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Rheological Properties Of (NR / SBR / CMC / C.B) Nanocomposites

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Abstract This research focuses on the impact of adding materials such as carbon black and polymer of carboxyl methylcellulose on the the rheological properties of styrene butadiene rubber (SBR) and natural rubber (NR) which was studied as a matrix. The present study was a carried out by two groups according to the loading level of carboxyl methylcellulose (CMC) and carbon black(C.B) its molecular weight (N660) which their used as stiffeners in the composites. on the other side, rheometer tests carried according to ASTM D 2705 For the purpose use these composites in various tire making and fender ship. All composites are consisting of carbon black (C.B) N660 (0, 10, 10, 10, 10) pphr and carboxyl methyl cellulose (CMC) (0, 0, 10, 20, 30) pphr respectively for the first group (A) and (0, 20, 20, 20, 20) pphr for C.B , (0, 0, 10, 20, 30) pphr for CMC for the second group (B). The maximum torque, minimum torque, scorch time, viscosity and Tc90 optimum curing time were checked. The results revealed that the parameters differ according to the level of loading. Viscosity, lower torque, maximum torque and optimal curing were reduced for increasing loading ratio of the C.B and CMC. As well, an optimal curing time of the TC90 burning time was reduced as addition ratios of the carbon black (C.B) and carboxyl methyl cellulose (CMC) increased.

Key words :Rheological properties , Natural rubber (NR) , synthetic rubber (SBR) , carboxyl methyl cellulose (CMC) , Carbon black (C.B), Torque, Scorch time, Min. torque, Max. torque, viscosity.

Introduction

Rheological is the science for flow and deformation; Briefly, the deformation is linked to elasticity , and flow is linked to viscosity . The term rheology is a same (synonymous) to the term viscoelasticity. Although these terms are often used interchangeably, a pharmaceutical suspension's rheological properties determine its performance. Gum rubbers and compounds' viscoelastic conduct has already been extensively studied[1]. in recent years, Fiber-reinforced composite materials have been widely used as engineering materials in structural sections of the marine industry due to favorable properties such as high strength to weight ratio, high modulus, chemical resistance, fatigue tolerance, and ease of manufacturing, such as submarines, harbor Submarine domes, fishing trawlers, and machinery and floating platforms. Also flax filler reinforcement in polypropylene was also discovered to increased dielectric permittivity. The torque used to oscillate the rotor is measured as a function of time[2]. The torque versus cure time curve can be used to measure all of the rubber compound's vulcanization properties. Rheography is divided into three stages, each of which is listed below in Figure (1) [3]:

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1- Stage -1- : It represents the rubber compound's the processing behavior.
2- Stage -2- : It displays the rubber compounds' curing properties.
3- Stage -3- : It gives us an indication on the rubber compound's physical properties.

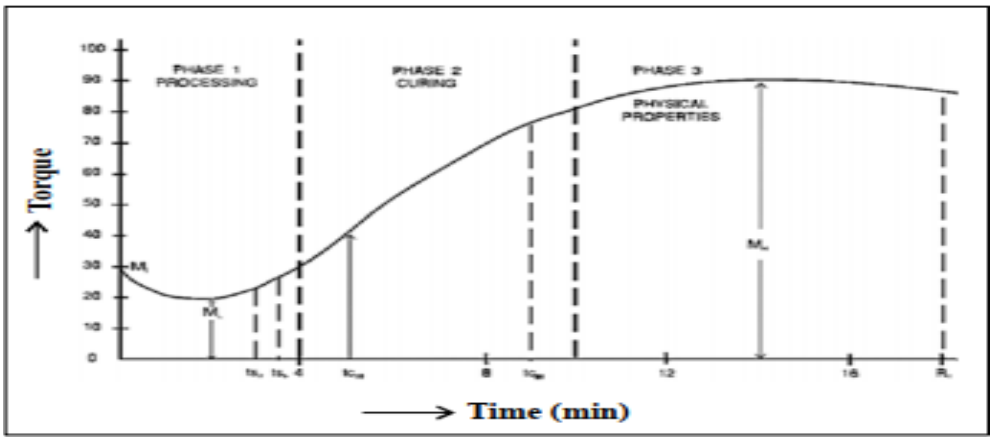


Figure (1) : Rheography cure curve [2].

