

## Preparation of (Rubber Blend/Oyster Shell Powder) Composites and Study Rheological Properties

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**Abstract:** This research includes preparation (NR50/SBR50/Oyster Shell Powder OSP) composites while the loading ratio of OSP were 0, 5, 10, 15, 20, 25, 30, 40, 60, 80, 100 pphr. The examination of FTIR (Fourier Transform Infrared analysis) of some specimen composites were carried out and study the effect of calcium carbonate (Oyster Shell Powder OSP) grain size  $<225 \mu$  on the rheological properties of (NR50/SBR50/OSP) composites with different loading ratio of (OSP). The device used to examine the characteristics is oscillating disc rheometer according ASTM D-2705 and temperature  $185^{\circ}\text{C}$ , pressure 10 bar and time 6 min. These rheological properties included the scorch time ( $t_{s2}$ ), cure time ( $t_{c90}$ ), viscosity, Maximum torque (MH), Minimum torque (ML) while the results of all these properties were decreasing with increase the loading ratio of OSP with or without C.B 10 pphr also all these properties were decreasing after addition C.B = 10 pphr for the same loading ratio of OSP except maximum and minimum torque at high loading ratio.

**Key words:** Natural rubber, synthetic rubber, oyster shell powder, FTIR and rheological properties, temperature, ASTM

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### INTRODUCTION

Rubbers play very important role in modern technology. They are presently used in wide areas of application such as cables, tire, adhesives, domestic appliances, coatings, packaging materials, textile and sporting goods to transportations, building infrastructures, medical and optical devices, etc., due to their light weight, elastic and other properties. There are many types of rubber such as Natural Rubber (NR), Synthetic Rubber (SBR), nitrile rubber and etc. The properties of a particular rubber are determined by the compound composition. A mix of raw rubbers with additives and the vulcanization process is important to adjustment of rubber with requirement application (Erich, 1978).

The vulcanization is one of the key factors in the technology of rubbers. It involves the conversion of raw rubber into a network through the formation of cross link between chains of rubber. This network is not sticky like raw rubber does not harden with cold weather or soften much except at very high temperatures is elastic is highly resistant to abrasion and becomes tighter and the forces necessary to achieve a given deformation increase (Hofmann, 1990; Mark, 1994).

Most commonly used for its high mechanical properties due to its density and ease of manufacture. In addition to lightweight, high durability and low manufacturing cost. The polymeric basis was divided into materials, thermoplastics and thermosetting materials (Kaw, 2005). The term it was used as an alternative to

rubber where previously the term rubber was a rubber band is used to refer to synthetic rubber. Flexible materials differ from other polymers with special specifications where they have the ability to deform when shedding stress on them and then regain their dimensions, quickly after removing these stresses and their mechanical properties can be significantly improved such as elasticity resistance to melting and bloating in the presence of temperature and appropriate vulcanization conditions (Ciesielski, 1999). The rubber material they are not only flexible but also energy-dispersing materials because of the flexible viscous nature, yet plasticization reduces plasticity (Mitchell, 2004).

Rheology is a study of deformation and flow in a simplistic way the deformation may be associated with elasticity and the flow with viscosity. Then, rheology is synonymous to viscoelasticity. Indeed, sometimes these terms are used interchangeably the performance characteristic of a pharmaceutical suspension depends upon its rheological properties (Al-Nesrawy *et al.*, 2016a, b). High elastic polymer composites are very important in the applications of rubber industries such as tires transportation belts, pipes for fluids and fender. Damping and support parts in the mobiles as well as diaphragm as mentioned above. Rubber composite materials with different type of rubber are used in dampers and support applications (Al-Nesrawy *et al.*, 2016a, b). The aim of the study is from X-rays and other rays the possibility of making a protective suit of rubber overlapping material.

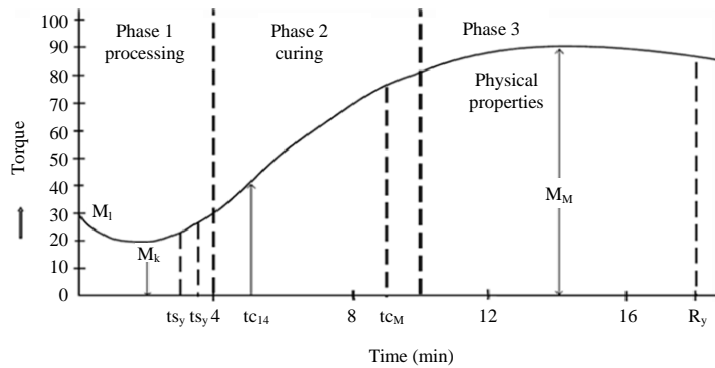


Fig. 1: Rheograph (cure curve) Singhal (2003)

Rheograph is cure curve obtained by a “Oscillating Disc Rheometer”. From this curve of torque vs. cure time, all the vulcanization characteristics of the rubber composite can be determined directly. Rheograph is divided into 3 phases which are explained in Fig. 1, the firstly phase gives an indication of processing behavior of the rubber composite, second phase describes the curing characteristics of the rubber composite and third phase gives an indication of physical properties of the rubber composite (Singhal, 2003).

