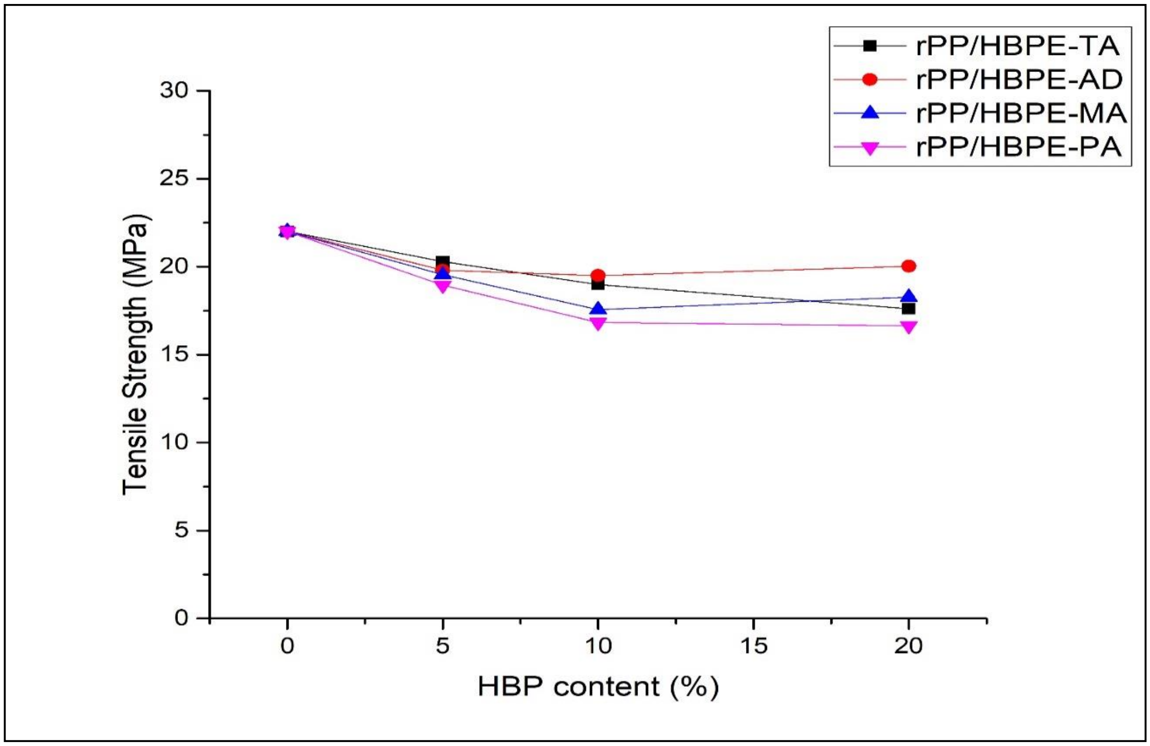


**Figure (4-18): Tensile strength of rPP/HBPE vs. HBPE content.**

These results are due to the weak interfacial adhesion between HBPE and PP, as well as the lack of entanglements between PP and HBPE with various polarities, results in inadequate stress transfer between dispersed phase HBPE and matrix PP, these results are in agreement with Zuhair [146, 147] and with Nevera and Wu [148, 149]. The HBPE molecules increase the distance between PP chains and allow the chains to move more freely past each other. These results indicate that the blends of PP and HBPE are immiscible as indicated by SEM images. In addition, from the above results, it was found that VPP has a higher tensile strength than rPP, which is attributed to the higher chain lengths of VPP that result in more entanglements and thus higher strength. rPP has a short chain with a large number, while VPP has a long chain with a small number.

The effect of HBPE on the elastic modulus of PP/HBPE blends are shown in Figure (4-19) and Figure (4-20). It is shown that elastic modulus of PP/HBPE blends decreases with the increase of HBPE content. From Figure (4-19) for VPP/HBPE blends, it was found that elastic modulus decreased by 0.13 GPa, 0.18 GPa, and 0.4 GPa for the 5%, 10% and 20% of HBPE-TA, and decreased by 0.22 GPa, 0.28 GPa, and 0.42 GPa for the 5%, 10% and 20% of HBPE-AD. While, it was decreased by 0.29 GPa, 0.2 GPa, and 0.27 GPa for the 5%, 10% and 20% of HBPE-MA, and decreased by 0.16 GPa, 0.07 GPa, and 0.29 GPa for the 5%, 10% and 20% of HBPE-PA.

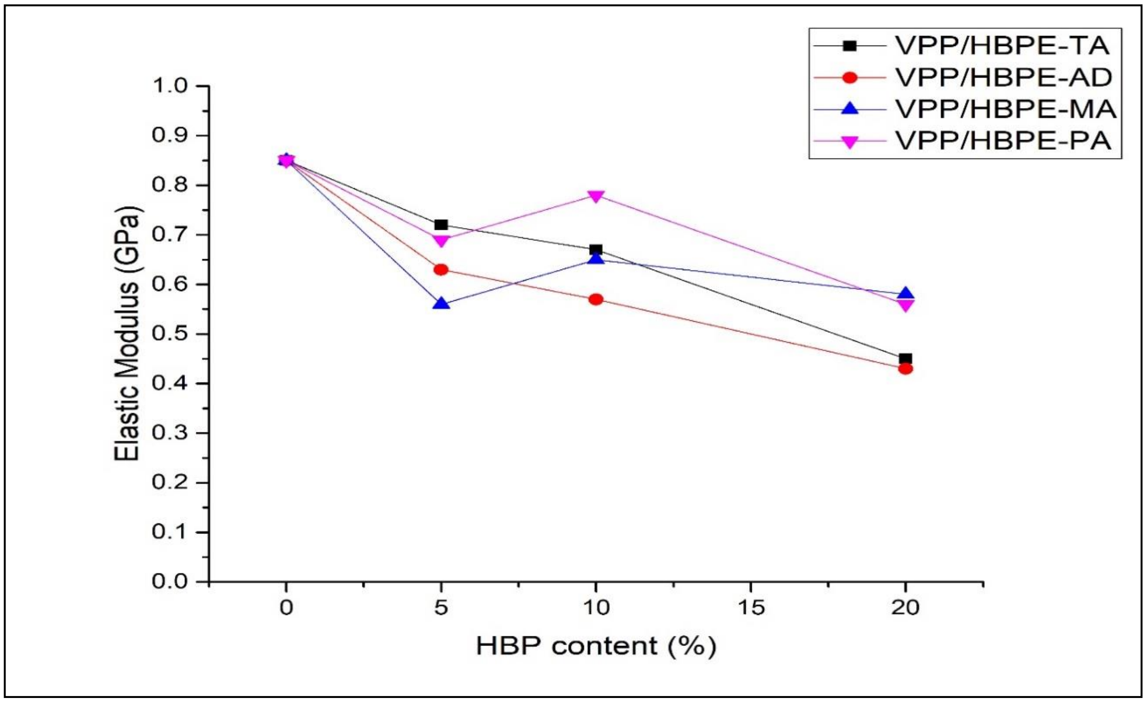


**Figure (4-19): Elastic modulus of VPP/HBPE blends with HBPE content.**

For rPP/HBPE blends shown in Figure (4-20), it was found that the elastic modulus decreased by 0.17 GPa, 0.23 GPa and 0.25 GPa for the 5%, 10% and 20% of HBPE-TA, and decreased by 0.12 GPa, 0.19 GPa, and 0.28 GPa for the 5%, 10% and 20% of HBPE-AD. While it decreased by 0.21 GPa. 0.24 GPa, and 0.31 GPa for the 5%, 10% and 20% of HBPE-MA, and decreased by 0.22 GPa, 0.26 GPa, and 0.33 GPa for the 5%, 10% and 20% of HBPE-PA.

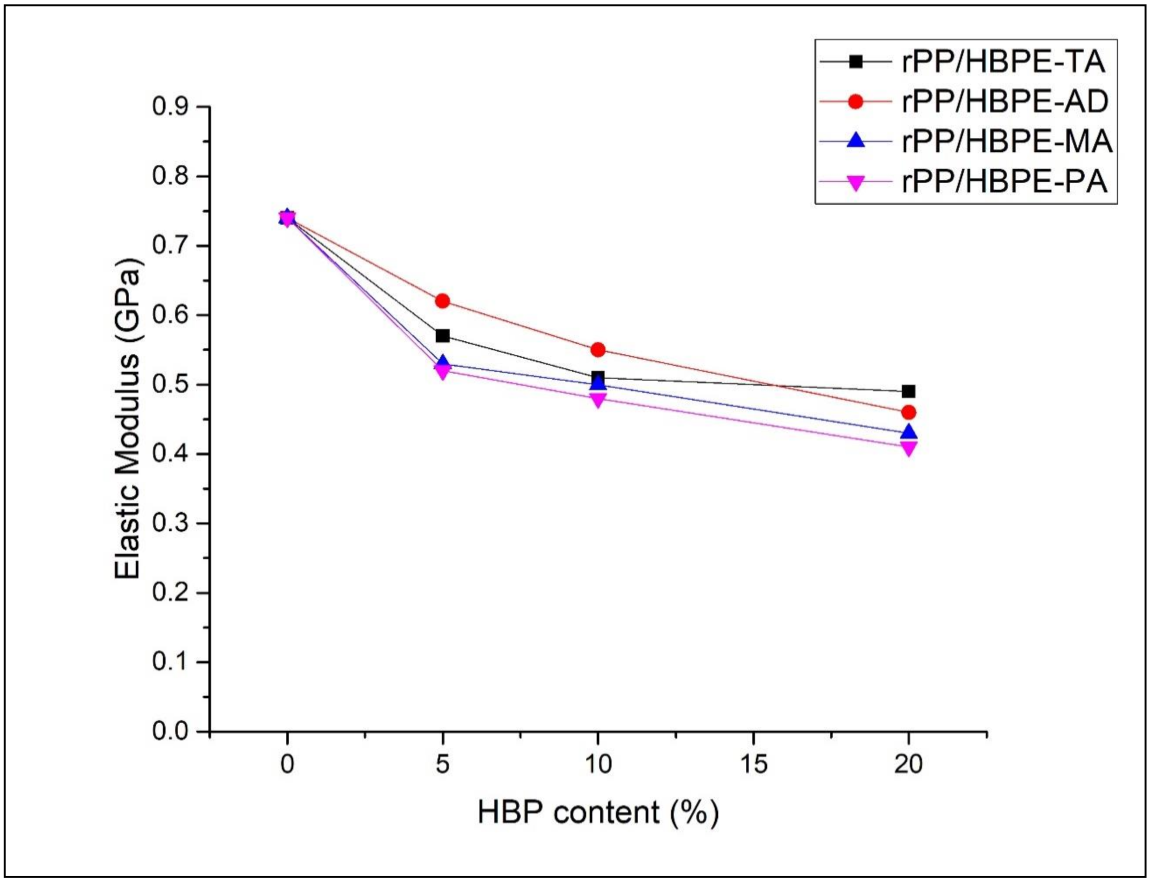


**Figure (4-20): Elastic modulus of rPP/HBPE blends with HBPE content.**

This behavior could be attributed to the stiffening effect and absence of entanglements of HBPE, resulting in a brittle material with poor mechanical properties these results are in agreement with Diao [150] and [151]. Also to the same reason as indicated in tensile strength results.

The influence of HBPE on the elongation at the break of PP/HBPE blends is shown in Figure (4-21) and Figure (4-22). It is found that the elongation at break for all blends decreased with the increase of HBPE content. From Figure (4-21) for VPP/HBPE blends, it was found that the elongation at break dropped by 17.56 %, 20.1 %, and 7.26 % for the 5%, 10% and 20% of HBPE-TA, and dropped by 17.1 %, 16.2 %, and 12 % for the 5%, 10% and 20% of HBPE-AD. While, it is dropped by 22.7 %, 23.4 %, and 19.4 % for the 5%, 10% and 20% of HBPE-MA, and is dropped by 14.1 %, 19.6 %, and 21 % for the 5%, 10% and 20% of HBPE-PA.

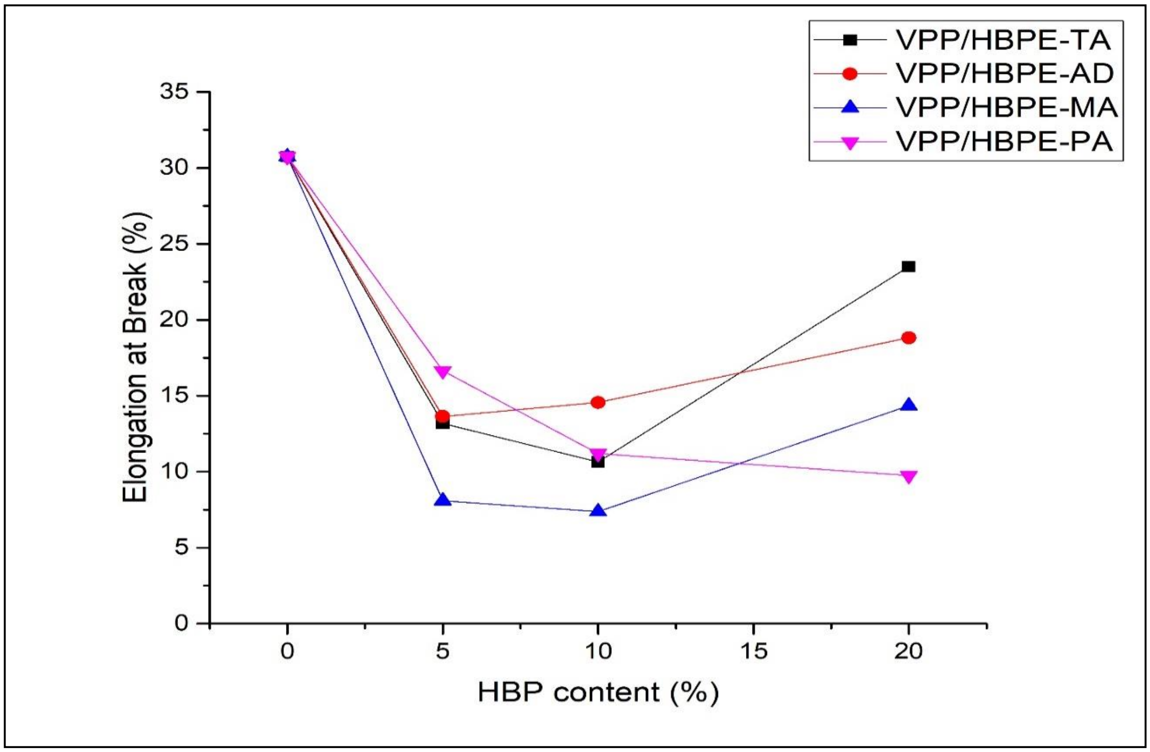


**Figure (4-21): The elongation at break of VPP/HBPE blends with HBPE content.**

While, for rPP/HBPE blends shown in Figure (4-22), it was found that the elongation at break decreased by 15 %, 7.5 %, and 12.3 % for the 5%, 10% and 20% of HBPE-TA, and decreased by 8.4 %, 12.7 %, and 16.6 % for the 5%, 10% and 20% of HBPE-AD. While, it is decreased by 22.4 %, 20.4 %, and 18.5 % for the 5%, 10% and 20% of HBPE-MA, and is decreased by 17 %, 5.4 %, and 8.3 % for the 5%, 10% and 20% of HBPE-PA.