The scheme torque with time is analyzed to get the differ consequences. In oscillating disc (Rheometer) ,the rheography was shown in Actual time, when the test end, the program analyzes the graph, computes the results , which either shown on the screen or printed. The Rheography findings are divided into three types of papers. [4,5] :

1. Torque report (Ib-in).
2. Time reports (minute).
3. Derived reports.

1. **Torque reports**

- **Minimum Torque (ML)**

If the compound is heated under pressure, the viscosity decreases, and the torque decreases. ML refers to the torque value that has been registered at the lowest level. It is essentially a measure of the stiffness and viscosity of vulcanized compound based on torque values using the relationship:

$$\boldsymbol{Viscosity = ML * 2.7} \quad \text{---------- (1)}$$

- **Maximum torque (MH)**

When the curing process starts, the torque increasing in proportionately. Depending on the form of compound, the slope of rising torque varies. For a time, the torque usually reaches its optimum value and plateaus; this is referred to as the torque plateau (plateau curve). If the test is run long enough, the remedy will reverse and the torque will begin to decline. This is the name for this kind of curve and reversion (reverting curve). Occasionally, the torque begins to rise in a steady upward direction over the course of the record duration. This kind of curve is referred to as (rising or marching curve). The highest torque registered in the plateau curve is MH (Maximum torque). The maximum torque recorded during curve reversion is abbreviated as MHR. The maximum torque can be expressed as a measure of the vulcanized rubber's stiffness.

2. Time reports

- **Scorch time (TS2)**

TS2 is detected when the torque rises two units above the minimum torque during the cure phase. Early vulcanization, also known as scorch, happens when rubber is partially vulcanized before being primed for vulcanization. It causes the plastic properties of the compound to degrade to the point that it can no longer be recycled. scorching is caused by a rise in temperature during fermentation as well as the length 6of time the compound is subjected to high temperatures. This time interval before vulcanization begins is called "scorch time." Since scorching destroys rubber, It is important that vulcanization doesn't begin until this process is completed. [6].

- **Optimum Cure Time (TC90)**

It is the point (time) at which 90 percent for the treatment has occurred [7].

- **Reversion Time (RT)**

Since reaching MH, its time to cross 99 percent of maximum torque (MH). When a substance is exposed to heat aging, how long it preserves its physical properties and give with an Signal of the compound's quality. occurs reversion at over cure, which results in a reduction in tensile and modulus power.

3. Derived values

- **Cure rate index (CR)**

Cure rate is a basically of the linear slope of an increasing curve. The properties of the material transform from a soft plastic to a tough elastic substance necessary for use when it is heated past the scorch point. The rate of cure is the rate at which cross-linking and the development of stiffness (Modulus) of the compound occurs. Rubber's long polymer chains are linked together by crosslinks. the rate of cure is an important vulcanization parameter since it indicates how long it takes to complete the whole curing process. To measure the cure rate table, use the following equation[4].

$$\boldsymbol{C.R} = \frac{\mathbf{100}}{\boldsymbol{TC90-TS2}} \qquad \text{----------(2)}$$

- **The differ between MH and ML torques (ΔM)**

The differ between ML and MH torque might possibly be expressed as a parameter of crosslink density. In crosslink density tests, we used this value as an indicator for measuring crosslink density.