The plot of torque against time is analyzed to obtain the various results. In “Oscillating Disc Remoter”, the rheograph is displayed in real time and at the end of test time, computer analyses the graph and results are automatically computed and displayed on the screen or the printer. Displayed results of rheograph are categorized into three columns:

- Torque values with units lb-in
- Time values with unit minutes
- Derived values

**Torque values**

**ML (Minimum torque):** As the composites gets heated under pressure, the viscosity decreases and the torque fall. The lowest value of torque recorded is called ML. Basically, it is a measure of the stiffness and viscosity of unvulcanized composite, so, the viscosity obtained by the relation (Singhal, 2003):

$$\text{Viscosity} = \text{ML} * 2.7 \tag{1}$$

**MH (Maximum Torque):** As the curing starts, the torque increases proportionately (Al-Husnawi, 2014). Depending upon the type of compound, the slope of rising torque varies. After a while the torque typically attains maximum value and it plateaus out. It is called “plateau curve”. If test is continued for sufficient time, the reversion of cure

occurs and torque tends to fall. This type of curve with reversion is called “reverting curve”. At times, the torque shows continuous rising trend during the period of record. Such type of curve is called “rising or marching curve”. MH (max. torque) is the highest torque recorded in plateau curve. In reverting curve, the max. Torque recorded is abbreviated as MH. maximum torque can be expressed measure of stiffness of vulcanized rubber (Singhal, 2003).

**Time values**

**Ts2 (scorch time):** After attaining minimum torque, during cure phase, scorch time  $t_{s2}$  is recorded as the torque rises 2 units above ML (Singhal, 2003; Al-Husnawi, 2014).

Scorch is premature vulcanization in which the rubber becomes partly vulcanized before the product is in its final form and ready for vulcanization. It reduces the plastic properties of the compound, so that, it can no longer be processed. Scorching is the result of both the raising of temperature during processing and the amount of time the compound is exposed to elevated temperatures. This period before vulcanization starts is generally referred to as “scorch time”. Since, scorching ruins the rubber, it is important that vulcanization does not start until this process is complete (Al-Husnawi, 2014; De Bever, 1992).

**Tc90 (Optimum cure time):** It is the time at which 90% of cure has taken place (Singhal, 2003; De Bever, 1992).

**Derived values**

**Cure rate index:** The cure rate index is an essentially a measure of the linear slope of the rising curve. The rate of cure is the rate at which cross-linking and the development of stiffness modulus of the compound occur after the scorch point. When the compound is heated beyond the scorch point, the properties of the compound

changes from a soft plastic to a tough elastic material required for use. During the curing phase cross-links are connect the long polymer chains of the rubber together. As more crosslinks are formed, the polymer chains become more firmly connected and the stiffness (modulus) of the compound increases. The rate of cure is an important vulcanization parameter since it determines the required time for complete curing process (Singhal, 2003). Cure rate index is simplified parameter can be given by Eq. 2-4, replacing measure the slope of curing curve due to measuring slope may be had significant error (Al-Husnawi, 2014):

$$CR = 100(tc_{90}-ts_2) \quad (2)$$

**Difference between maximum and minimum torques**

**ΔM:** The difference between maximum and minimum torques can be expressed as a parameter of crosslink density (Al-Husnawi, 2014). The researchers are use this value in their studies of crosslink density as indicator for evaluating the crosslink density.

**MATERIALS AND METHODS**

**Experimental part:** The materials which were used in this research are:

- Natural Rubber NR and industrial rubber SBR
- Zinc Oxide (ZnO)
- Citric acid
- MBS (M–maleimidobenzoyl-N-hydroxysuccinimide ester)

- 6PPD (Para-Phenylenediamines)
- Sulfur vulcanization
- Process oil
- Carbon black C.B N375
- Oyster Shell Powder (OSP)

**Equipment**

**FTIR system**

**Laboratory mill:** Baby mill was used in this study to prepare the batches. It has two roll mills having provisions for passing cold water, these rolls are cylindrical in shape and of 150 mm diameter and 300 mm in length in the other hand the roll speed is 20 rpm.