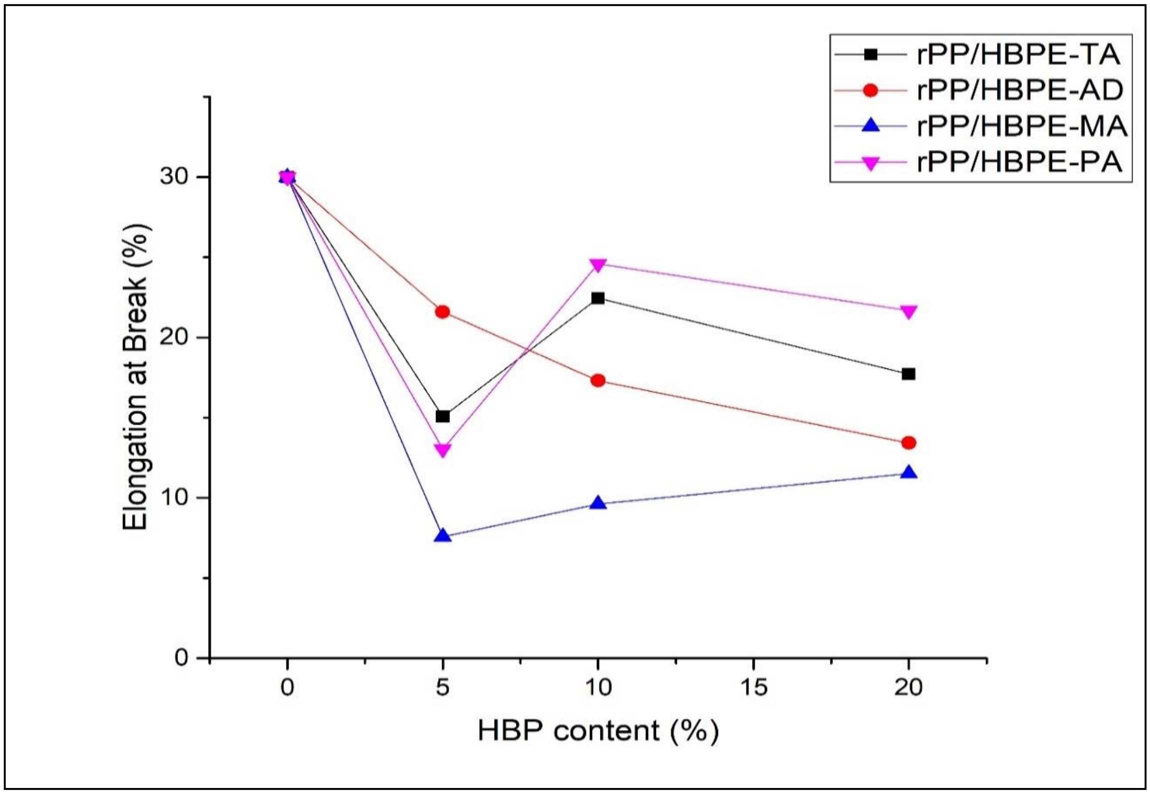


**Figure (4-22): The elongation at break of rPP/HBPE blends with HBPE content.**

This happen, because there is no interaction between HBPE (dispersed phase) and PP matrix, the HBPE remained as a free particle, reducing the PP ability to elongate as in [152, 153]. In addition, it is found that VPP blends have higher elongation than rPP, which may be attributed to the higher chain lengths of VPP when compared with rPP, and that the length of the chain can affect the ability of chains to be aligned and so affect the elongation.

### 4.3.3. Impact Test Results

The toughness is the ability of material to absorb energy and deform without break is referred to as impact strength. The influence of HBPE on the impact strength of PP/HBPE blends is shown in Figure (4.23) and (4-24). The results show that the addition of HBPE enhanced the impact strength of all blends PP/HBPE. From Figure (4-23) for VPP/HBPE blends, it was found that the impact strength increased by 5.1 kJ/m$^2$, 15.1 kJ/m$^2$, and 7.3 kJ/m$^2$ for the 5%, 10% and 20% of HBPE-TA, and increased by 8.3 kJ/m$^2$, 10.5 kJ/m$^2$, and 2.7 kJ/m$^2$ for the 5%, 10% and 20% of HBPE-AD. While, it is increased by 9.8 kJ/m$^2$, 9.6 kJ/m$^2$, and 5.2 kJ/m$^2$ for the 5%, 10% and 20% of HBPE-MA, and increased by 9.4 kJ/m$^2$, 10.6 kJ/m$^2$, and 11.74 kJ/m$^2$ for the 5%, 10% and 20% of HBPE-PA respectively compared to PP.

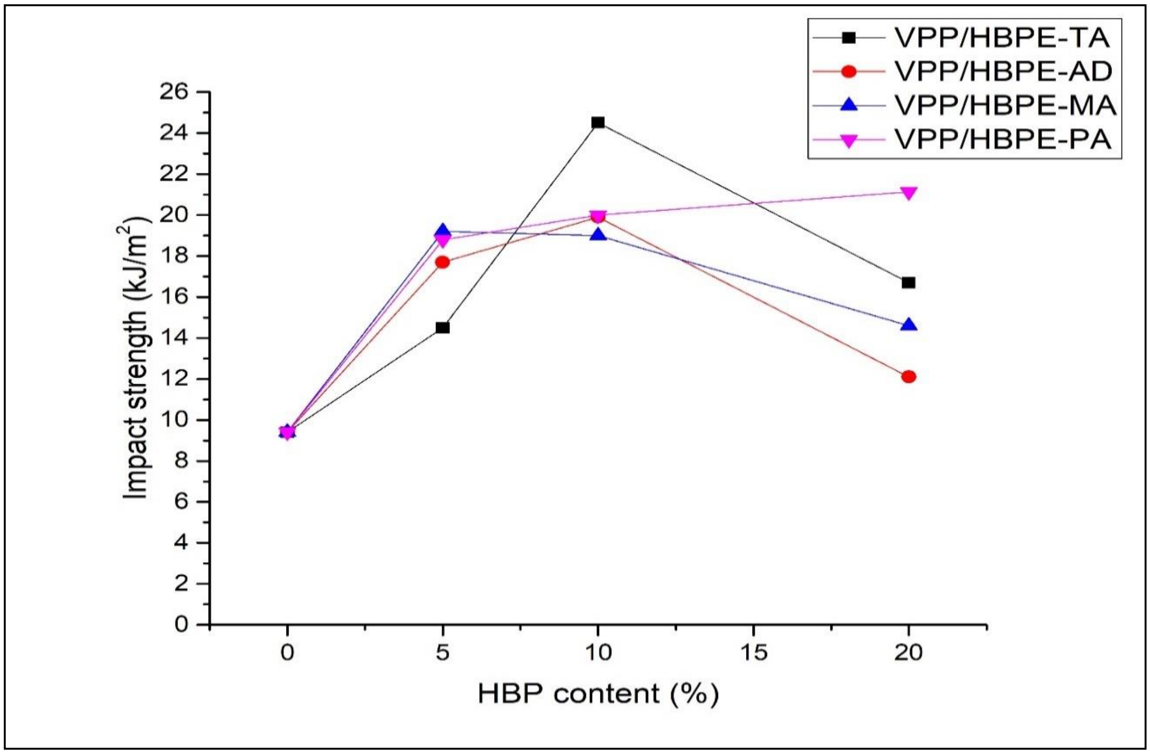


**Figure (4-23): The impact strength of VPP/HBPE with HBPE content.**

While, for rPP/HBPE blends shown in Figure (4-24), it was found that the impact strength enhanced by 7.3 kJ/m$^2$, 13.3 kJ/m$^2$, and 11.6 kJ/m$^2$ for the 5%, 10% and 20% of HBPE-TA, and enhanced by 7.9 kJ/m$^2$, 9.1 kJ/m$^2$, and 4.1 kJ/m$^2$ for the 5%, 10% and 20% of HBPE-AD. While, it is enhanced by 6.4 kJ/m$^2$, 8.3 kJ/m$^2$, and 8 kJ/m$^2$ for the 5%, 10% and 20% of HBPE-MA, and is enhanced by 4.7 kJ/m$^2$, 6.7 kJ/m$^2$, and 1.84 kJ/m$^2$ for the 5%, 10% and 20% of HBPE-PA respectively compared to rPP.

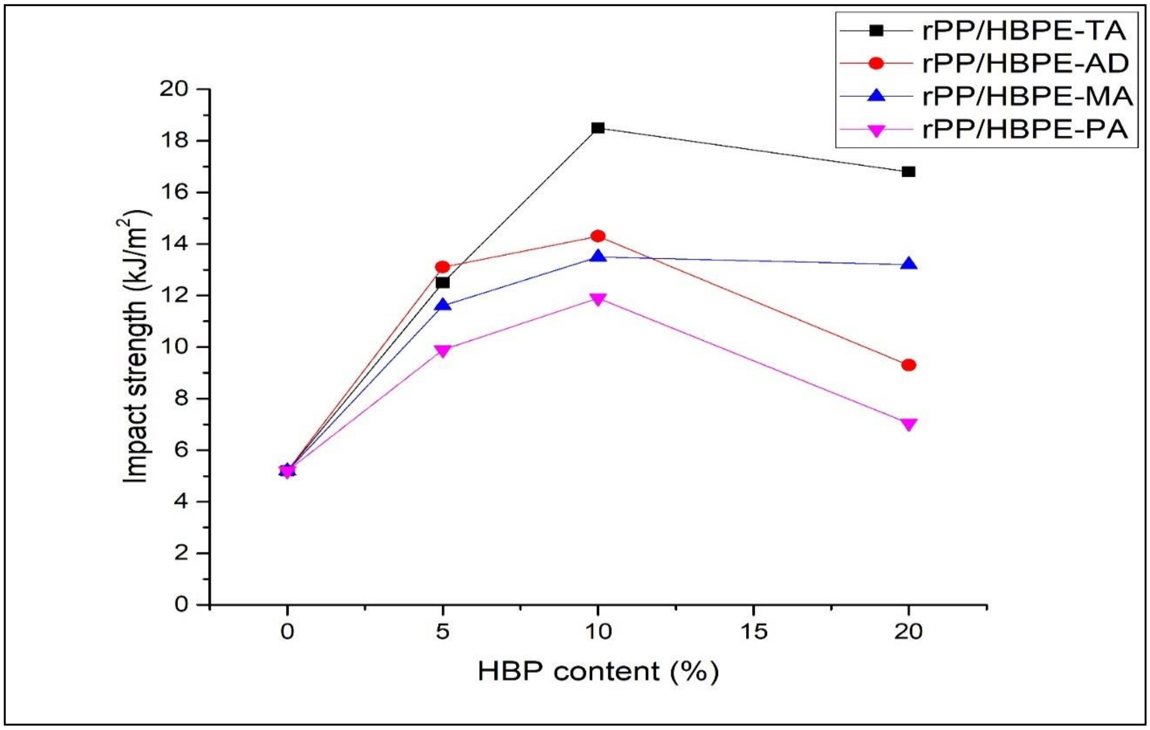


**Figure (4-24): The impact strength of rPP/HBPE with HBPE content.**

The addition of HBPE, up to a certain level, increases the impact strength of PP due to the improved flexibility that results from the increase in chain spaces that result from the branches within the HBPE molecule. This result agrees with the findings in[154, 155]. In addition, it is found that VPP and its blends has higher impact strength than rPP, which is due to the higher chain lengths and entanglements as compared with rPP and its blends.

### 4.3.4. Hardness Test Results

Hardness is defined as the resistance of a material to scratch or penetration. The presence of plasticizers in materials reduces their hardness, while crosslinks increase it. Figure (4-25) and (4-26) show the influence of HBPE on the Shore D hardness of the PP/HBPE blends. It is found that the

Shore D hardness of all blends has been increased when the amount of HBPE increased. From Figure (4-25) for VPP/HBPE blends, it was found that the Shore D hardness increases by 1.26, 3.86, and 2 as the amount of HBPE-TA increases from 5% to 20% respectively, and increases by 2.1, 3.5, and 2.4 as the amount of HBPE-AD increases from 5% to 20% respectively. While, it increases by 1.5, 3, and 2.1 as the amount of HBPE-MA increases from 5% to 20% respectively, and increases by 0.7, 5.18, and 3.58 as the amount of HBPE-PA increases from 5% to 20% respectively.

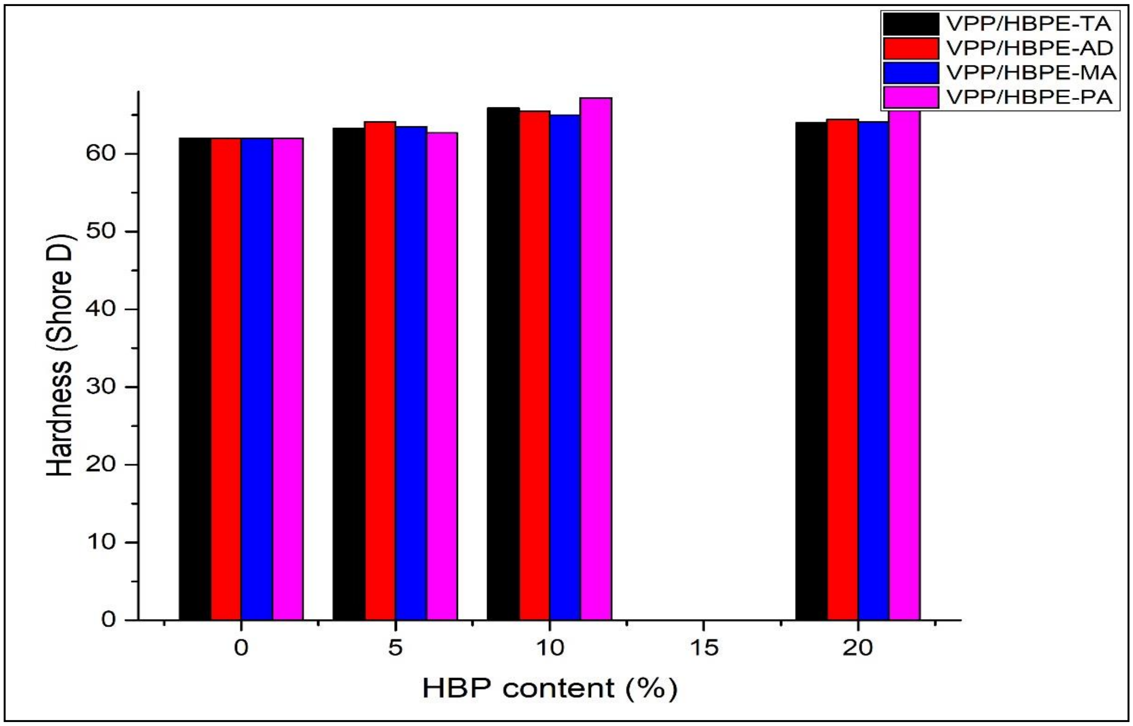


**Figure (4-25): Shore D hardness of VPP/HBPE with HBPE content.**

While, for rPP/HBPE blends shown in Figure (4-26), it was found that the Shore D hardness improved by 1.1, 1.7, and 3.2 as the amount of HBPE-TA increases from 5% to 20% respectively, and improved by 1.2, 3.4, and 3.5 as the amount of HBPE-AD increases from 5% to 20% respectively. While, it is improved by 1.4, 2.2, and 3.2 as the amount of HBPE-MA increases from 5% to 20% respectively, and is improved by 1.2, 3.1, and 4.5 as the amount of HBPE-PA increases from 5% to 20% respectively.