EXPERIMENTAL Part

1. Materials :

- **SBR :** used in these search is a rubber (SBR1502), consist of 23.50 percent styrene and butadiene. From a company Petkim, Turkey, supplied his basic gravity (0.95 g/cm3).
- **NR :** is only natural product. It is a cis-polyisoprene, has a very high molecular weight and contains long branches[56], Natural rubber is collected in the form of latex that exudes from the bark of the tree when it is cut. The tree Havea Braziliensis [8].
- **Carbon black N660 :** imported by a company Douda, Iran. It was tested for iodine absorption (ASTM D135) and DBP absorption (according to ASTM D135) (ASTM D136).
- **CMC :** Carboxyl methylcellulose or carboxymethylcellulose is a carboxymethyl group (-CH2-COOH) cellulose derivative bound to certain glycopyranose mononide hydroxyl groups that make up the cellulose chain. It is widely found in the form of sodium salts, such as methylcellulose carboxylic sodium[9].

- Zn (Zinc oxide , 97%) and S-acid (stearic acid - 99.40%) imported by a company Dorham - U.K, MBS (N-oxydiethylenebenzothiazole 2-sulfonamide; 98.20%) imported by a company lTT- India. S (Sulfur) imported from Al-Meshrak CO - Iraq.

2. Equipment

Laboratory mill : The batches in this sample were prepared using a Laboratory mill. It has two roll mills, each of which can pass cold water between them . The roll cylindrical have a diameter of 150 mm and a length of 300 mm, and they are cylindrical in form.

Rheometer : Rheometers were used to calculate the scorch time, compound torques, and the optimum vulcanization time. A company MV-ODR-(Micro vision Enterprises-India) calculated the cure properties of the different compounds at (165^{o}, 175^{o}, and 185° C) at time = 12 min, according to ASTM D2705[7].

Hydraulic press : According to the specification test, the vulcanization processes are a result of strain, heat, and time. The hydraulic press, which has a high pressure of 700 bar and is fitted with a thermocouple, was used to prepare the samples. The maximum temperature of the hydraulic press was 300°C.

3. Preparation of recipes :

The ingredient of all the batches was show in Table 1 represents group (A) and Table 2 represents group (B) carbon black 10 pphr.

Table 1: Batches recipe of group,(A) in pphr

Material	A1	A2	A3	A4	A5
NR	60	60	60	60	60
SBR	40	40	40	40	40
Carbon black	0	10	10	10	10
CMC	0	0	10	20	30
Zinc Oxid	3	3	3	3	3
Stearic Acid	2	2	2	2	2
MBS	0.75	0.75	0.75	0.75	0.75
Sulfur	2	2	2	2	2

Table 2: Batches recipe for group, (B) in pphr

Material	B1	B2	B3	B4	B5
NR	60	60	60	60	60
SBR	40	40	40	40	40
Carbon black	0	20	20	20	20
CMC	0	0	10	20	30
Zinc Oxid	3	3	3	3	3
Stearic Acid	2	2	2	2	2
MBS	0.75	0.75	0.75	0.75	0.75
Sulfur	2	2	2	2	2

Results and discussion

Figure (2), The viscosity of rubber reduces as it is heated, resulting in a reduction in maximum torque, but the increase observed in the scheme is due to the increase in the loading ratios for CMC and C.B of the second group CMC=(0 , 0 , 10 , 20 , 30) pphr and C.B=(0 , 20 , 20 , 20 , 20) pphr respectively. Equally, the rubber compound starts to volcanize and converted to elastic solid and the torque increase. Molecular chain detachment may occur. this behavior agreement with the researcher [11].

An growing maximum torque showed that cross-linking was the controlling, and when torque reached a plateauing, and this indicated meant the curing process had completed and a stable network had formed [10]. So, maximum torque, minimum torque and the time values such as optimum cure time , scorch time and the derived properties such as viscosity and treatment rate index . Someone can notes from these schemes that properties values and rheography curves were varied by rises the loading ratio of (C.B) carbon black and carboxyl methylcellulose (CMC) and at same time this values were varies with differ loading ratio of CMC for the same loading level.

