Study of rheological, viscoelastic and vulcanization behavior of sponge EPDM/NR blended nano-composites

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Abstract. In this research paper the effect of blending ratio of natural rubber (NR) with Ethylene Propylene Diene Monomer (EPDM) were investigated. Different samples of EPDM/NR ratio were prepared to study the variation of NR in EPDM on rheology, curing characteristics, tangent δ, and viscosity variation during vulcanization of sponge nano composites. The main aim of present research is to develop elastomeric based sponge composites with the blending ratio of base elastomers along with the carbon nano particles for high energy absorbing and damping applications. The curing characteristics, rheology and viscoelastic nature of the composite is remarkably influenced with the progressive blending ratio of the base elastomeric matrix.

1. Introduction
Elastomeric based composites have attracted the attention of engineers and scientists for their versatile nature. They are light weight, easy processing, low cost and have high strength to weight ratio, most suitable for aerodynamics applications. Relatively, more impact energy absorption and damping efficiency make them unique for personal, building and armour protection[1].

Reinforcing fillers such as carbon black and silica are used during processing for the improvements in mechanical, thermal and aging characteristics[2]. Vulcanization and curing behavior including scorch safety, viscoelastic nature, damping efficiency are also influenced by the fillers. Concentration, size and morphology are the salient features of the fillers for the variation in the physical properties of finished elastomeric composites[3].

Elastomeric blends have gained much attention in the industry due to the improvements in the features as compared individual partner. Natural Rubber (NR) has high tensile strength as it crystallizes on stretching and resists thermal degradation due to existence of double bonds in molecular backbone. Oil resistance of NR is low as compared to other synthetic rubbers like EPDM, chloroprene rubber (CR) and nitrile butadiene rubber (NBR) etc[4]. To overcome this shortcomings NR is blended with other synthetic polymers. Mechanical properties and curing behaviour of blended polymers are affected due to the difference in the polarity and interfacial interaction of the blended partners. The major important feature of blending is to attain the intermediate properties which are necessary in some applications[5].

The deformation and flow behavior of the elastomeric composite during vulcanization is known as rheology. The elastomers possess both viscous and elastic nature simultaneously so it is necessary to
determine its rate of flow under various conditions of stress, temperature, time for the application of the stress and the elastic recovery on the removal of applied stress[6].

Viscoelasticity is an important property of elastomers. These materials exhibit both elastic and viscous behavior on deformation. Elastic part is recoverable while energy is dissipated in viscous part during stress application[7].

The novelty of present research is the significant execution of various NR blending ratio in EPDM in the presence of blowing agent and carbon nano particles on the sponge structure formation, curing rate index, viscosity variation during vulcanization, viscous and elastic torque with the variation of NR ratio in EPDM/NR sponge composites.

2. Materials
Blowing Agent (ACPW) was purchased from Qingdao Xiangsheng, Shandong, China. EPDM (KELTAN 4331) and NR received from Technical Rubber Products, China. Carbon Black (N330) from Continental Carbon USA. Mercaptobenzthiazole (MBTS) and Diphenylguanidine (DPG) were purchased from Dalian Richon Chemical Co.Ltd. China. Stearic acid, sulphur, and zinc oxide were supplied by Merck, Germany. Aromatic oil was purchased from International Petrochemicals (Pvt.) Ltd. Pakistan.

2.2 EPDM/NR Blends Preparation
Two-roll mixing mill was used for the preparation of EPDM/NR blends along with reinforcing fillers, accelerators, activators and processing aids according to ASTM 3182 [8]. Blending of the elastomers completed in two stages, the compounding of fillers and processing aids are carried in the first stage. In the second stage, accelerators, cross linkers and activators are incorporated into the previous mixture at the controlled temperature. Temperature control is very necessary at this stage so chilled water is passed through the rolls at a regulated flow rate to remove the excessive heat to avoid the premature vulcanization at the processing stage. Lateral shearing is caused the uniform distribution of the fillers within the blending mixture. Rubber sheet was cut diagonally and folded back at the nip frequently for uniform blending [1].