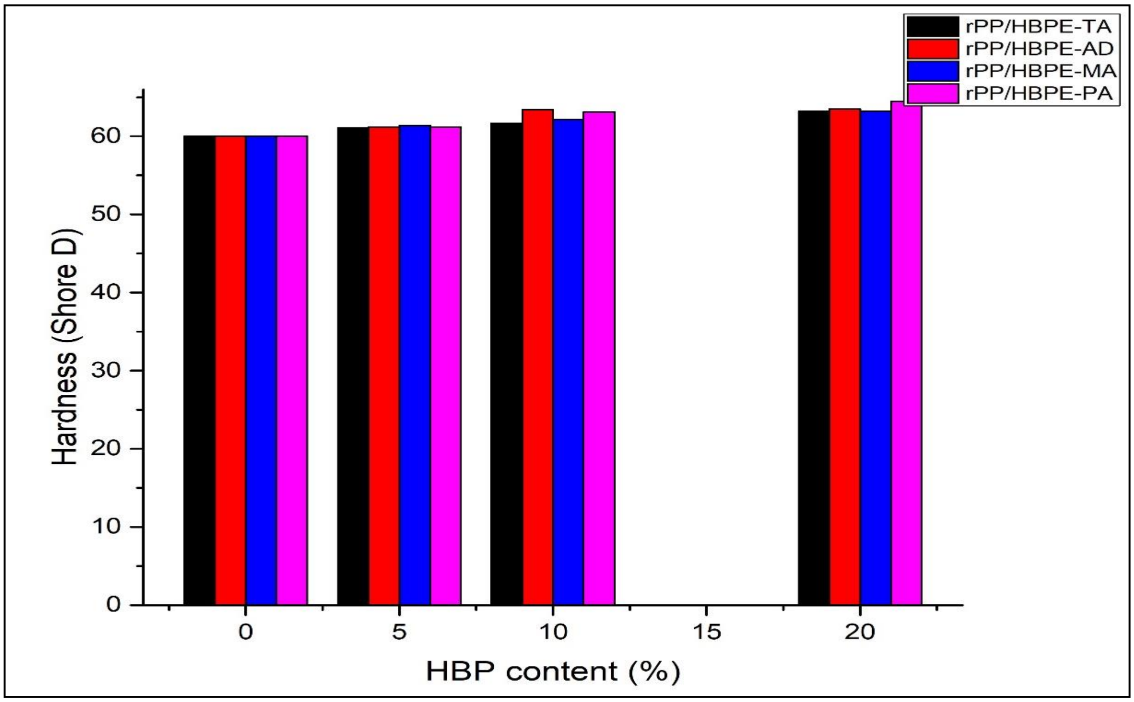
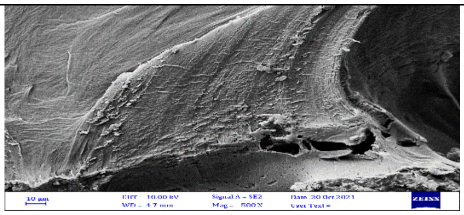
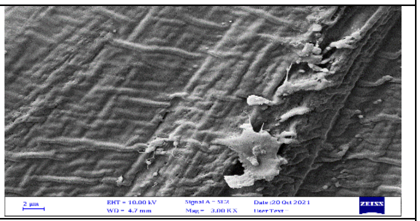
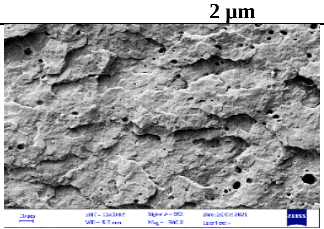
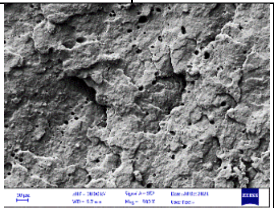
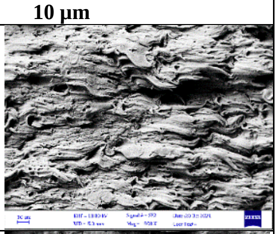
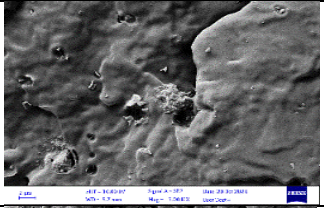
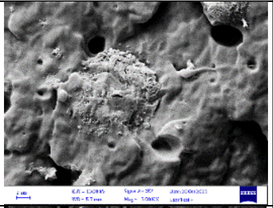
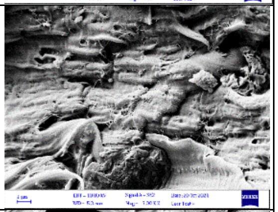
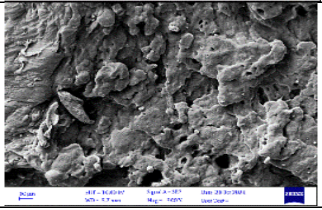
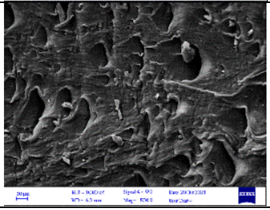
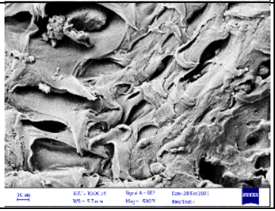


**Figure (4-26): Shore D hardness of rPP/HBPE with HBPE content.**

This increment in the hardness attributed to the HBPE molecule's stiffness and to the increase in surface smoothness with the increase in HBPE addition. These results are in agreement with S. Mahapatra and Y.Jin [152, 156]. The addition of HBPE to PP increases the flow properties, which are reflected on the surface properties as indicated in the MFR results.

### 4.3.5. SEM Results

Figure (4-27) and Figure (4-28) show the FE-SEM images of PP (VPP, and rPP) and PP/HBPE blend samples at two magnification (10 µm and 2 µm). It has shown from Figure (4-27) and (4-28) that PP (VPP and rPP) sample has smooth, continuous, and uniform surface. When HBPE polymer was added to the PP with different percentages (5, 10, and 20 wt %) it is found that the surface of blends losses its smoothness and becomes rough and non-uniform surface with some voids and cavities. In addition, it is found that as the HBPE polymer content increases in the blends the HBPE polymer tend to agglomerate so a heterogeneous blends are formed (the minor phase HBPE are surrounded by continuous phase PP). The size of HBPE polymer domain is of sub-micron order. However, it is found that there is a homogenous dispersion only at small content of HBPE polymer while the material becomes inhomogeneous at higher content of HBPE. These results are due to the difference in the polarities of PP and HBPE polymer, which result in poor interfacial adhesion between the two polymers (PP and HBPE). The lack of miscibility and the difference in polarity are the cause of weak mechanical properties as shown above. These results are in agreement with Froehling, Fan, Yan, and Diao [155], [157–159].

| Material | Scale | HBPE content | | |
|---|---|---|---|---|
| **VPP** | |  |  | |
| | | **2 µm** | **10 µm** | |
| **VPP/HBPE-TA** | **10 µm** |  |  |  |
| | **2 µm** |  |  |  |
| **VPP/HBPE-AD** | **10 µm** |  |  |  |

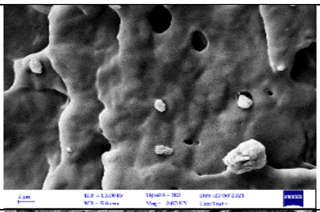
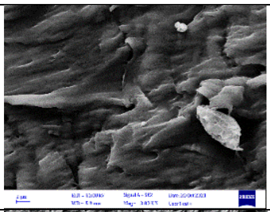
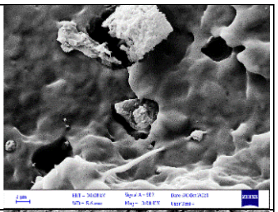
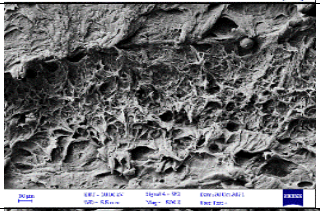
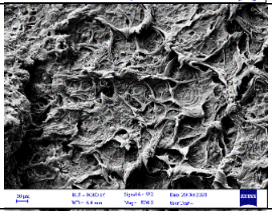
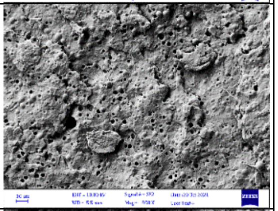
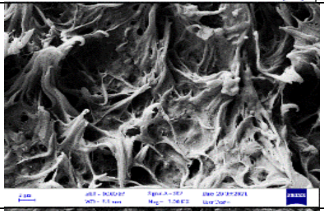
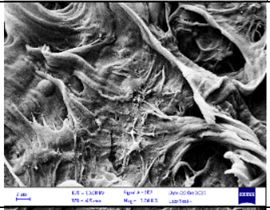
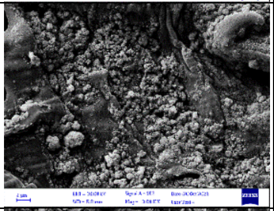
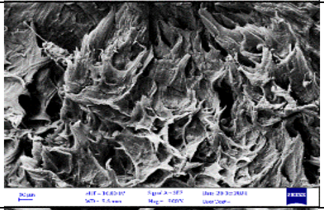
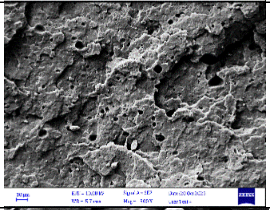
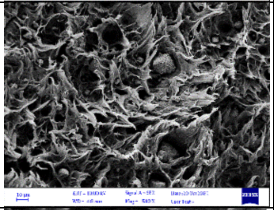
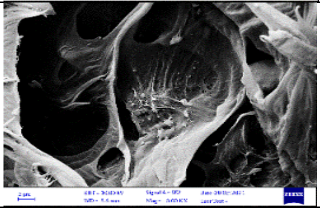
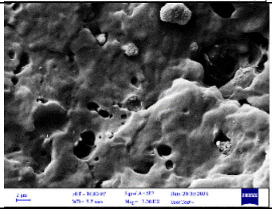
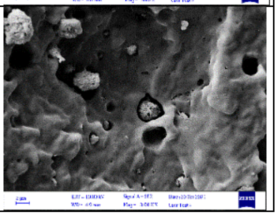
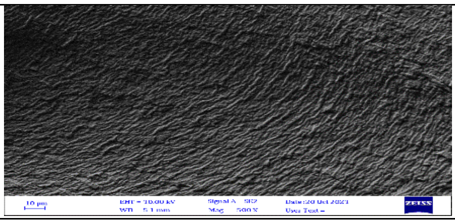
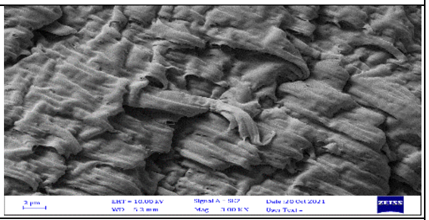
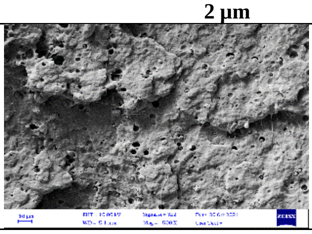
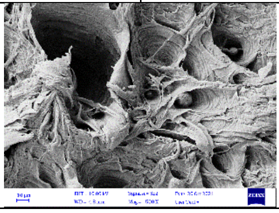
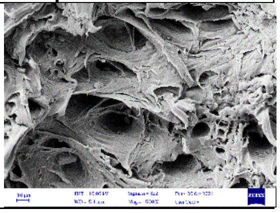
| | | | | |
|---|---|---|---|---|
| | **2 µm** |  |  |  |
| **VPP/HBPE-MA** | **10 µm** |  |  |  |
| | **2 µm** |  |  |  |
| **VPP/HBPE-PA** | **10 µm** |  |  |  |
| | **2 µm** |  |  |  |

**Figure (4-27): FESEM images of VPP and VPP/HBPE.**

| **Material** | **Scale** | **HBPE content** | | |
|---|---|---|---|---|
| **rPP** | |  |  | |
| | | **2 µm** | **10 µm** | |
| **rPP/HBPE-TA** | **10 µm** |  |  |  |

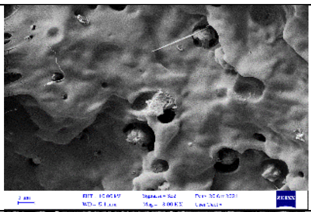
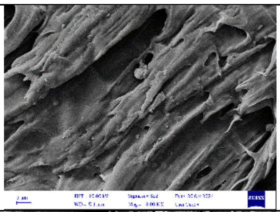
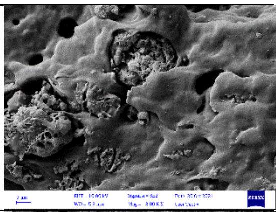
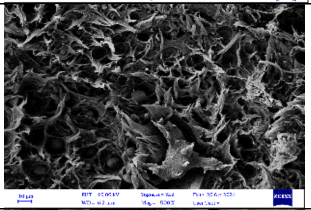
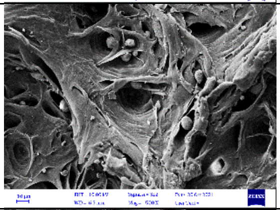
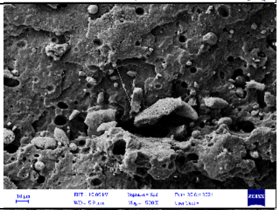
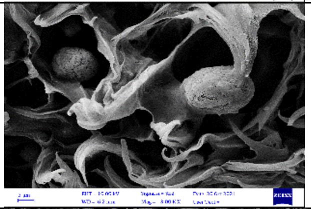
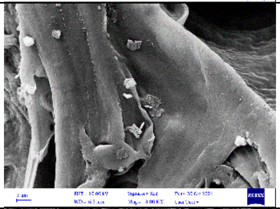
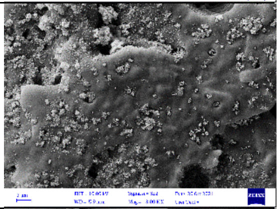
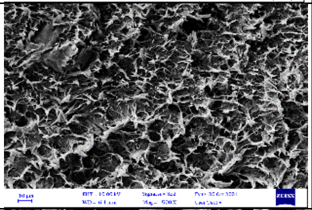
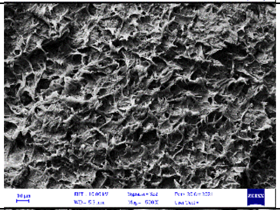
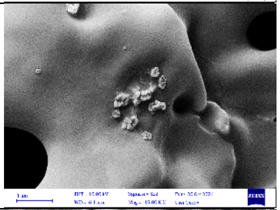
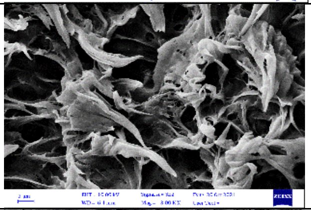
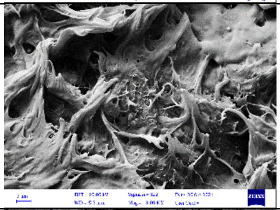
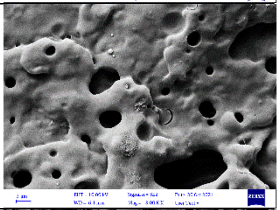
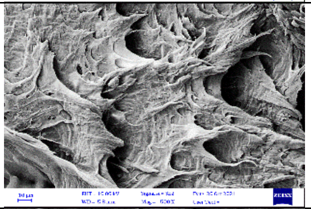
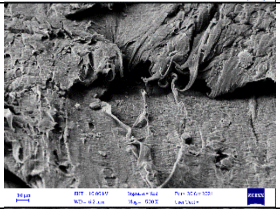
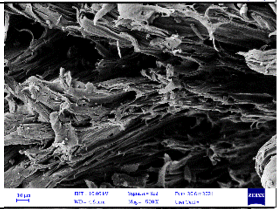
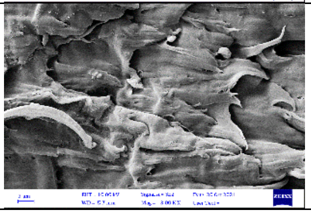
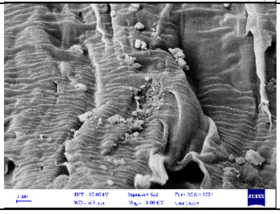
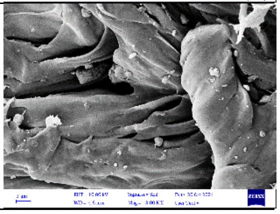
| | | | | |
|---|---|---|---|---|
| | 2 µm |  |  |  |
| **rPP/HBPE-AD** | **10 µm** |  |  |  |
| | **2 µm** |  |  |  |
| **rPP/HBPE-MA** | **10 µm** |  |  |  |
| | **2 µm** |  |  |  |
| **rPP/HBPE-PA** | **10 µm** |  |  |  |
| | **2 µm** |  |  |  |

**Figure (4-28): FESEM images of rPP and rPP/HBPE.**

### 4.3.6. DSC Test Results

The effect of HBPE content on the melting ($T_m$) and crystallization ($T_c$) temperature of PP and its blends were studied using DSC. The polymer's crystallization can be affected by the addition of a heterogeneous or inorganic material. Figure (4-29) shows the melting temperature of the prepared HBPE. It is found that the melting temperature of HBPE-TA is 168.81 °C, for HBPE-AD is 155.49 °C, for HBPE-MA is 148.27 °C, and for HBPE-PA is 197.49 °C. from these results it is found that the HBPE-PA has the highest melting temperature over the other prepared polymers due to the presence of aromatic rings in its structure, while HBPE-TA and HBPE-AD have the lower melting temperatures than HBPE-PA, due to the presence of hydroxyl groups in HBPE-TA and $CH_2$ in the main chain of HBPE-AD. While HBPE-MA has the lowest melting temperature over the four polymers, this may be due to the short chains of this polymer and to the low functional groups (OH) within it is structure.

