Morphology, Mechanical and Neutron attenuating properties of carbon black filled EPDM / HDPE composites

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Abstract. Flexible polymer composites have been the focus of demanding interest in classical studies of neutron radiation shielding applications. The influence of varied loading of carbon black on the morphology, mechanical and neutron shielding properties of Ethylene Diene Monomer Rubber/High-Density Polyethylene (100/30) blends are observed through this experimental work. EPDM and HDPE were blended in a Brabender type internal mixer and other functional additives were dispersed using two roll mill and later cured using a compression molding, on determining the cure time on rubber rheometer. The carbon black addition enhanced HDPE dispersion in the EPDM matrix, as evidenced through morphological and mechanical analysis. The improvement in the tensile parameters indicates the reinforcing efficiency of the carbon black in EPDM/HDPE blends. Lower tear resistance suggests a weak interface within the EPDM / HDPE blend at low black carbon concentration. Carbon black filled EPDM/HDPE composites displayed a total neutron macroscopic cross-section of 0.28 cm⁻¹ for 2 MeV energy neutrons.

Keywords: EPDM rubber, Carbon black, Mechanical properties, Neutron shielding, Thermoplastic elastomer

1. Introduction

Ethylene propylene diene monomer (EPDM) rubber-based composites are widely studied due to its peculiar nature of shielding the neutron radiations in the curved and irregular surfaces. The excellent thermal characteristics of the EPDM rubber makes it suitable in applications such as cables, tires, etc. In the neutron shielding mechanism, elastic scattering between the neutrons and atoms plays a significant role in the reduction of energy of the fast-incoming neutrons. Elements such as hydrogen and carbon can moderate the fast neutrons due to their large inelastic and elastic scattering cross-sections. Low atomic weight hydrogen-rich materials such as EPDM rubber proves its crucial role in this scenario. The conventional EPDM rubber composites possess hydrogen atomic density in between ~ 4 ×10²² atoms/cc with very low tensile characteristics [1–3]. These reports were focused on the influence of boron atomic density in the EPDM rubber with the addition of various boron compounds. However, to the best of our knowledge, no attempts were reported to improve the hydrogen atomic density of EPDM rubber.
A study on neutron transport through the cement mortar, PCC mortar, normal weight, and magnetite heavyweight concretes indicate that a 1% increase in moisture can enhance the shielding by 10% due to an increase in hydrogen atomic density. Moreover, only a marginal increase in fast neutron attenuation was noticed with the density of concrete that indicates heavyweight concrete is not an effective candidate for fast neutron shielding [4]. The carbon aggregates, iron ores (hematite), barium, lead, etc. are extensively used to enhance the fast neutron moderation properties of the concrete [5].

Among the polymers, conventional high-density polyethylene (HDPE) possesses greater hydrogen atomic density, and are preferred rigid neutron attenuating material [6,7]. The blending of the thermoplastics with rubber enhances the chemical, thermal and mechanical properties [8,9]. HAF carbon black, due to its average particle size and specific surface structure is the most common reinforcing filler used in the polymer materials, owing to its compatibility in polymers for improving mechanical properties [10,11]. Husnan et.al noticed the increase in tensile strength, modulus, and hardness of the virgin and recycled NBR blends with an increase in carbon black loading with a reduction in the elongation at break[12].

In this work, our objective was to prepare carbon black filled EPDM/HDPE composites with varied “phr” of carbon black using peroxide as a curing agent. Surface morphology, mechanical properties along with their neutron shielding characteristics are corroborated and discussed. The theoretical neutron shielding characteristics based on the experimental atomic density values are also evaluated in this work.

2. Materials and Methods

2.1. Materials

Ethylene-propylene diene monomer rubber (EPDM) Keltan ® 9565Q (specific gravity - 0.87) was purchased from LANXESS Elastomers. Trimethyl quinone of industrial-grade was procured from Sameera chemicals, India. The curing agent Dicumyl peroxide and the coagent Trimethylolpropane triacrylate (TMPMA) was procured from Sigma Aldrich. High-density polyethylene (HDPE) HD50MA180 (specific gravity - 0.96) was purchased from Reliance Polymers, India. Reinforcing filler High abrasive furnace carbon black of grade N330 (specific gravity – 1.7) was obtained from Philips Carbon black, Kerala, India.

2.2. Preparation

EPDM/HDPE with varying carbon black was prepared using a 100/30 blend matrix as illustrated in Table 1. EPDM and HDPE were melted mixed in the Brabender internal mixer with a chamber temperature of150°C with 60rpm for 8 minutes. The incorporation of functional additives was done on two roll mixing mills. The samples were labeled as EH 0, EH 10, EH 20, EH 30 and EH 40 with respect to the “phr” of carbon black loaded in EPDM/HDPE blend.