**Rheometer:** The cure characteristics of the different compounds were measured at 165, 175, 185°C at time equal 6 min by MV-ODR-(Micro Vision Enterprises-India) the composites were determined by this rheometer.

**Hydraulic press:** The vulcanization processes are function of pressure, heat and time according to the specification test. The preparation processes of samples were carried out by the hydraulic press has maximum pressure equal to 700 bar, the hydraulic press is equipped with thermocouple and maximum temperature is equal to 300°C.

**Preparation of recipes:** The ingredient of all the batches was show in Table 1 represents group (A) with the addition of OSP and Table 2 represents group (B) with the presence OSP and carbon black 10 pphr.

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

Material	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11
NR	50	50	50	50	50	50	50	50	50	50	50
SBR	50	50	50	50	50	50	50	50	50	50	50
ZnO oxide	3	3	3	3	3	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
MBS	1	1	1	1	1	1	1	1	1	1	1
6PPD	1	1	1	1	1	1	1	1	1	1	1
Process oil	3	3	3	3	3	3	3	3	3	3	3
Oyster shell powder	0	5	10	15	20	25	30	40	60	80	100
Sulfur	2	2	2	2	2	2	2	2	2	2	2

Table 2: Batches recipe of group (B) in pphr

Material	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11
NR	50	50	50	50	50	50	50	50	50	50	50
SBR	50	50	50	50	50	50	50	50	50	50	50
ZnO oxide	3	3	3	3	3	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
MBS	1	1	1	1	1	1	1	1	1	1	1
6PPD	1	1	1	1	1	1	1	1	1	1	1
Carbon black	10	10	10	10	10	10	10	10	10	10	10
Process oil	3	3	3	3	3	3	3	3	3	3	3
Oyster shell powder	0	5	10	15	20	25	30	40	60	80	100
Sulfur	2	2	2	2	2	2	2	2	2	2	2

**RESULTS AND DISCUSSION**

**FTIR analysis:** The FTIR spectra of (NR50/SBR50/OSP) (NR50/SBR50/OSP/CB) composites reinforced with the different ratio of OSP and 10 pphr C.B are recorded at room temperature in the region 600-4000  $\text{cm}^{-1}$  as shown in Fig. 2a-e and represented in Table 3 from the infrared spectra. It can be noticed that the variation of C.B ratio causes some observable changes in the spectrum of (NR50-SBR50). The spectra exhibited characteristic bands of stretching and bending vibrations of the functional groups formed in composites. From

this spectra it can be noted that the bands of the  $-\text{CH}_2$  and  $-\text{CH}_3$  asymmetrical and symmetrical stretching at 2916 and 2848  $\text{cm}^{-1}$ , respectively, the band at 1539  $\text{cm}^{-1}$  can be assigned to the aromatic ring  $\text{C} = \text{C}$  stretching and  $\text{CH}_3$  band at 1452  $\text{cm}^{-1}$  be attributed to the b asymmetrical bending vibration. The two peaks at 964 and 698  $\text{cm}^{-1}$  were attributed to the bending vibration.

**Rheological properties:** All the rheological properties were measured by oscillating disc rheometer according ASTM D-2705 (ASTM., 2012) and temperature 185°C,