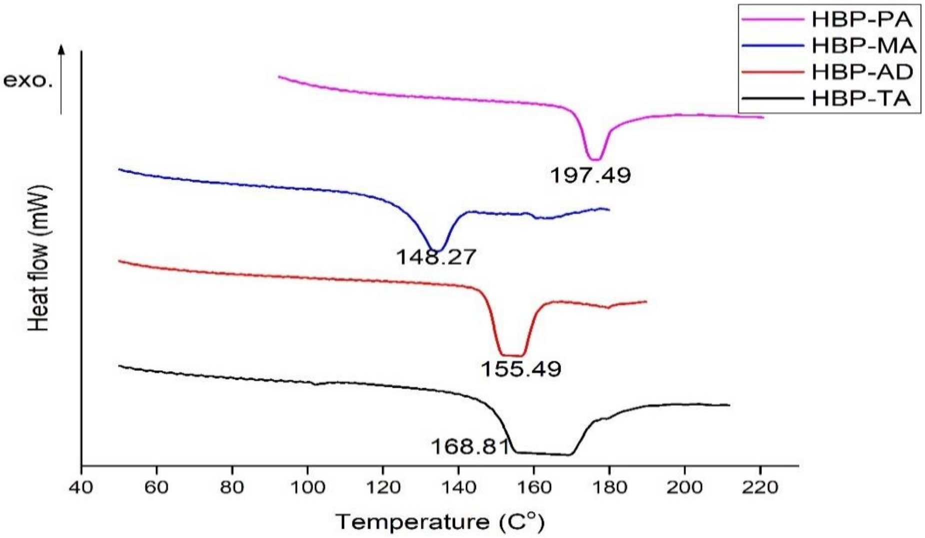


**Figure (4-29): DSC curves of the prepared HBPE polymers.**

**Table (4-5): DSC data for the prepared HBPEs.**

| **Samples** | **$T_m$ (°C)** | **ΔH (J/g)** |
|---|---|---|
| HBPE-TA | 168.81 | 123.72 |
| HBPE-AD | 155.49 | 81.97 |
| HBPE-MA | 148.27 | 56.49 |
| HBPE-PA | 197.49 | 95.22 |

Figure (4-30) and Figure (4-31) show the heating and cooling thermographs of VPP, rPP, and their blends with HBPE (VPP/HBPE, and rPP/HBPE). The effect of the addition of HBPE on the melting and the crystallization temperature of VPP are shown in Figure (4-30). It is found that the melting temperature of VPP/HBPE blends with the four prepared HBPE polymers have slightly improved when the amount of HBPE increased from 0 to 20% of HBPE, as shown in table (4-6). However, the crystallization temperature of VPP/HBPE blends have shifted the crystallization temperature of neat VPP to a higher value when the HBPE content increased from 0 to 20% of HBPE. This increment may be due to that the addition of HBPE can act as effective nucleating agents and accelerate the crystallization of PP matrix which permit to a better arrangement and alignment in the chains than in the case of neat VPP and thus the crystallization temperature became higher as shown in table (4-6). Additionally, it is found that as the HBPE content increased the crystallinity of VPP/HBPE blends which were decreased and these results are related with mechanical properties, these results are in agreement with Chaoqin [160] and Jiang[161].

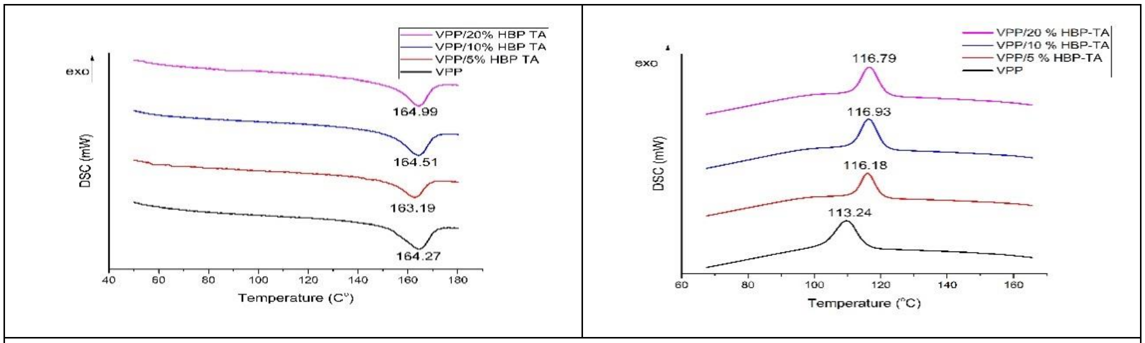
Figure (4-31) shows the effect of the addition of HBPE on the melting and the crystallization temperature of rPP. It is found that the melting temperature of rPP/HBPE blends with the four prepared polymers have slightly improved when the amount of HBPE increased from 0 to 20% of HBPE as shown in table (4-7). However, the crystallization temperature of rPP/HBPE blends have shifted the crystallization temperature of neat rPP to a lower value when the HBPE content increased from 0 to 20% of HBPE. This reduction may be due to absence of chain arrangements that result from recycling which reduces the chain entanglements and causes lower crystals formation, the presence of HBPE has no ability to form perfect crystals as shown in table (4-7). Additionally, it is found that as the HBPE content increased the crystallinity of rPP/HBPE blends which were decreased and these results are related with mechanical properties, these results are in agreement with Mastalygina [162] and Aumnate [163].

**Table (4-6): DSC data of VPP and VPP/HBPE blends.**

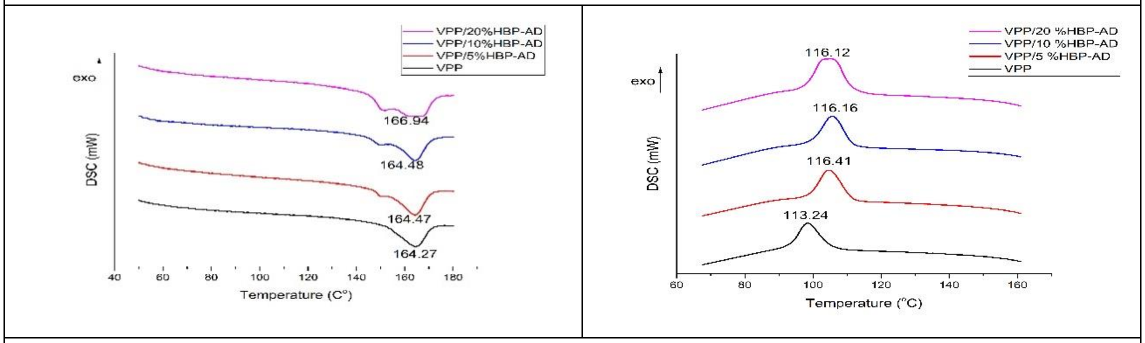
| Samples | $T_m$ (°C) | $\Delta H_m$ (J/g) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $X_c$ % |
|---|---|---|---|---|---|
| VPP | 164.27 | 40.97 | 113.24 | 73.91 | 19.6 |
| VPP/5%HBPE-TA | 163.19 | 25.84 | 116.18 | 83.18 | 11.74 |
| VPP/10%HBPE-TA | 164.51 | 40.6 | 116.93 | 84.41 | 17.48 |
| VPP/20%HBPE-TA | 164.99 | 37.51 | 116.79 | 79.2 | 14.36 |
| VPP/5%HBPE-AD | 164.47 | 34.82 | 116.41 | 96.41 | 15.83 |
| VPP/10%HBPE-AD | 164.48 | 31.95 | 116.16 | 93.37 | 13.76 |
| VPP/20%HBPE-AD | 166.94 | 42.18 | 116.12 | 94.07 | 16.15 |
| VPP/5%HBPE-MA | 165.31 | 28.2 | 111.41 | 104.3 | 12.8 |
| VPP/10%HBPE-MA | 166.5 | 17.86 | 111.39 | 82.04 | 7.7 |
| VPP/20%HBPE-MA | 165.76 | 27.61 | 114.03 | 86.97 | 10.6 |
| VPP/5%HBPE-PA | 165.2 | 22 | 117.99 | 95.38 | 10 |
| VPP/10%HBPE-PA | 164.37 | 30.29 | 111.25 | 87.24 | 13.04 |
| VPP/20%HBPE-PA | 164.17 | 25.35 | 122.89 | 90.99 | 9.7 |

**Table (4-7): DSC data of rPP and rPP/HBPE blends.**

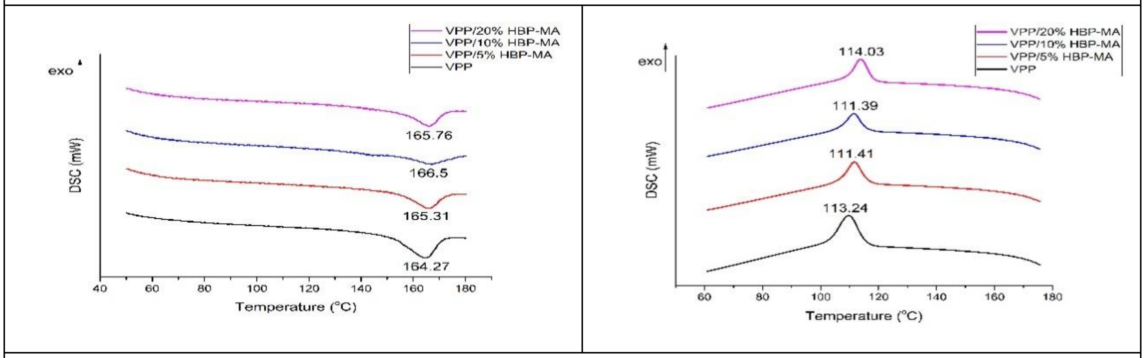
| Samples | $T_m$ (°C) | $\Delta H_m$ (J/g) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $X_c$ % |
|---|---|---|---|---|---|
| rPP | 149.46 | 37.28 | 116.86 | 103.4 | 16.9 |
| rPP/5%HBPE-TA | 150.66 | 9.23 | 105.84 | 71.33 | 4.2 |
| rPP/10%HBPE-TA | 150.96 | 16.89 | 102.05 | 59.1 | 7.3 |
| rPP/20%HBPE-TA | 153.24 | 21.09 | 106.04 | 60.34 | 8.1 |
| rPP/5%HBPE-AD | 150.29 | 29.17 | 101.91 | 64.42 | 13.3 |
| rPP/10%HBPE-AD | 149.38 | 28.54 | 107.02 | 69.85 | 12.3 |
| rPP/20%HBPE-AD | 150.22 | 29.44 | 107.03 | 61.76 | 11.3 |
| rPP/5%HBPE-MA | 150.01 | 36.7 | 102.12 | 77.18 | 16.6 |
| rPP/10%HBPE-MA | 149.8 | 25.94 | 102.58 | 64.62 | 11.2 |
| rPP/20%HBPE-MA | 151.13 | 31.13 | 100.49 | 63.66 | 11.9 |
| rPP/5%HBPE-PA | 150.71 | 19.35 | 101.02 | 63.57 | 8.8 |
| rPP/10%HBPE-PA | 149.96 | 29.75 | 101.03 | 73.84 | 12.8 |
| rPP/20%HBPE-PA | 150.01 | 16.43 | 102.17 | 64.86 | 6.2 |