2.3. Characterization techniques

Cryogenic fractured surface of specimens was observed under the Field Emission Scanning Electron Microscope of Model ZEISS Gemini SEM 300. Tensile and tear properties of the composites were tested using Universal Testing Machine (Tinius Olson, H25K, UK) according to ASTM D-412 and ASTM D-624 respectively. Shore hardness tests were performed using a shore A digital durometer according to the ASTM D2240. The experimental density of composites was evaluated on a densitometer (Shimadzu) using Archimedes principles.

3. Results and Discussion

3.1. Morphology

Cryofracturing and gold sputtering was done on specimen before analyzing the specimens for morphology details. SEM micrographs of the composites with various “phr” of carbon black in
EPDM/HDPE are shown in Figure 1. The surface of EPDM/HDPE (100/30) with no carbon black appears irregular, with HDPE as a dispersed phase in the continuous EPDM rubber matrix. Droplet morphology for HDPE was observed in the continuous EPDM matrix for unfilled EPDM/HDPE blends. The incorporation of carbon black changes the morphology of HDPE in EPDM matrix to a more continuous, due to reduction in droplet size and smooth appearance. This can be attributed to slight disappearance of phase border owing to presence of carbon black, indicating a partial compatibilization among HDPE and EPDM matrix. In minor areas of the SEM microphotograph, we can also observe a reduction in HDPE droplet size and uniform distribution throughout the EPDM matrix with increasing “phr” of carbon black. Reduction in droplet morphology of HDPE can be attributed to the fragmentation of HDPE domains owing to huge mechanical friction during the two-roll mixing.

![SEM images of cryocut specimens of the composites](image)

**Figure 1.** SEM images of cryocut specimens of the composites (a) EH 0 (b) EH 20 and (c) EH 40 at 2000 magnification

3.2. Mechanical Properties

The influence of the HAF carbon black on the EPDM/HDPE blends to the tensile load was tested by using the Universal Testing Machine as per ASTM D 412. The dumbbell-shaped samples were punched out from the standard sheet and tested to determine tensile properties. The stress-strain curves of EPDM/HDPE blend with 0, 10, 20, 30 and 40phr carbon black can be seen in Figure 2 (a). The tensile properties of the composites enhanced steadily with the incorporation of carbon black. It is well known that the unequal stress distribution in the polymer was overcome by the reinforcing ability of the carbon black, owing to which tensile strength increased with an increase in “phr” of carbon black. Addition of carbon black in EPDM/HDPE blends leads to the strong adherence of the rubber chains to the carbon black surface, which enables the composites to bear the applied tensile load effectively.
Figure 2. Tensile test (a) Stress-strain curves (b) Tensile strength and 100% modulus of carbon black EPDM/HDPE composites

Modulus at 100 %, 200 %, 300 % strain was greatly enhanced on the addition of carbon black as indicated in Table 1. An increase in the modulus values determines the increase in stiffness, i.e. rigidity of the EPDM/HDPE blends, with the addition of carbon black. The addition of carbon black adsorbs the rubber chains on its surface and contributes to compatibilization between EPDM and HDPE. Adding carbon black also increases the rigidity of the blends by forming strong interfacial interactions between surface of carbon black and the polymer chains. An increase in modulus was observed that can be contributed to the better load-bearing capacity owing to synergistic effect between carbon black and polymer chains. One may observe an increase in tensile strength of the composites with increase in “phr” of carbon black and gradual decrement in elongation at the break indicating the presence of true physical force between carbon black and EPDM/HDPE matrix. Another reason can be the chemical interaction at the interfacial sites of the carbon black and polymer chains. Above the 20phr of carbon black, steep increase in tensile strength with marginal reduction in the elongation break was observed, which can be attributed to immobilization of rubber chains through filler network formation. Corroborating tensile properties with morphological images one can observe that decrease in the HDPE droplet size in continuous EPDM matrix increases the tensile modulus and tensile strength of the EPDM/HDPE composites in presence of carbon black. But a gradual decrease in elongation at break can be attributed to increase in stiffness due to reduction in HDPE droplet size with the addition of carbon black. One may also observe the decrease in elongation at break is not significant, owing to the true physical and chemical interaction within EPDM, HDPE, and carbon black in the composites.