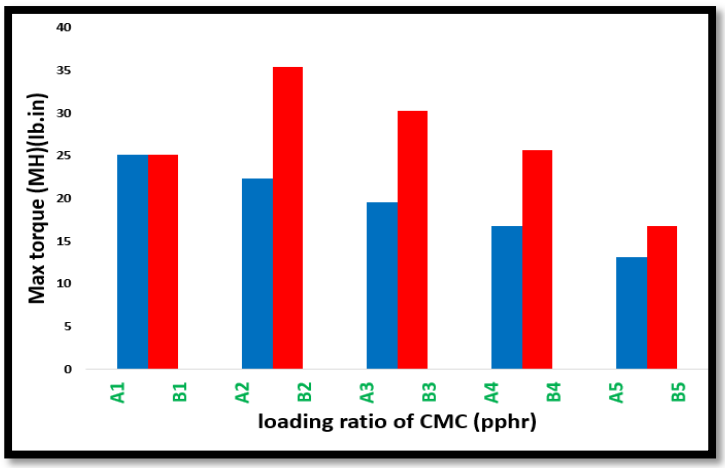
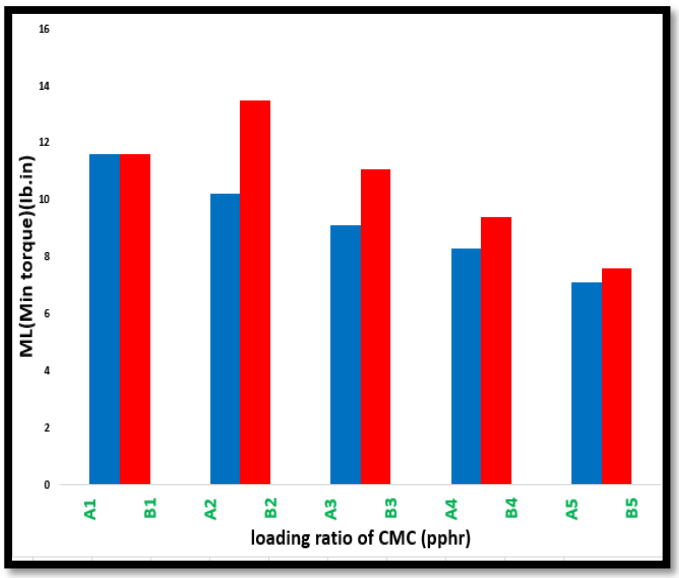


Figure (2) Relation between Max torque (MH) (lb.in) and loading ratio of CMC (pphr)

An growing maximum torque showed that cross-linking was the controlling, and when torque reached a plateauing, and this indicated meant the curing process had completed and a stable network had formed [10]. So, maximum torque, minimum torque and the time values such as optimum cure time , scorch time and the derived properties such as viscosity and treatment rate index . Someone can notes from these schemes that properties values and rheography curves were varied by rises the loading ratio of (C.B) carbon black and carboxyl methylcellulose (CMC) and at same time this values were varies with differ loading ratio of CMC for the same loading level

Figure (3) show the relation between min. torque against loading ratios for CMC. It is clear from the figures, that this property was increase decreased with increasing loading ratio of CMC=(0 , 0 , 10 , 20 , 30) pphr and C.B=(0 , 20 , 20 , 20 , 20) pphr. this behavior agreement with the researcher [11].

This behavior was due to a rise in cross linking density and correlations between the rubber chain and ratios of C.B and CMC then, cause torque and viscosity to decrease, allowing the vulcanization process to speed up. As a result, the consequence of a continuous rise in CMC loading ratios on



these samples was to increase the rate of vulcanization in a short period of time.

Figure (3) Relation between Min torque (ML) (lb.in) and loadi ratio of CMC (pphr)

Figure (4) show that the relation between scorch time TS2 against loading ratio of CMC, and means the start of the treatment against continuous increasing the loading ratio of CMC. as can be observe , this property increased with CMC increased and decrease as the loading speed for C.B. increased. This was due to an increase in the rate of vulcanization and a decrease in the values of the treatment time and optimum scorch time TS2. this behavior agreement with the researcher [11].