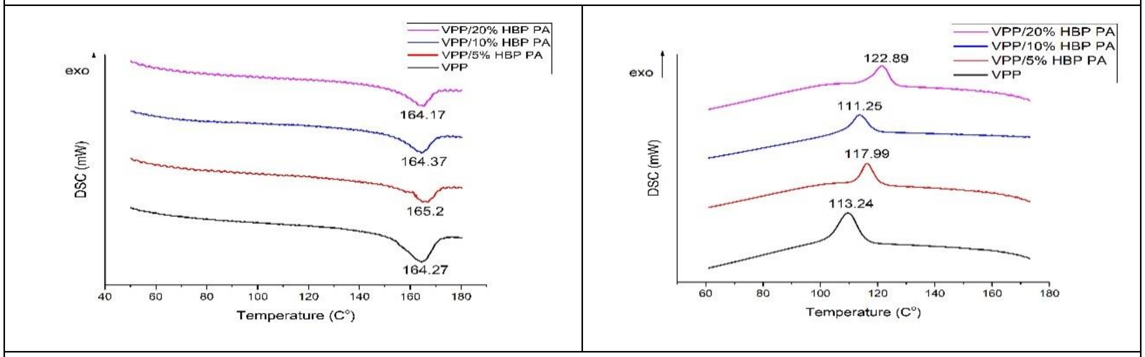
A. VPP/HBPE-TA



B. VPP/HBPE-AD

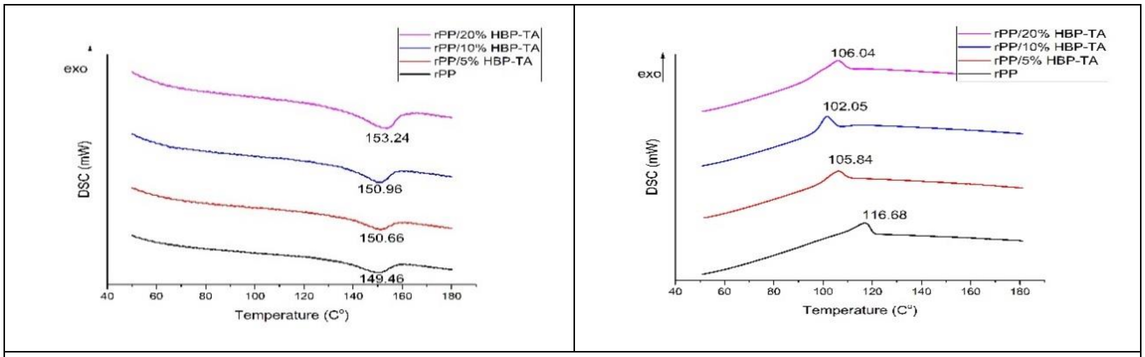


C. VPP/HBPE-MA

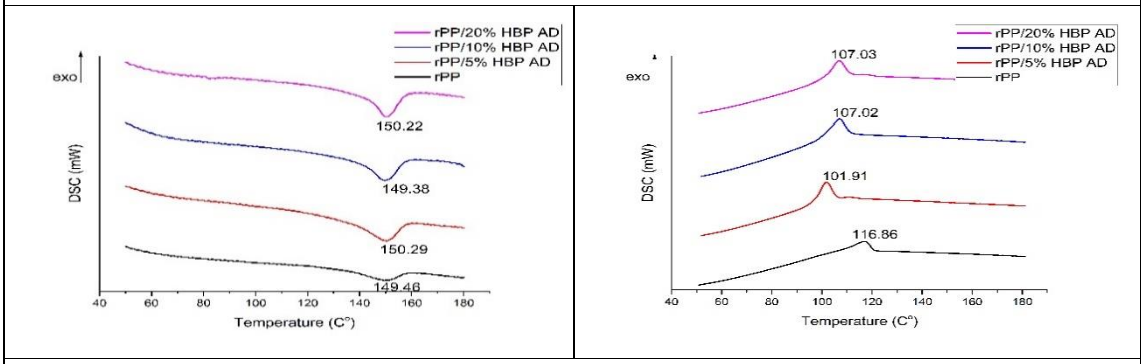


D. VPP/HBPE-PA

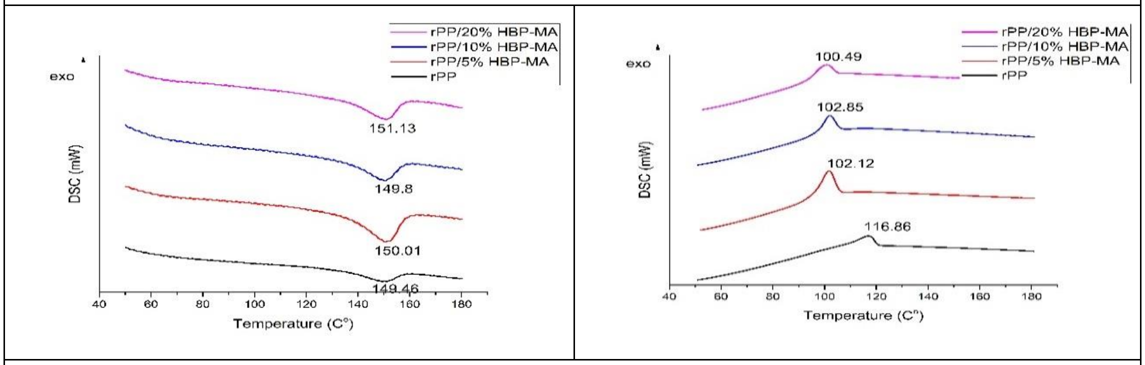
**Figure (4-30): DSC heating and cooling thermographs for VPP and VPP/HBPE blends.**



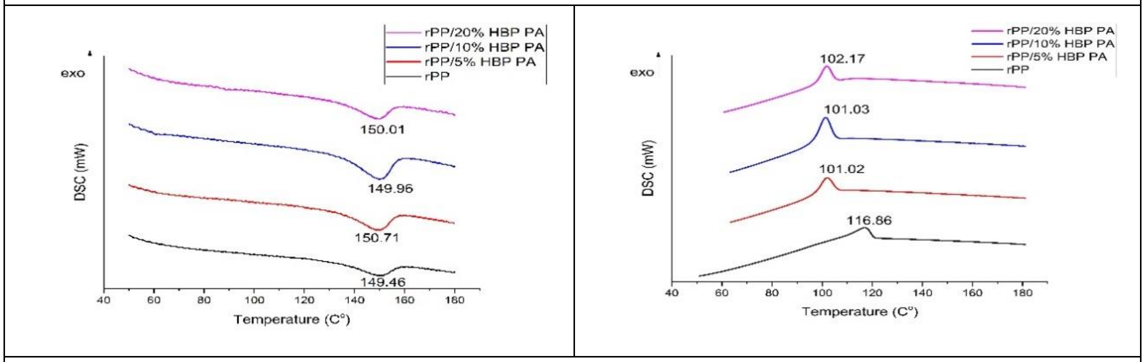
A. rPP/HBPE-TA



B. rPP/HBPE-AD



C. rPP/HBPE-MA



D. rPP/HBPE-PA

Figure (4-31): DSC heating and cooling thermographs for rPP and rPP/HBPE blends.

### 4.3.7. TGA Test Results

The thermal stability of a polymer can provide an important guidance for its processing and application. The studies of thermal behavior not only can explain the behavior of a polymer at high temperature, but also provide assistance for the establishment of selection criteria for specific applications of polymer materials.

Figure (4-32) shows the TGA and DTG curves for the prepared HBPE. It is found that both HBPE-TA and HBPE-AD showed a two stage degradation process, while HBPE-MA and HBPE-PA showed three stage degradation process. For HBPE-TA the first stage degradation starts between 201 to 276 $^{o}$C with 49.5% weight loss and the second stage degradation starts between 285 to 584 $^{o}$C with 27.9% weight loss, while for HBPE-AD the first stage starts between 131 to 338 $^{o}$C with 64.6% weight loss and the second stage degradation starts between 347 to 597 $^{o}$C with 24.3% weight loss. From these results it is found that HBPE-TA has better thermal stability than that HBPE-AD, because HBPE-TA has higher molecular weight than that HBPE-AD which also has higher OH content and lower branch length.

For HBPE-MA the first stage degradation process starts between 104 to 176 $^{o}$C with 7.2% weight loss, the second stage degradation process starts between 193 to 289 $^{o}$C with 32.6% weight loss, and the third stage degradation process starts between 292 to 595 $^{o}$C with 25.9% weight loss. While, for HBPE-PA the first stage degradation process starts between 113 to 319 $^{o}$C with 73.42% weight loss, the second stage starts between 328 to 452 $^{o}$C with 9.4% weight loss, and the third stage starts between 465 to 581 $^{o}$C with 9.61 weight loss. From these results, it is found that the HBPE-PA has better thermal stability than HBPE-MA which may attributed to the presence of aromatic ring within its structure, also to the higher melting enthalpy as indicated by table (4-5).

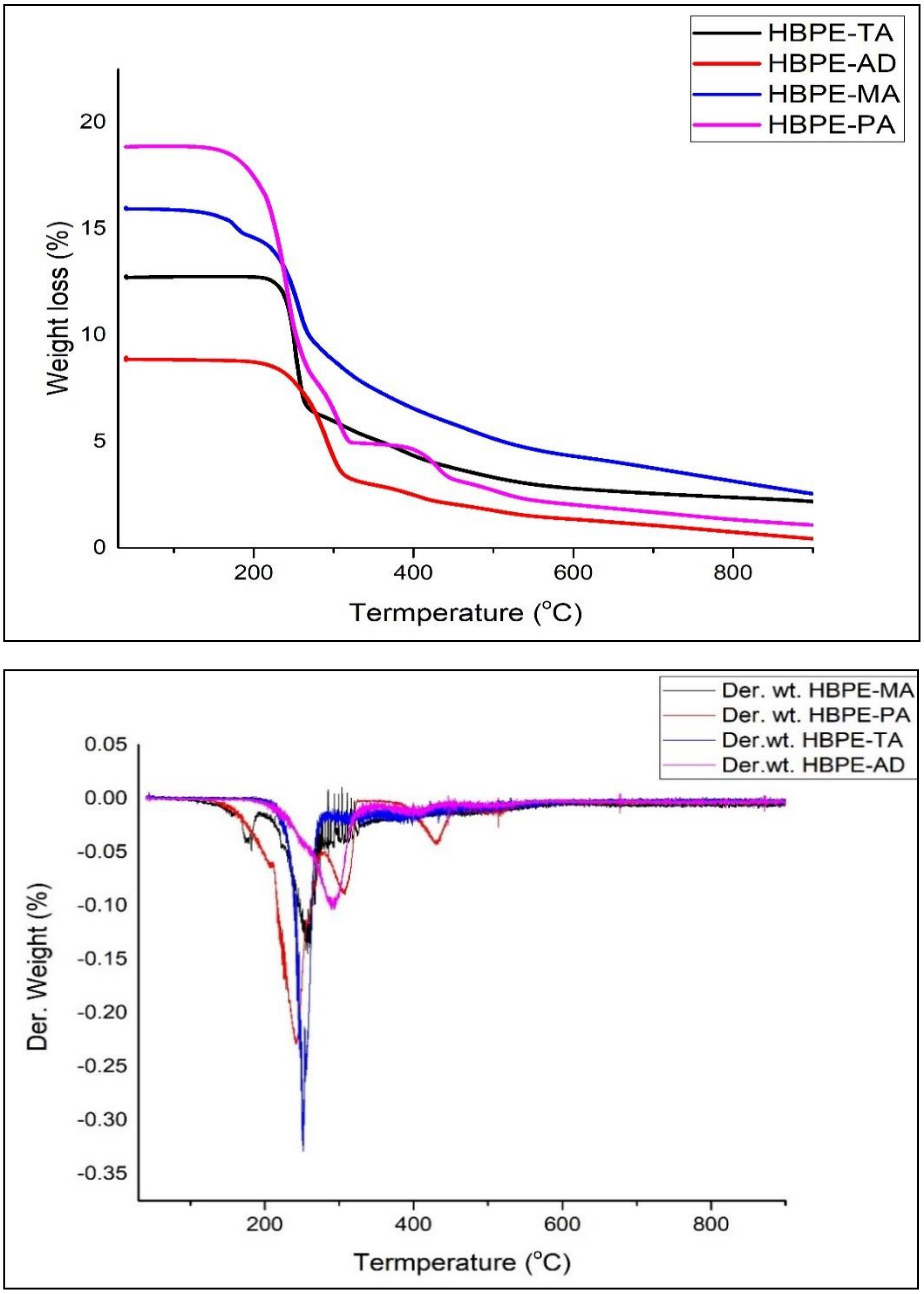


**Figure (4-32): TGA and DTA curves for the prepared HBPE.**

Figure (4-33) and Figure (4-34) show the TGA curves for PP/HBPE blends. Figure (4-33) shows TGA and DTA curves for VPP and VPP/HBPE blends, it is found that VPP has single step degradation process starts between 317 to 511 ºC with 95.9% weight loss [164], while for blends of VPP/HBPE it is found that there are two step degradation process. For VPP/HBPE-AD blend, the first step starts between 240 to 337 ºC with 5.53% weight loss and the second step starts between 349 to 518 ºC with 94.5% weight loss, while for VPP/HBPE-TA blend, it is found that the first step starts between 189 to 298 ºC with 3.1% weight loss and second step starts between 336 to 519 ºC with 84.4% weight loss. For VPP/HBPE-MA blend, it is found that the first step starts between 206 to 294 ºC with 4.5% weight loss and second step starts between 320 to 514 ºC with 85.5% weight loss, while for VPP/HBPE-PA blend, it is found that the first step starts between 199 to 315 ºC with 4.7% weight loss and second step starts between 343 to 522 ºC with 86.4% weight loss.

Figure (4-34) shows TGA and DTA curves for rPP and rPP/HBPE blends, it is found that rPP has single step degradation process that starts between 314 to 510 ºC with 99.7% weight loss [165], while for blends of rPP/HBPE it is found that there are two step degradation process. For rPP/HBPE-AD blend, the first step starts between 237 to 336 ºC with 7.7% weight loss and the second step starts between 372 to 512 ºC with 80.5% weight loss, while for rPP/HBPE-TA blend, it is found that the first step starts between 180 to 293 ºC with 7.04% weight loss and second step starts between 318 to 511 ºC with 92% weight loss. For rPP/HBPE-MA blend, it is found that the first step starts between 196 to 298 ºC with 4.6% weight loss and second step starts between 332 to 514 ºC with 90.2% weight loss, while for rPP/HBPE-PA blend, it is found that the first step starts between 193 to 311 ºC with 6.1% weight loss and second step starts between 353 to 513 ºC with 81.7% weight loss.

From the above results of VPP, rPP, and their blends with the prepared HBPE, it is found that the addition of HBPE to VPP and rPP has improved the thermal stability of blends when compared to neat polymers, this improvement may be due to good dispersion of HBPE particles within PP matrix also due to the presence of some compatibility between HBPE and PP as indicating by SEM results.

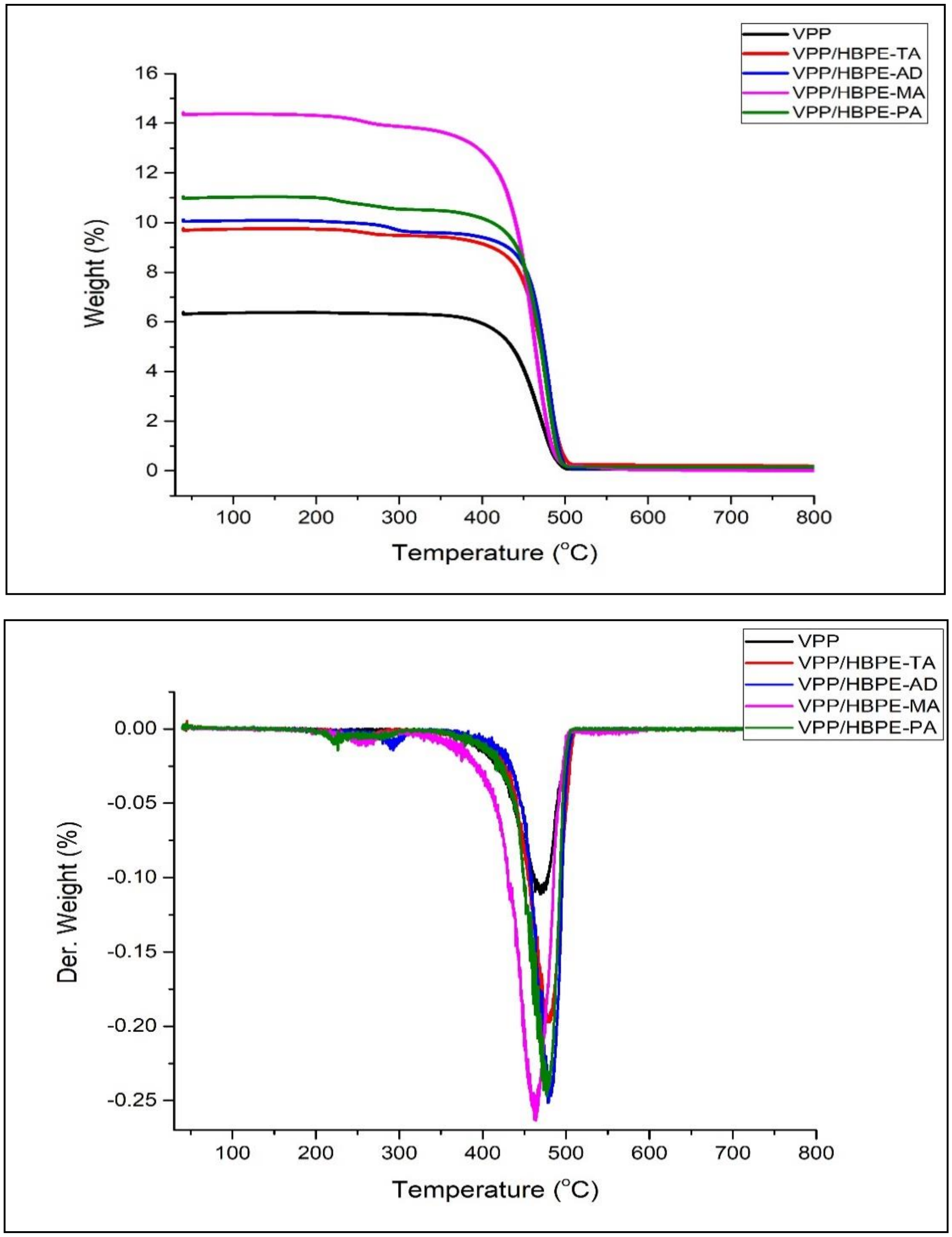
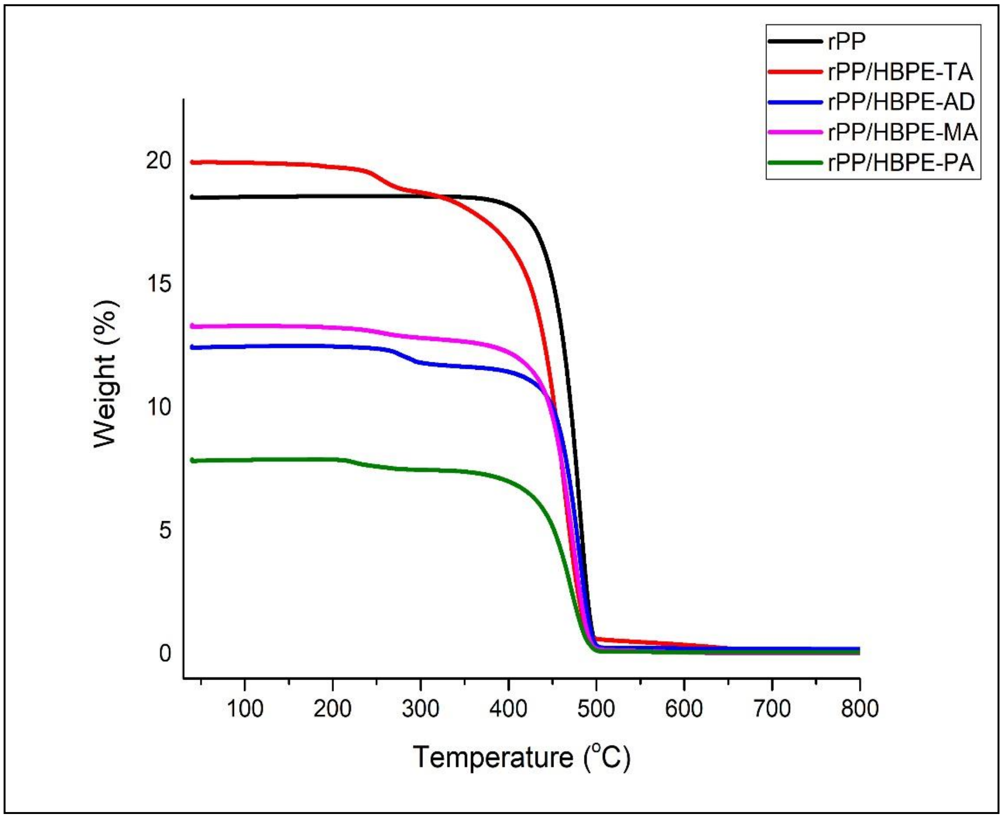