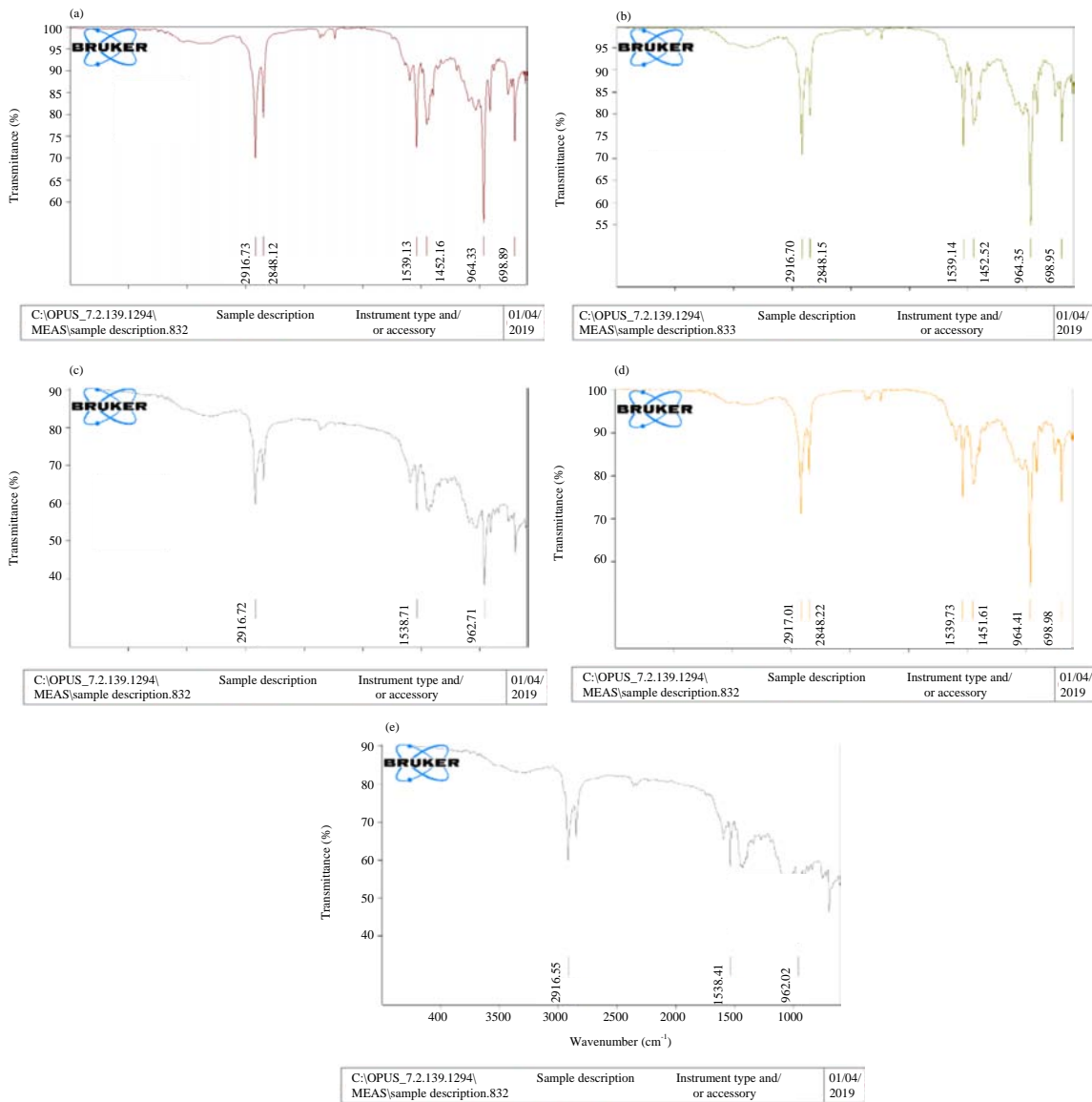


Fig. 2: FTIR spectra for (NR50/SBR50/OSP/C.B) composites: (a) For(NR50/SBR50/0OSP), (b) (NR50/SBR50/10OSP), (c) (NR50/SBR50/20OSP) (d) (NR50/SBR50/10OSP/10C.B) and (e) (NR50/SBR50/20OSP/10C.B)

Table 3: FTIR transmittance bands positions and their assignments for (NR50/SBR50/OSP/C.B) composites with different ratio of OSP and C.B = 10 pphr

Band assignment	Wave number (cm <sup>-1</sup> )				
	NR50+SBR50 pphr	10 OSP+0 CB pphr	20 OSP+0 CB pphr	10 OSP+10 CB pphr	20 OSP+10 CB pphr
CH <sub>2</sub> asy.str	2916	2916	2916	2916	2916
CH <sub>2</sub> sy.str	2848	2848	2848	2848	2848
C = C arom.str	1539	1539	1539	1539	1539
CH <sub>2</sub> asy.bend	1452	1452	1452	1452	1452
CH bend 964	964	964	964	964	964
CH bend 698	698	698	698	698	698

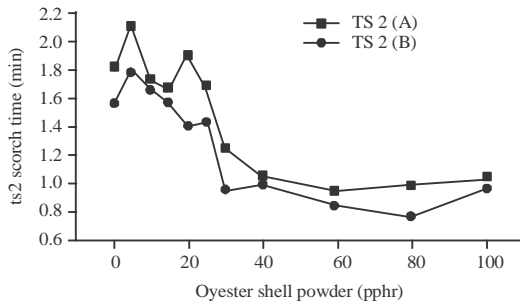


Fig. 3: Relationship between scorch time and (OSP) loading of (NR50/SBR50/OSP) composite

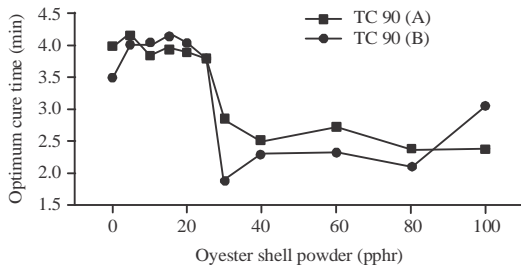


Fig. 4: Relationship between optimum cure time tc90 and OSP loading of (NR50/SBR50/OSP) composite

pressure 10 bar and time 6 min while (Fig. 3) represent scorch time which shows the reduction of Scorch time values with the addition or increasing the loading ratio of the oyster shell powder except the high loading ratio. However, it is necessary to have a high scorch time to ensure flow full material in mold cavities and no defects in final product (Zaman *et al.*, 1995).