| Table 1. Blending scheme of EPDM/NR | Blended samples |
|-------------------------------------|-----------------|
| Ingredients (wt%)                  | S1  | S2  | S3  | S4  |
| EPDM                               | 100 | 90  | 80  | 70  |
| NR                                 | 0   | 10  | 20  | 30  |
| Carbon black                       | 5   | 5   | 5   | 5   |
| Aromatic Oil                       | 10  | 10  | 10  | 10  |
| Stearic Acid                       | 1   | 1   | 1   | 1   |
| Activator                          | 5   | 5   | 5   | 5   |
| Blowing agent                      | 5   | 5   | 5   | 5   |
| MBTS                               | 1   | 1   | 1   | 1   |
| DPG                                | 1   | 1   | 1   | 1   |
| Cross linker                       | 1.5 | 1.5 | 1.5 | 1.5 |
2.3 Rheological Characterization
Rheocheck profile-MD, Gibitire Instruments S.R.I, Italy was used to investigate \( \tan \delta \), scorch time \((t_{s1} \& t_{s2})\), viscous torques at minimum and maximum viscosity according to ASTM 6204.

2.3.1 Curing behavior
Permanent cross linking between the polymer chains and ingredients is known as the curing or vulcanization. The elastomeric blended composites converts into viscous liquid as the heating starts and at this stage lowest torque is measure by the moving die (Rheocheck-MD). Cross linking proceeds gradually with time and at the final stage of vulcanization maximum torque value is recorded. This effect is known as the cure rate index (CRI) and calculated by the relation
\[
\text{Cure Rate Index} \ (\text{CRI}) = \frac{100}{t_{90}-t_{10}} \quad (\text{Eq.1})[9]
\]
Where \( t_{90} \) and \( t_{10} \) are the completion of 90% and 10% vulcanization respectively.

3. Results and Discussion
In figure-1, \( t_{s1} \) is the time duration between the closure of die and increase torque up to 1dN.m, \( t_{s2} \) is the time for premature vulcanization up to 2 dN.m. Both \( t_{s1} \) and \( t_{s2} \) are longer for pure EPDM (S1) and it shortens gradually with the increase in blending ratio of natural rubber in EPDM as displayed in Figure 1. This decrease in time durations is due to difference in reaction strategy of the both major components of polymer blends with the accelerators, activators, cross linkers and other ingredients which fastens the curing rate and shortens the scorch safety \((t_{s2})\) and \( t_{s1} \) as well.

![Figure1](image_url)  
**Figure1.** Effect of blending ratio of Natural Rubber in EPDM on \( t_{s1} \) and scorch time \( t_{s2} \)
Figure 2. Viscosity variation of the blended composite with the incorporation of natural rubber component in EPDM

The variation in the viscosity of the blended composite, measured in torques at the initial and final stages of vulcanization as shown in Figure 2. Both lowest and maximum torques reduced with the augmentation of the blending of NR in EPDM which is due to the enhancement of viscous portion of the blended portion of NR [10].

Figure 3. Variation in % curing of EPDM/NR blended composite with blending ratio of NR

The curing behaviour of the blended composite is found to be high as compared to pure EPDM(S1) as shown in Figure 3. This enhancement in the percent curing of the blended composite is due to the increase in blending part of NR due to more filler- polymer chains and chains network interactions of the composite.
Polymers inherently possess both viscous and elastic parts. The variation in viscous torques at minimum and maximum viscosity of the samples during vulcanization is displayed in Figure 4. The torque values increased gradually with the incorporation of NR component which is due to the augmentation of the viscous part of the blended NR component.

Tangent delta (tan δ) is the ratio of loss modulus to storage modulus. Both tan δ values at minimum and maximum viscosities enhanced. The blending part causes the enhancement in loss modulus, reduction in storage modulus and elastic recovery of the blended composite as expressed in Figure 5. The blending of NR in EPDM increases in viscous part and reduces elastic component and as a result the tan δ values increases[11].
4. Conclusions
EPDM sponge blended with variant part of natural rubber studied the effect on the rheological, curing and visco-elastic properties of the composite. Curing rate, ts1, ts2, lowest torque, maximum torque diminish on the addition of natural rubber component in the EPDM. Viscous torque and tan delta of the blended composite augmented 3% and 550% respectively with the 30 % incorporation of natural rubber in the EPDM based blended composite. The enhancement in the % curing of the composite was also observed with the increase of blending ratio of NR in EPDM.

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