**Figure (4-33): TGA and DTA of VPP and VPP/HBPE blends.**



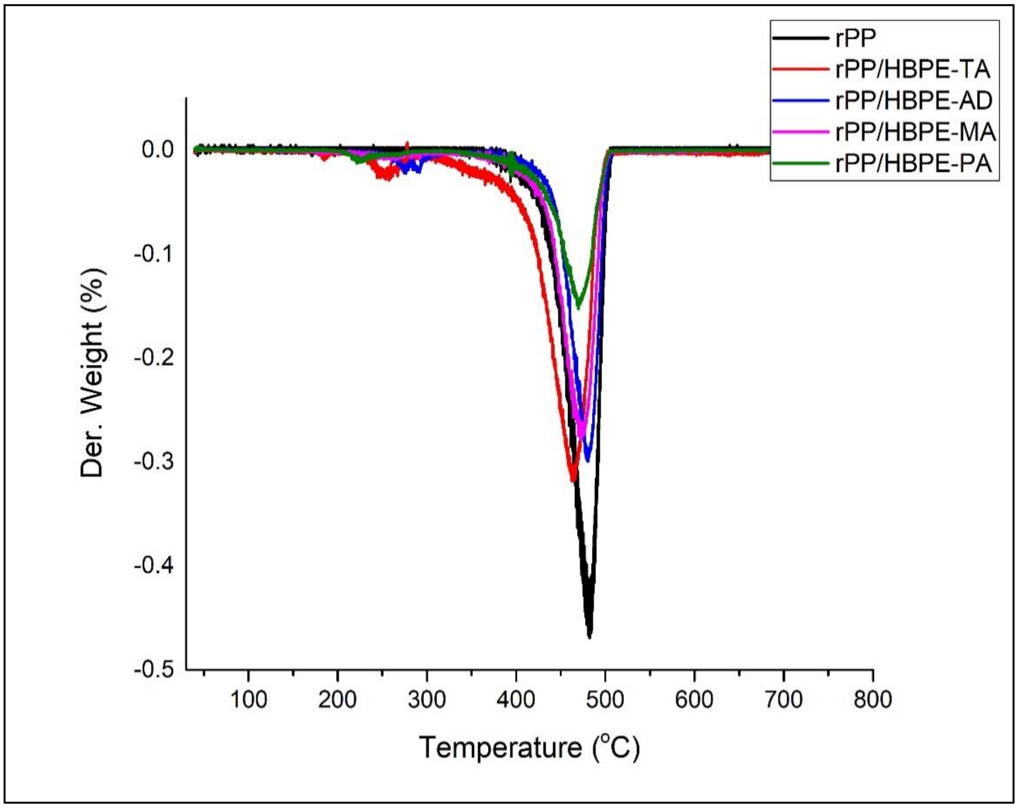


**Figure (4-34): TGA and DTA of rPP and rPP/HBPE blends.**

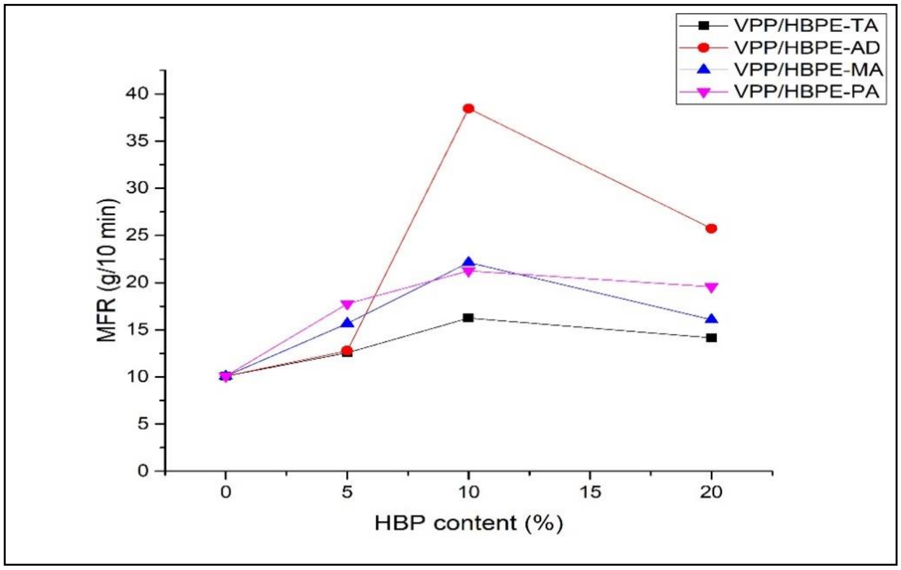
### 4.3.8. MFR Results

The rheological properties (MFR, viscosity, and shear rate) of PP and its blends with HBPE have been characterized using MFR. The MFR of PP and PP/HBPE blends shown by Figure (4-35). From figure (4-35) A for VPP and VPP/HBPE blends, it is found that the MFR of all blends has been increased with the increase of HBPE content. It is shown that the VPP has MFR of 10 (g/10min), as the HBPE blended with VPP the MFR was increased by 2.6, 6.23, and 4.14 g/10min for 5%, 10%, and 20% of HBPE-TA samples and increased by 2.8, 28.5, and 15.7 g/10min for 5%, 10%, and 20% of HBPE-AD samples respectively. While, it is increased by 5.7, 12.1, and 6.1 g/10min for 5%, 10%, and 20% of HBPE-MA samples and increased by 7.8, 11.24, and 9.6 g/10min for 5%, 10%, and 20% of HBPE-PA samples respectively.

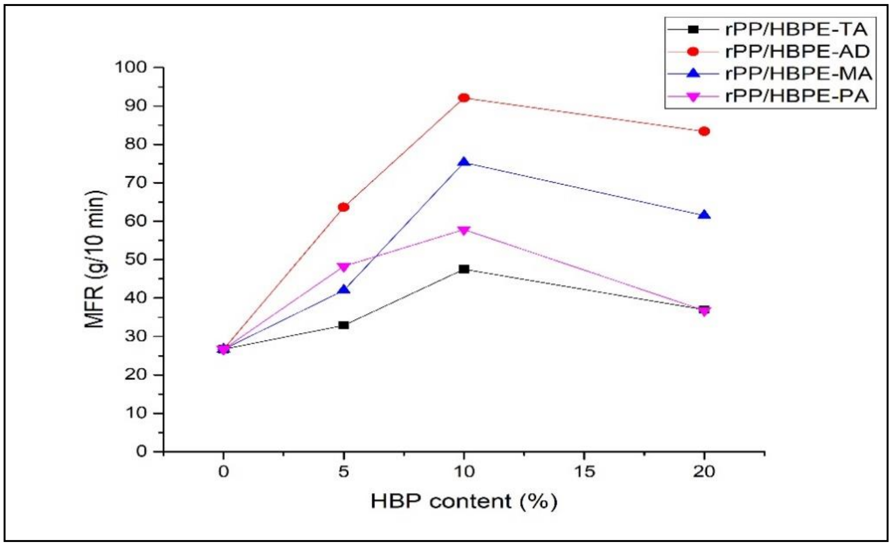
However, for rPP and rPP/HBPE blends shown in Figure (4-35) B, it was found that the MFR improved by the addition of HBPE. The MFR of rPP is 26.7 g/10min, as the HBPE added the MFR improved by 6.2, 20.8, and 10.3 g/10min for 5%, 10%, and 20% of HBPE-TA samples and improved by 37, 65.45, and 56.8 g/10min for 5%, 10%, and 20% of HBPE-AD samples respectively. While, it is improved by 15.4, 48.7 and 34.9 g/10min for 5%, 10%, and 20% of HBPE-MA samples and is improved by 21.7, 31.2 and 10.1 g/10min for 5%, 10%, and 20% of HBPE-PA samples respectively.

From the above results, it is found that HBPE addition improves the MFR for rPP better that VPP due to the less entanglements and shorter chains of rPP. In addition, it is found that 10% of HBPE has the highest MFR value for VPP and rPP blends due to the better compatibility and distribution of HBPE within PP matrix as indicated by SEM.

These results attributed to the fact that hyperbranched polymers HBPE have relatively lower viscosity than linear polymers PP, which mean that these additives act as viscosity reducers (processing aids additives). So that the presence of HBPE in the molten PP generate a rolling effect which facilitates sliding of melt on the cylinder wall of MFI tester, serve as ball bearings, and reducing the interlayer interaction.



**A-VPP/HBPE**



**B-rPP/HBPE**

**Figure (4-35): MFR of VPP, rPP, and their blends with HBPE.**

According to the results above, the viscosity, shear rate and the power law index (n) of VPP, rPP, and their blends were calculated easily from equations (3.4) and (3.5) to give the data in table (4-8).

**Table (4-8): The calculated data from the MFR for VPP, rPP, and their blends.**

| **Samples** | **Viscosity (Pa.s)** | **Shear rate ($S^{-1}$)** | **Power law index (n)** |
|---|---|---|---|
| VPP | 34903.5 | 21002.4 | 0.43 |
| VPP/5%HBPE-TA | 28836.2 | 25421.4 | 0.392 |
| VPP/10%HBPE-TA | 22382.1 | 32752 | 0.343 |
| VPP/20%HBPE-TA | 26326.2 | 27845.1 | 0.374 |
| VPP/5%HBPE-AD | 28205.97 | 21002.4 | 0.388 |
| VPP/10%HBPE-AD | 9564.3 | 25989.4 | 0.195 |
| VPP/20%HBPE-AD | 14281.42 | 76645.1 | 0.262 |
| VPP/5%HBPE-MA | 22888.92 | 32026.7 | 0.348 |
| VPP/10%HBPE-MA | 16896.91 | 43384.03 | 0.292 |
| VPP/20%HBPE-MA | 23388.7 | 31342.4 | 0.352 |
| VPP/5%HBPE-PA | 20471.84 | 35808.02 | 0.327 |
| VPP/10%HBPE-PA | 17215.23 | 42581.83 | 0.295 |
| VPP/20%HBPE-PA | 18097.1 | 40506.92 | 0.304 |
| rPP | 13141 | 55783.9 | 0.39 |
| rPP/5%HBPE-TA | 10850.8 | 67557.8 | 0.366 |
| rPP/10%HBPE-TA | 7713.2 | 95039.3 | 0.311 |
| rPP/20%HBPE-TA | 10205.7 | 71828.2 | 0.355 |
| rPP/5%HBPE-AD | 5619.28 | 130453.73 | 0.263 |
| rPP/10%HBPE-AD | 3891.9 | 188356.12 | 0.211 |
| rPP/20%HBPE-AD | 4432.6 | 165379.9 | 0.229 |
| rPP/5%HBPE-MA | 8537.14 | 85866.7 | 0.327 |
| rPP/10%HBPE-MA | 4808.84 | 152439.21 | 0.24 |
| rPP/20%HBPE-MA | 6073.82 | 120691.13 | 0.275 |
| rPP/5%HBPE-PA | 7364.21 | 99543.01 | 0.303 |
| rPP/10%HBPE-PA | 6288.02 | 116579.7 | 0.28 |
| rPP/20%HBPE-PA | 10242.1 | 71572.9 | 0.356 |

From table (4-8) it is shown that the viscosity of all blends PP/HBPE was decreased by the increase of HBPE while the shear rate was increased with HBPE increasing, which proves that HBPE addition increases the flow behavior for PP. The shear thinning was increased with the increase of HBPE content as indicated by table (4-8), the values of power law index were decreased for all blends.

From these results, it can be concluded that the addition of HBPE has improved the processability of PP and the energy consumption during the preparation of blends, these results are in agreement with Guzmán [166] and Mesias [167].

### 4.3.9. Contact Angle Results

The water contact angle gives an indication of the nature of the surface, whether it is hydrophilic or hydrophobic. The higher the contact angle the lower the wettability and the surface is hydrophobic and vice versa. In table (4-9) and (4-10), the water contact angle data for PP and PP/HBPE blends is shown at different time intervals. For VPP and its blends with HBPE, it is found that the contact angle was decreased with the increase of HBPE content from 0% to 20%, the contact angle after 3 sec for VPP was decreased from 78.38° to 60.17° for HBPE-TA and was decreased to 62.1° for HBPE-AD and decreased to 61.61° and 67.87° for HBPE-MA and HBPE-PA respectively after 60 sec the contact angle for VPP was decreased from 78.38° to 69.4° and was decreased further for the other blends, as shown in Table (4-9) and Figure (4-36).

For rPP and rPP/HBPE blends, it is found that the contact angle also was decreased with HBPE increasing. The contact angle after 3 sec for rPP was decreased from 70.77° to 58.23° and 65.37° for HBPE-TA and HBPE-AD respectively and was decreased to 64.1° and 68.2° for HBPE-MA and HBPE-PA respectively after 60 sec the contact angle for rPP was decreased from 70.77° to 66.5° and was decreased further for the other blends, as shown in Table (4-10) and Figure (4-36).