Figure 4 represents the curve of group (A) and the Table 1 of Appendix (A), the addition of oyster shell powder reduces the optimum cure time (t90) due to the role of oyster shell powder in vulcanization process. The addition of (OSP) into the compound increases the speed of vulcanization. The accelerator (MBS) is decomposed into amine part and (MBS) radical under the influence of the heat. All two radicals of (MBS) react to form the accelerator (MBS). The addition of (OSP) is increase the rate of the increase of the amount of sulphur atoms embedded in the accelerator (MBS). According to the

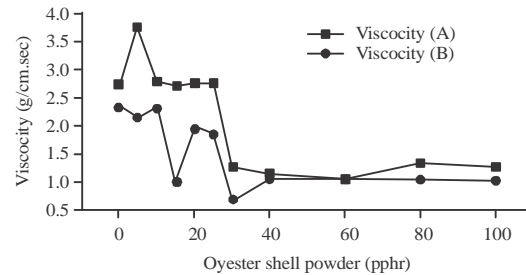


Fig. 5: Relationship between viscosity and OSP loading of (NR50/SBR50/OSP) composite

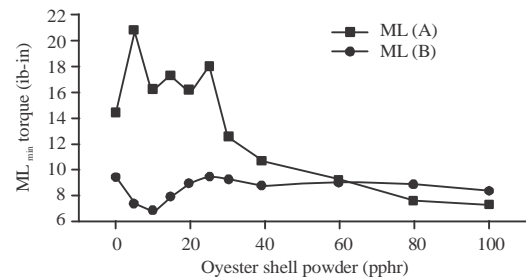


Fig. 6: Relationship between minimum torque (ML) and OSP loading of (NR50/SBR50/OSP) composites

curve of (B) group of the Fig. 4 and Table 2 of Appendix (A), the addition of the carbon black with the (OSP) is effect on the optimum cure time (t90). Since, the carbon black is increase the optimum cure time (t90).

Figure 5 the effect of oyster shell powder on the viscosity that measured in Eq. 1 of the rubber composites where the viscosity decreases with increasing the percentage of addition of OSP in the curve (A) or with the addition of C.B10 pphr on the rubber composites, so, the decreasing of viscosity in the second case with the same loading ratio. This behavior attributed to an increasing the cross linking density and correlations between the mix of oyster shell powder and the rubber chain, this leads to increasing the torque and viscosity and then leads to increase the vulcanization process.

Figure 6 represents relationship between minimum torque (ML) and OSP loading of (NR50/SBR50/OSP) composites. While it was demonstrated decreasing the

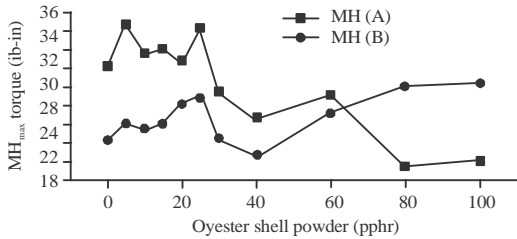


Fig. 7: Relationship between maximum torque (MH) and OSP loading of (NR50/SBR50/OSP) composites

value of minimum torque recorded ML with increasing the loading percent of OSP. It is a measure of the stiffness and viscosity of vulcanized composites (Singhal, 2003).

With respect (Fig. 7) it was represented the effect of oyster shell powder at maximum torque MH where we note from the shape increase the value of max. torque when adding of oyster shell powder. So, the maximum torque value decreases when adding C.B10 pphr for the same loading ratio of OSP except the high loading ratios. The difference between Maximum (MH) and Minimum (ML) torques can be expressed as a parameter of crosslink density. It was used this value in the studies of crosslink density as indicator for evaluating the cross linking density (Zaman *et al.*, 1995).

### CONCLUSION

Decreasing the results of all these properties with increase the loading ratio of OSP with or without C.B 10 pphr. All these properties were decreasing after addition C.B = 10 pphr for the same loading ratio of SPO except maximum and minimum torque at high loading ratios.

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