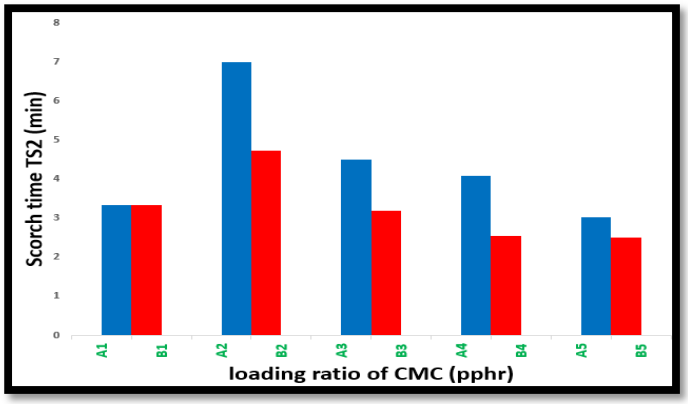


Figure (4) Relation between Scorch time (TS2) (min) and loading ratio of CMC (pphr)

Figure (5) show the relation between scorch time (TS5) and loading ratio of CMC. We can notice that this property was increase by increasing CMC and decrease by increasing loading level for C-B. This behavior was due to higher vulcanization rates and lower scorch time TS5 and treatment time values.

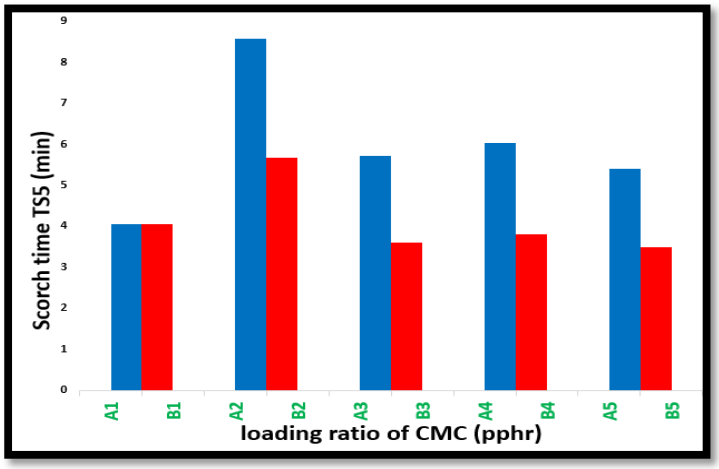


Figure (5) Relation between Scorch time (TS5) (min) and loading ratio of CMC (pphr)

Figure (6) show the relation between cure time (TC50) and loading ratio of CMC. We can notice that this property was increase with increasing CMC and decrease with increasing C.B loading speed. This behavior was due to an increase in vulcanization rate and a decrease in cure time values (TC5). this behavior agreement with the researcher [11].

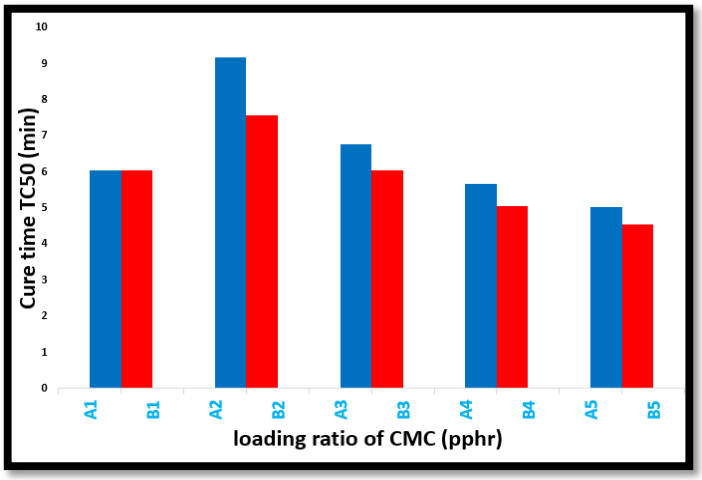


Figure (6) Relation between Cure time (TC50) (min) and loading ratio of CMC (pphr)

Figure (7) show that the relation between optimum cure time TC90 against the loading ratio for CMC. these properties decreased because increased the loading ratio for CMC and C.B . This was due to an increase in the rate of vulcanization and a decrease in the values of the Optimum treatment time (TC90). this behavior agreement with the researcher [11].