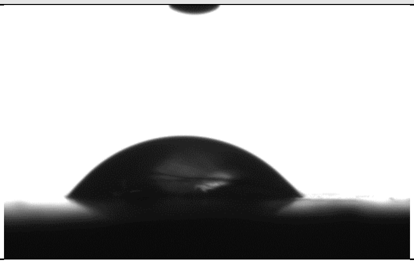
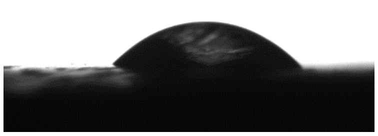
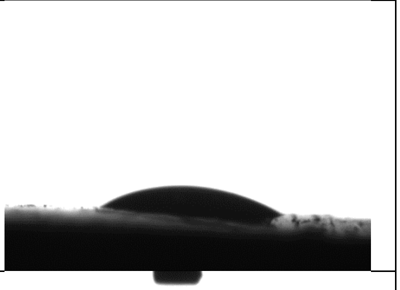
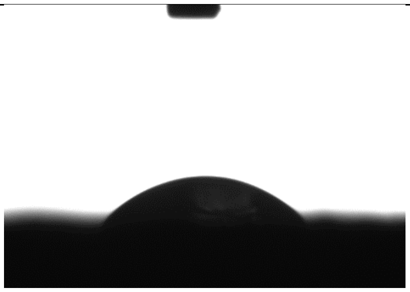
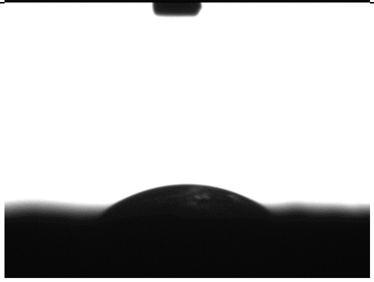
From the results, it is found that the addition of HBPE to PP has improved its hydrophilicity (the surface wettability increased) by reducing the contact angle, this improvement is due to the presence of large number of hydroxyl group and carboxyl group in the prepared HBPE (the presence of polar group can improve the wettability and hydrophilicity of the surface) these results are in agreement with Zhang [168] and Caicedo [169]. Also it is found that the rPP/HBPE blends have better wettability and lower contact angle than VPP/HBPE, this due to the shorter chains and the less entanglement in rPP than VPP. In addition, the blends with HBPE-TA have the lowest contact angle, the best surface wettability and the best hydrophilicity; this is due to the higher content of hydroxyl and carboxyl group in HBPE-TA when compared with the other types of the prepared HBPEs.

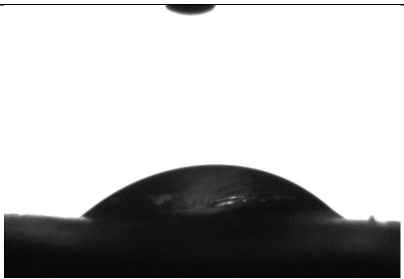
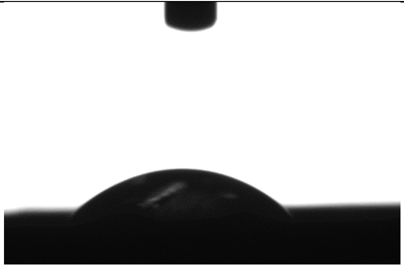
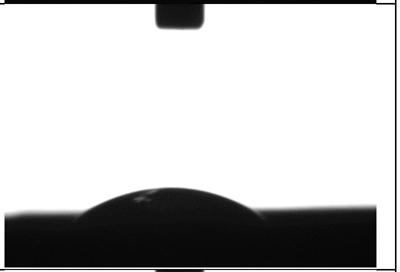
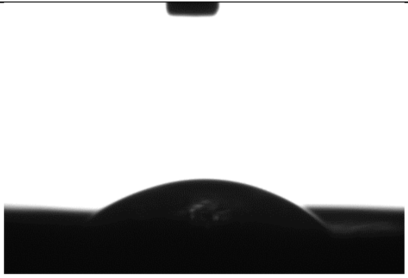
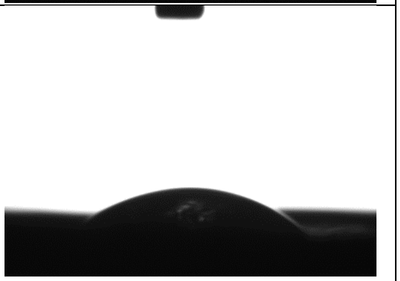
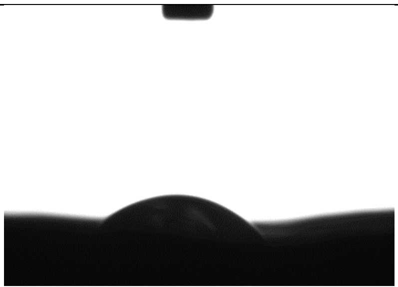
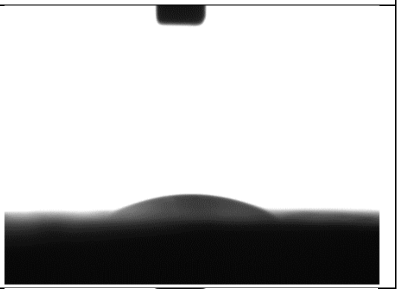
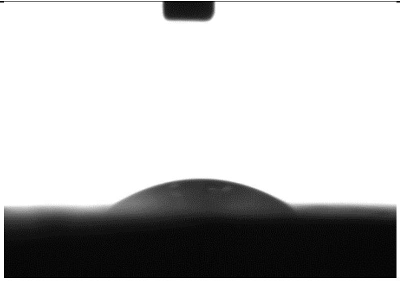
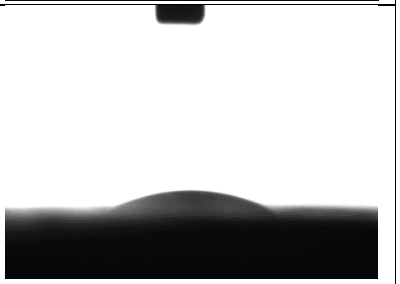
**Table (4-9): Contact angle data for VPP, and their blends with HBPE.**

| **Samples** | **Contact angle** | **Wettability** |
|---|---|---|
| | **After 3 sec** | **After 60 sec** |
| VPP | 78.38° | 69.4° |
| VPP/5%HBPE-TA | 65.66° | 54.8° |
| VPP/10%HBPE-TA | 63.18° | 54.18° |
| VPP/20%HBPE-TA | 60.17° | 49.95° |
| VPP/5%HBPE-AD | 62.24° | 60.32° |
| VPP/10%HBPE-AD | 61.68° | 57.07° |
| VPP/20%HBPE-AD | 62.1° | 58.12° |
| VPP/5%HBPE-MA | 65.51° | 59.06° |
| VPP/10%HBPE-MA | 63.36° | 58.85° |
| VPP/20%HBPE-MA | 61.61° | 57.32° |
| VPP/5%HBPE-PA | 65.95° | 61.24° |
| VPP/10%HBPE-PA | 63.89° | 61.43° |
| VPP/20%HBPE-PA | 67.87° | 64.05° |

Table (4-10): Contact angle data for rPP, and their blends with HBPE.

| Samples | Contact angle | Wettability |
|---|---|---|
| | After 3 sec | After 60 sec |
| rPP | 70.77° | 66.5° |
| rPP/5%HBPE-TA | 65.02° | 48.82° |
| rPP/10%HBPE-TA | 63.92° | 42.57° |
| rPP/20%HBPE-TA | 58.23° | 47.95° |
| rPP/5%HBPE-AD | 68.2° | 59.25° |
| rPP/10%HBPE-AD | 65.89° | 53.33° |
| rPP/20%HBPE-AD | 65.37° | 58.53° |
| rPP/5%HBPE-MA | 65.41° | 58.49° |
| rPP/10%HBPE-MA | 63.38° | 55.57° |
| rPP/20%HBPE-MA | 64.1° | 55.21° |
| rPP/5%HBPE-PA | 68.23° | 59.61° |
| rPP/10%HBPE-PA | 67.3° | 55.45° |
| rPP/20%HBPE-PA | 68.2° | 59.85° |

| Material | Contact Angle° | Wettability |
|---|---|---|
| | 3 sec | 60 sec |
| VPP |  |  |
| VPP/5%HBPE-TA |  |  |
| VPP/10%HBPE-TA |  |  |

| | | |
|---|---|---|
| **VPP/20%HBPE-TA** |  |  |
| **VPP/5%HBPE-AD** |  |  |
| **VPP/10%HBPE-AD** |  |  |
| **VPP/20%HBPE-AD** |  |  |
| **VPP/5%HBPE-MA** |  |  |

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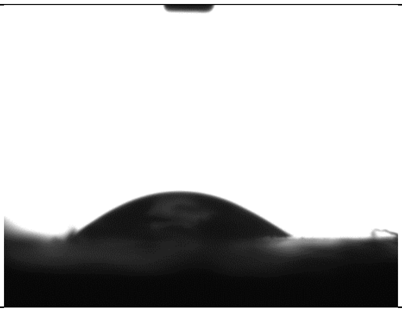
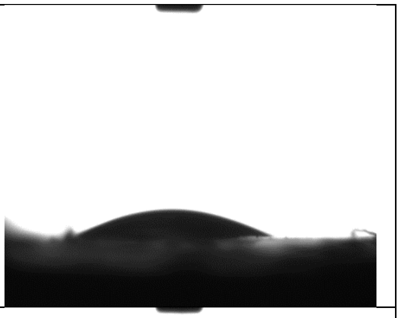
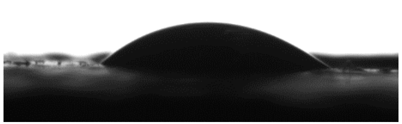
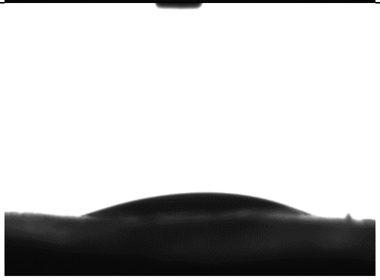
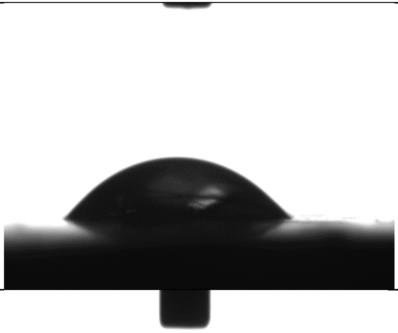
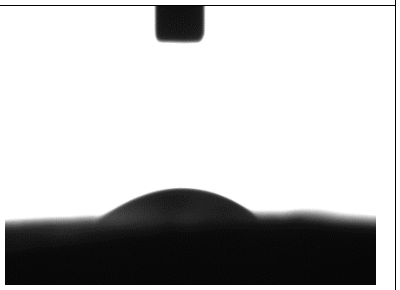
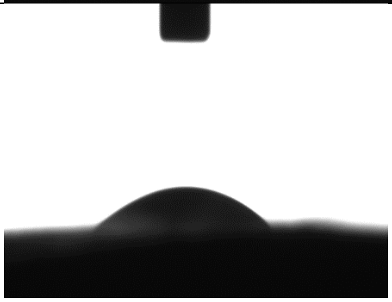
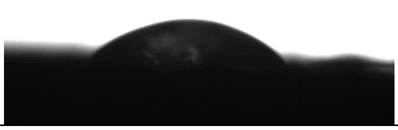
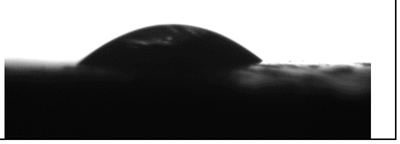
|---|---|---|
| **VPP/10%HBPE-MA** |  |  |
| **VPP/20%HBPE-MA** |  |  |
| **VPP/5%HBPE-PA** |  |  |
| **VPP/10%HBPE-PA** |  |  |
| **VPP/20%HBPE-PA** |  |  |

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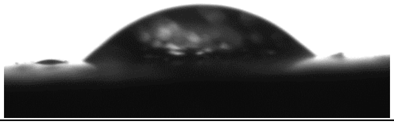
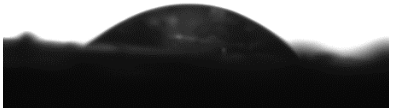
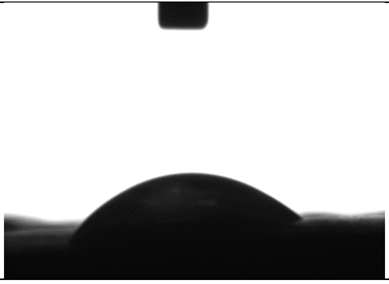
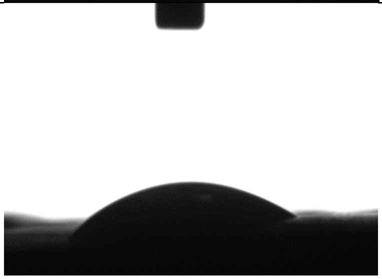
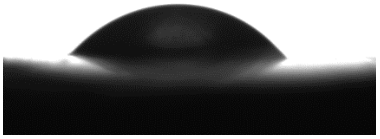
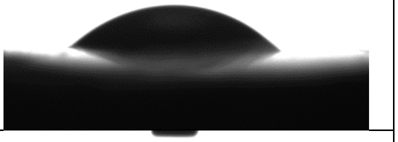
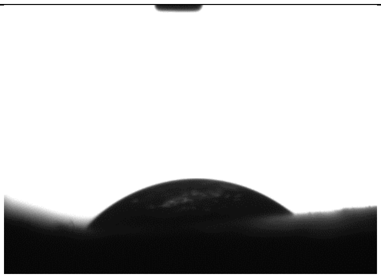
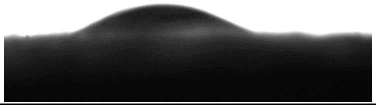
|---|---|---|
| **rPP** |  |  |
| **rPP/5%HBPE-TA** |  |  |
| **rPP/10%HBPE-TA** |  |  |
| **rPP/20%HBPE-TA** |  |  |
| **rPP/5%HBPE-AD** |  |  |
| **rPP/10%HBPE-AD** |  |  |

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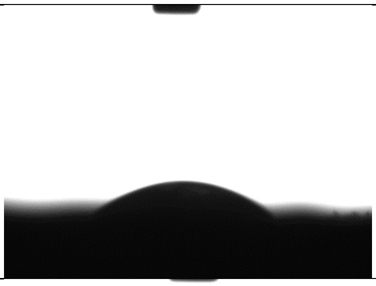
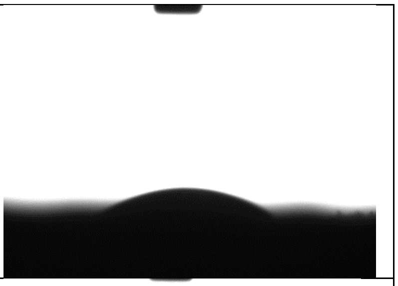
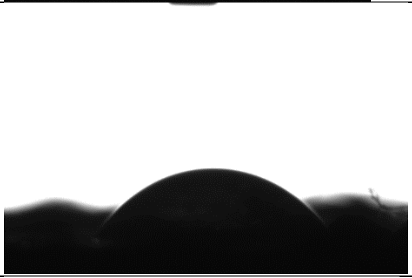
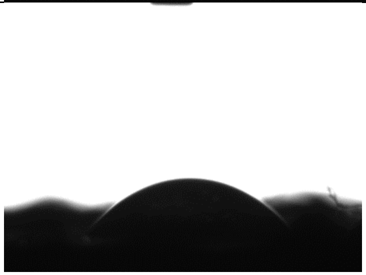
|---|---|---|
| **rPP/20%HBPE-AD** |  |  |
| **rPP/5%HBPE-MA** |  |  |
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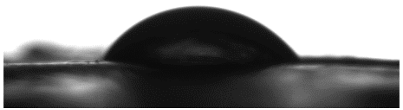
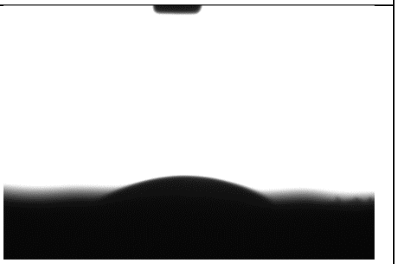
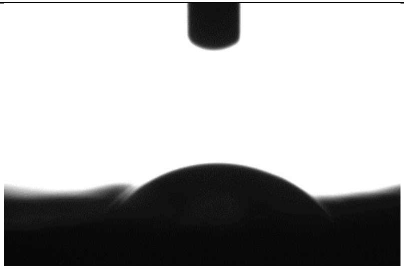
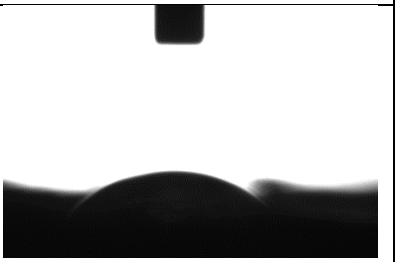
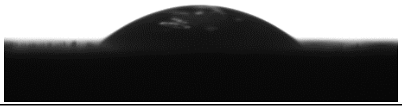
| **rPP/20%HBPE-MA** |  |  |
| **rPP/5%HBPE-PA** |  |  |
| **rPP/10%HBPE-PA** |  |  |