Table 1. Mechanical properties of the EPDM/HDPE composites with varying HAF loading

| Sample | Modulus @100 (MPa) | Modulus @200 (MPa) | Modulus @300 (MPa) | Tensile Strength (MPa) | % Elongation @ break | Tear Strength (kN/m) | Shore A Hardness | Cross-link density (10^-5 gmol/cc) |
|--------|-------------------|-------------------|-------------------|----------------------|----------------------|---------------------|-----------------|------------------|
| H 0    | 2.51              | 3.05              | 3.51              | 5.92                 | 685.9                | 32.6                | 77.46           | 21.7             |
| H 10   | 2.7               | 3.16              | 3.82              | 7.46                 | 586.8                | 27.5                | 77.88           | 31.4             |
| H 20   | 3.31              | 4.02              | 5.06              | 8.48                 | 548.9                | 30.7                | 81.66           | 39.4             |
| H 30   | 3.68              | 5.03              | 6.88              | 13.08                | 539.9                | 42.6                | 83.28           | 54.7             |
Tear strength value that represents the ability of the material to resist the crack propagation was tabulated in Table 1. Unlike tensile properties, the tear strength decreased at 10phr HAF incorporation and further steadily increased. The decrease in tear strength in EPDM/HDPE blends at 10phr and 20phr can be related to, the non-uniform distribution and larger droplet size of the HDPE domain, which forms a weak interface among EPDM and HDPE. This will impart weak resistance to the tear action thereby induces early crack propagation. With the increase in loading of carbon black, the droplet size of HDPE in EPDM matrix decreases and distribution of carbon black within the blend matrix became nearly homogenous with true physical and chemical interactions. Hence, it improves the ability of the carbon black filled matrix to resist the tearing action.

The shore hardness values were analyzed by using the digital Shore A Durometer following ASTM D 2240. The different areas on the surface of each composite button were tested to determine the hardness. The hardness of the EPDM/HDPE composites were gradually increased with the increase in carbon black loading. The addition of carbon black to the EPDM/HDPE blends formed adhered layers, which increased the density and simultaneously the hardness of the composites. Hence an increase in carbon black content increased the probability of formation of adhered layers that leads to enhance the hardness of the composites. Crosslink density experimented and calculated showed a rise with increase in phr of carbon black, this can be attributed to the increase in number of three-dimensional networks with increasing carbon black. Curing agent and coagent also contribute to crosslinking density through the formation of chemical crosslinks, while carbon black forms physical crosslinks. Hence combination of chemical and physical crosslinks increases the crosslink density of the EPDM/HDPE carbon black composites with increasing carbon black content.

The addition of carbon black above 20phr increases the stiffness of the composites with a slight reduction in elongation as observed from the tensile test result. These results were similar to Ghosh and Chakrabarti, 2000 [13], where saturation of mechanical properties at 30phr carbon black loading in EPDM was noticed.

3.3. Neutron Shielding Studies

The experimental density of the composites obtained using the Archimedes principle was compared with the theoretical values calculated based on the rule of mixtures as represented in Figure 3. The experimental values were lower than the theoretical density, which can be assigned to voids that are formed during its processing. The difference between the theoretical density and experimental density diminished with an increase in the concentration of carbon black that resembles the decrease in voids. Further, the atomic density of the composites was calculated using experimental density values and the corresponding neutron shielding characteristics of the composites were evaluated by using Beer-Lamberts law.
Figure 3. Comparison of theoretical and experimental density of the EPDM/HDPE composites with varying HAF loading

Table 2 shows the elemental information of the EPDM/HDPE with 20 phr carbon black. The corresponding neutron shielding cross-sections at 2 MeV were taken from the database [14]. Incident neutrons with high energies will undergo elastic or inelastic scattering while interacting with elements in the composites. The macroscopic cross-section and mean free path of the 20 phr carbon black filled EPDM/HDPE composites were 0.28 cm\(^{-1}\) and 3.6 cm respectively. The macroscopic cross-section is gradually decreased on addition of carbon black due to the corresponding decrease in the hydrogen atomic density possessing large interaction probability. Collision probability with neutrons is higher if the hydrogen atomic density is higher, because of the small and similar size of the hydrogen atoms and neutrons. EPDM/HDPE composites filled with 20 phr carbon black have the hydrogen atomic density of 7.2*10\(^{22}\) atom/cm\(^3\).