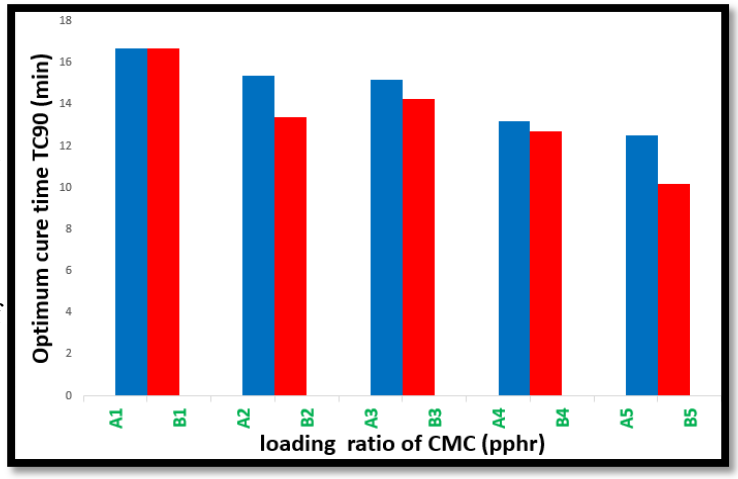


Figure (7) Relation between Optimum Cure time(TC90)(min) and loading ratio of CMC (pphr)

Figure (8) show the relation between viscosity and loading ratio of CMC. As can be shown, this property decreased as the loading ratio of C.B and CMC increased. This behavior was due to an increase in vulcanization intensity and a decrease in viscosity values.. this behavior agreement with the researcher [12].

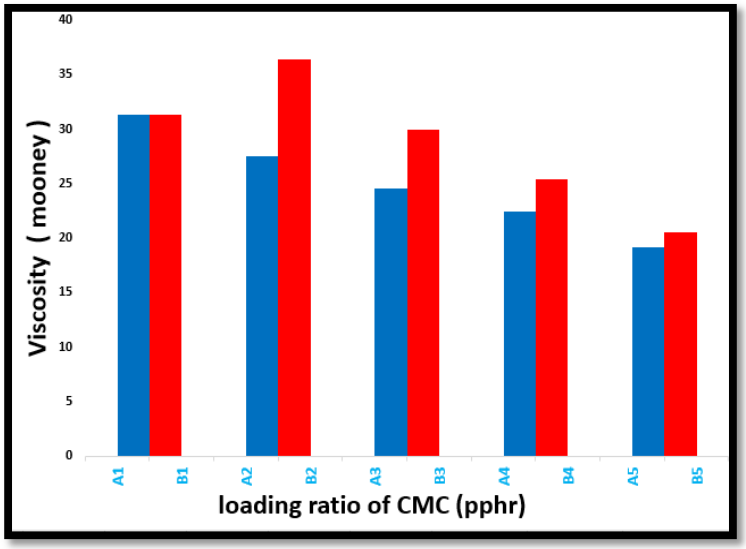


Figure (8) Relation between Viscosity (mooney) and loading ratio of CMC (pphr)

CONCLUSIONS

I. The observed increase in the plots of rheological properties is due to the increase in the loading ratios of CMC.

II. Decrease of optimum cure, viscosity, maximum torque and minimum torque with increase loading ratio for CB =(0, 20, 20, 20, 20)pphr and CMC=(0 ,0 ,10 ,20 ,30)pphr.

III. With increasing loading levels C.B and CMC, Optimum treatment time and scorch time decreased.

IV. The polymer CMC works as a filler because its melting point 255^{O}C, so the polymer did not melt, so we did not have a triple mixture.

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