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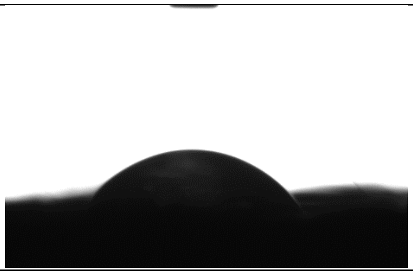
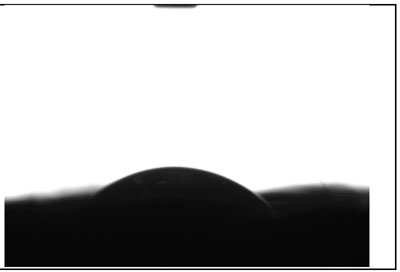
|---|---|---|
| **rPP/20%HBPE-PA** |  |  |

**Figure (4-36): Contact angle images for VPP, rPP and their blends with the prepared HBPEs polymers.**

### 4.3.10. Biodegradation Results (Soil Burial)

Most types of polymers when they meet the required need and after the expiry of their use, they will accumulate in large quantities, which will have a dangerous impact on the environment as well as on the general appearance. In order to reduce the accumulation of these materials, these polymers are usually mixed with other types of materials that have the ability to decompose in order to improve the decomposition of these polymers and to reduce their danger to the environment and human life.

The biodegradation through the weight loss of PP and its blends with HBPE in soil are shown in Figure (4-37) and (4-38). From the results, it is noted that both VPP and rPP did not show any weight loss during the 90-day examination period. These results indicate that this type of polymer does not have the ability to degrade in short periods, but needs very long periods, because the chemical structure of this type of polymer does not contain any groups that aid in degradation. For VPP/HBPE blends, it is found that there is an improvement in the degradation of PP through the test period. It is shown from Figure (4-37) that the weight loss increases as both test period and the amount of HBPE increase. It is found that the blend with HBPE-TA increases the weight loss to 6.5%, 7.7%, and 8.5% as the HBPE increases from 5% to 20%, and the blend with HBPE-MA increases the weight loss to

3.5%, 4.2%, and 4% as the HBPE increases from 5% to 20%. While for the blends with HBPE-AD and HBPE-PA it is found that the weight loss is in the range of 2.5% to 3.25%.

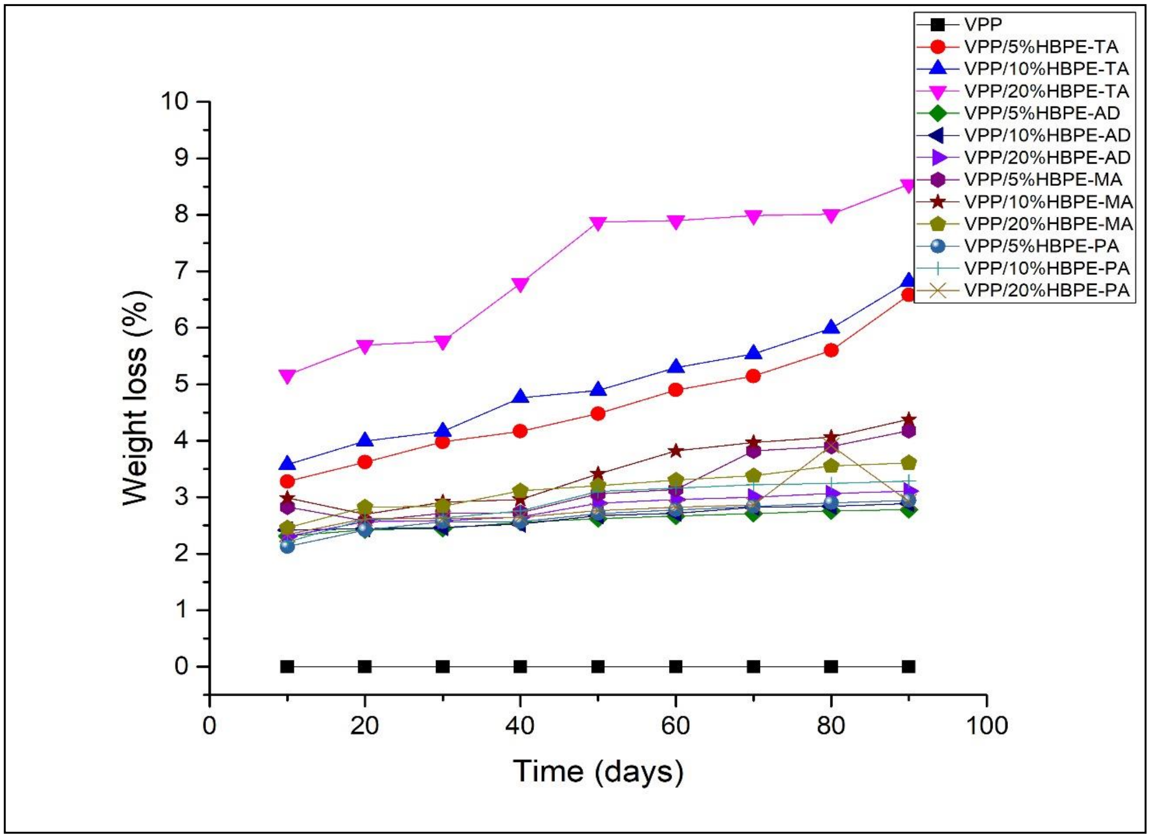


**Figure (4-37): The biodegradability of VPP and VPP/HBPE in soil environment.**

While in Figure (4-38), for rPP/HBPE blends it is found that the weight loss for blend with HBPE-TA is 9%, 12.2%, and 13.1% as the HBPE increases from 5% to 20%, and the blend with HBPE-MA increases the weight loss to 4.5%, 5.2%, and 5.8% as the HBPE increases from 5% to 20%. While for the blends with HBPE-AD and HBPE-PA it is found that the weight loss is in the range of 3.9% to 4.25% for blend with HBPE-AD and the weight loss is in the range of 4.8% to 5.4% for blend with HBPE-PA.

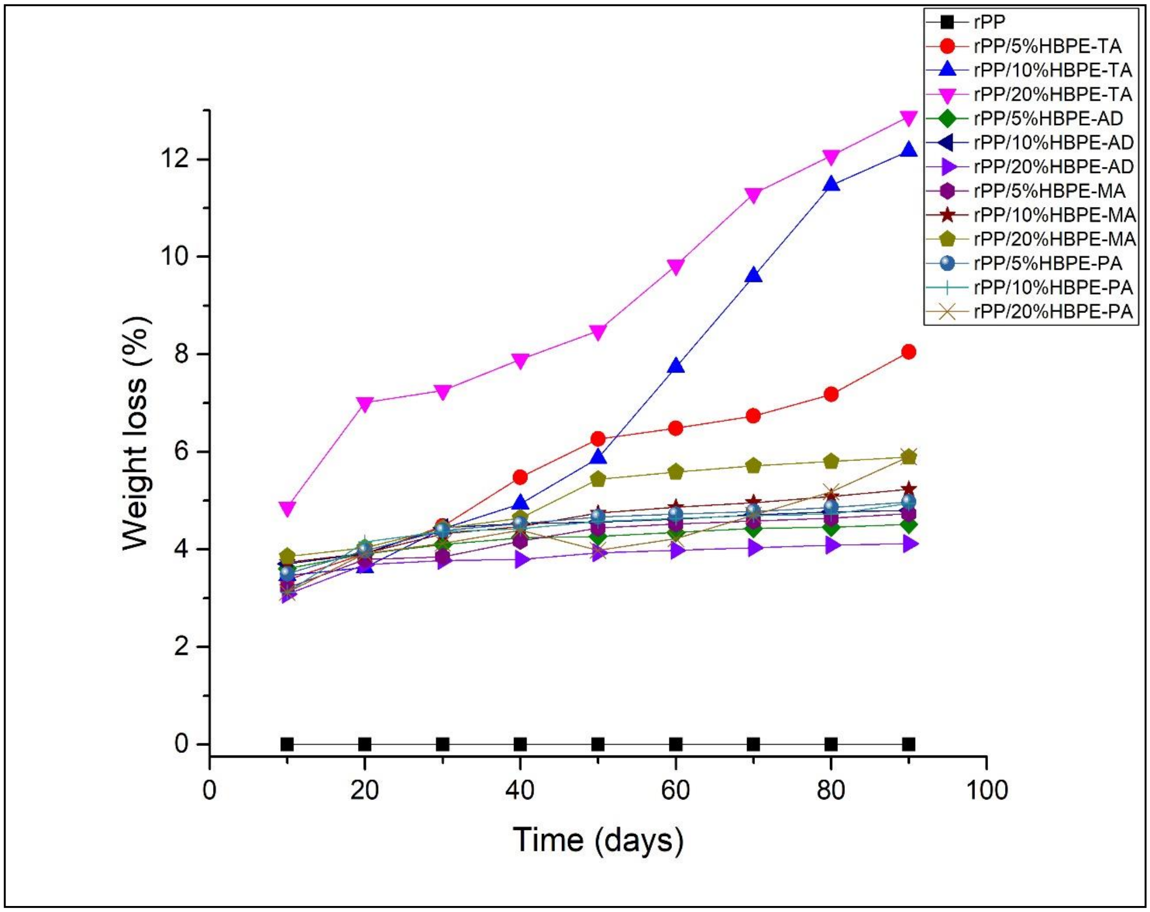


**Figure (4-38): The biodegradability of rPP and rPP/HBPE in soil environment.**

From the above results, it is found that the blends with HBPE-TA have the best results when compared with other blends this is due to the higher content of OH groups in HBPE-TA as indicated by FTIR analysis. In addition, it is found that the result of rPP is better than VPP this is because rPP has shorter chains and lower entanglements which permit in better absorption of water and make the degradation easier. The presence of HBPE molecule can reduce the polymer crystallinity as indicated by DSC results, the reduction in the crystallinity means the polymer ability to withstand the degradation was reduced, and the hydrolysis within amorphous regions are higher than crystalline regions. The presence of esters in HBPE can result in faster degradation, these results are in agreement with Bakhshi [170] and Weidong [171]. This is a good prove about the higher degradation that occurs in rPP blends rather than VPP blends, the crystallinity of rPP is much lower than VPP as shown in table (4-6) and (4-7) for DSC data.

## 5.1. Conclusions

From the results discussed in chapter four, the following conclusions can be summarized as shown below:

1. Both FTIR and $^1$H-NMR proves the starting material (B3 monomer) and the four hyperbranched polyester polymers HBPs have been synthesized successfully and showed the presence of different functional groups in the same molecule such as OH, C-N and C=O.
2. GPC showed that three of the four prepared HBPE polymers (HBPE-TA, HBPE-AD, and HBPE-PA) have narrow molecular weight and polydispersity index PDI except HBP-MA has higher molecular weight.
3. FTIR for both blends (VPP/HBPE and rPP/HBPE) showed that there is no chemical interaction between PP and HBP, only physical interaction with a slight shifting in PP bands.
4. The mechanical properties (tensile strength, elastic modulus, and elongation at break) were decreased with HBPE addition for both blends (VPP/HBPE and rPP/HBPE), while impact strength results were improved. In addition, shore D hardness slightly improved.
5. SEM showed that there is a homogenous distribution of HBPE particles within the PP matrix at a low content of 5%, while at higher HBPE content, the material tends to agglomerate form a nonhomogeneous material.
6. DSC showed that there is a slight improvement in melting temperature for both blends (VPP/HBPE and rPP/HBPE), while crystallization temperature increased for VPP blends and decreased for rPP blends. In addition the degree of crystallinity decreased for both blends (VPP/HBPE and rPP/HBPE).

7. The thermal stability by TGA showed that both HBPE-TA and HBPE-AD have two stage of thermal degradation, while HBPE-MA and HBPE-PA have three stage of thermal degradation. The thermal stability for both blends (VPP/HBPE and rPP/HBPE) improved by the addition of HBPE.
8. The processability for both the blends (VPP/HBPE and rPP/HBPE) were increased by the addition of HBPE, while the viscosity decreased and the shear rate increased as indicated by MFR.
9. Contact angle measurement showed that the addition of HBPE increases the hydrophilicity for both blends (VPP/HBPE and rPP/HBPE).
10. The biodegradation in soil environment was improved by the addition of HBPE for PP through the increase of the weight loss of samples over 90 days.

## 5.2. Recommendations

From the present study, the following recommendations can be helpful for further studies:

1. Studying the effect of different mixing ratios of monomers on the properties of hyperbranched polyester polymer.
2. Studying the degree of branching of the prepared monomers and how it will change by changing the monomers ratio.
3. Studying the antibacterial, optical properties, and UV resistance properties of the prepared polymers.
4. Studying the rheological properties of PP/HBPE blends using a capillary rheometer, and comparing the results theoretically using the Ansys program.

5. Studying the effect of the prepared HBPEs on the miscibility of PE/PVA blends (polar/non-polar blend).
6. Adding the prepared polymers to other polymers (polar) such as PVC, PVA, PET, and PC.
7. Preparing new types of hyperbranched polymers using more than one type of monomers (using multicomponent polymerization method).

# List of Symbols

| Symbols | Meaning | Unit |
|---|---|---|
| $X_c$ | Degree of Crystallinity | Dimensionless |
| $T_g$ | Glass transition temperature | $^{o}C$ |
| $\eta^*$ | Complex viscosity | Pa.s |
| $\sigma$ | Stress at break | MP.a |
| $\varepsilon$ | Elongation at break | Dimensionless |
| $T_m$ | Melting temperature | $^{o}C$ |
| $\Delta G_{mix}$ | Free energy of mixing | J/K.mol |
| $\Delta H_{mix}$ | Enthalpy of mixing | J/g |
| I.S | Impact resistance of the material | $J/m^2$ |
| $U_C$ | Impact energy | J |
| A | Cross-sectional area of the sample | $m^2$ |
| $\Delta H_m$ | melting enthalpy of polymer | J/g |
| $\Delta H_o$ | melting enthalpy of fully crystalline polymer | J/g |
| t | Time | min/sec |
| $\rho$ | Density | $kg\ /m^3$ |
| L | Length | mm |
| $\gamma^{\cdot}_{w}$ | Shear rate at the wall | $S^{-1}$ |
| $W_a$ | Weight before degradation | g |
| $W_b$ | Weight after degradation | g |

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