Table 2. Atomic density and macroscopic cross-section of EPDM/HDPE composites with 20 phr carbon black

| Elements | Moles | Mole Percentage (%) | Total Atoms | Atomic Density*E24 (atoms/cc) | Neutron Crosssection (barns) | Macroscopic Crosssection (cm\(^{-1}\)) | Total Macroscopic Crosssection (cm\(^{-1}\)) |
|----------|-------|----------------------|-------------|----------------------------|-------------------------------|--------------------------------|----------------------------------|
| C        | 11.42 | 34.8                 | 6.88        | 0.039                      | 0.171                         | 0.0668                         | 0.28                             |
| H        | 21.26 | 64.9                 | 12.81       | 0.0727                     | 0.29                          | 0.2109                         |                                  |
| O        | 0.039 | 0.12                 | 0.024       | 0.00014                    | 0.158                         | 0.0002                         |                                  |
| N        | 0.0057| 0.01                 | 0.003       | 0.000002                   | 0.156                         | 0.0000                         |                                  |
4. Conclusion

The smooth brittle surface and reduced size domains of HDPE in the EPDM matrix on addition of carbon black confirms the partial compatibilization of HDPE in EPDM matrix. The tensile strength and tensile modulus of the carbon black filled EPDM/HDPE increases with increase in carbon black with a slight decrease in elongation at break, which can be attributed to physical force and chemical interaction at interface of carbon black and polymer chains. A decrease in tear strength at a lower concentration of carbon black shows the inefficiency of carbon black to form strong interfacial adhesion at the interface of EPDM/HDPE blends. EPDM/HDPE with 20phr of carbon black showed total neutron cross-section of 0.28 cm\(^{-1}\) for 2 MeV energy neutrons. Our attempt in designing an EPDM/HDPE composites wherein phase distribution of HDPE in EPDM rubber, with carbon black was quite suitable to act as a flexible neutron shielding material to slow down the energy of 2 MeV neutrons.

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References

[1] Özdemir T, Akbay I K, Uzun H and Reyhancan I A 2016 Neutron shielding of EPDM rubber with boric acid: Mechanical, thermal properties and neutron absorption tests Prog. Nucl.Energy 89 102–9
[2] Özdemir T, Gungor A and Reyhancan A 2017 Flexible neutron shielding composite material of EPDM rubber with boron trioxide: Mechanical, thermal investigations and neutron shielding tests Radiat. Phys. Chem. 131 7–12
[3] Güngör A, Akbay I K and Özdemir T 2019 EPDM Rubber with hexagonal Boron Nitride: A Thermal Neutron Shielding Composite Radiat. Phys. Chem. 165 108391
[4] Piotrowski T, Mazgaj M, Zak A and Skubalski J 2015 Importance of atomic composition and moisture content of cement based composites in neutron radiation shielding Procedia Eng. 108
616–23

[5] Kharita M H, Yousef S and AlNassar M 2009 The effect of carbon powder addition on the properties of hematite radiation shielding concrete Prog. Nucl. Energy 51 388–92

[6] Shin J W, Lee J W, Yu S, Baek B K, Hong J P, Seo Y, Kim W N, Hong S M and Koo C M 2014 Polyethylene/boron-containing composites for radiation shielding Thermochim. Acta 585 5–9

[7] Harrison C, Weaver S, Bertelsen C, Burgett E, Hertel N and Grulke E 2008 Polyethylene/boron nitride composites for space radiation shielding J. Appl. Polym. Sci. 109 2529–38

[8] Stelescu D M, Airinei A, Homocianu M, Fifere N, Timpu D and Aflori M 2013 Structural characteristics of some high density polyethylene/EPDM blends Polym. Test. 32 187–96

[9] Sharma B K, Chowdhury S R, Jha A, Samanta A K, Mahanwar P and Sarma K S 2017 ENGAGE compatibilized HDPE / EPDM blends : Modification of some industrially pertinent properties and morphology upon incorporation of Mg ( OH ) 2 filler and electron beam crosslinked network 44922

[10] Jovanović V, Samaržija-Jovanović S, Budinski-Simendić J, Marković G and Marinović-Cincović M 2013 Composites based on carbon black reinforced NBR/EPDM rubber blends Compos. Part B Eng. 45 333–40

[11] Rane A V., Kanny K, Mathew A, Mohan T P and Thomas S 2019 Comparative Analysis of Processing Techniques’ Effect on the Strength of Carbon Black (N220)-Filled Poly (Lactic Acid) Composites Strength Mater. 51 476–89

[12] Husnan M A, Ismail H and Shuib R K 2018 The effect of carbon black (CB) loading on curing characteristics and mechanical properties of virgin acrylonitrile butadiene rubber (Nbrv)/recycled acrylonitrile butadiene rubber (Nbrr) blends IOP Conf. Ser. Mater. Sci. Eng. 309

[13] Ghosh P and Chakrabarti A 2000 Conducting carbon black ® lled EPDM vulcanizates : assessment of dependence of physical and mechanical properties and conducting character on variation of filler loading 36 1043–54

[14] International Atomic Energy Agency Data File Data File