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Thermal Aging of Bentonite-Filled Ethylene Propylene Diene Monomer Composites

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ABSTRACT: Bentonite-filled ethylene propylene diene monomer (EPDM/Bt) composites were prepared using two roll mill compounding method and the effect of Bt loading on the thermal aging, swelling resistance and crosslink density of EPDM/Bt composites were studied. The effect of *in situ* addition of different silane coupling agents (SCAs) on the above properties at optimum Bt loading of EPDM/Bt composite was also investigated. Thermal aging test results show that the tensile strength and tensile modulus at 100% elongation (M100) increase initially for 2 days aged composites and decrease slightly after 4 days of aging, meanwhile the elongation at break (E_b) decrease gradually with aging period as compared to the unaged composites. Upon aging, swelling resistance increase initially indicating increased crosslink density of EPDM/Bt composite due to post-curing and reduced after 4 days of aging due to crosslink destruction and EPDM chain scissioning. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

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INTRODUCTION

Ethylene propylene diene monomer (EPDM) is a low unsaturated polyolefin developed by DuPont in the 1960s.[1] EPDM has attracted much attention and showed a tremendous growth in market share due to its inherent resistance to heat, aging, irradiation, and oxidation compared with other synthetic rubbers resulted from its unsaturated hydrocarbon backbone with the presence of double bonds in the side chain. Besides, EPDM also shows high electrical and dynamic mechanical properties, low temperature flexibility, and excellent swelling resistance in several chemicals such as brake fluid and glycol. Other than that, EPDM is also capable of accepting high loading of filler, reinforcing materials and plasticizers while retaining its properties. All these outstanding properties of EPDM make it the most suitable rubber for outdoor applications, automotive sealing systems, building profiles, electrical power cables, and white side walls of tires, roofing sheets, belting, and sport goods. And recently, EPDM was used as ablative and insulator compounds in solid propellant rocket motors.[2–7]

However, the low mechanical properties become the drawback which limits the use of EPDM in most industrial applications. Therefore, filler reinforcement is required or necessary to improve the mechanical properties of EPDM to suit the high performance applications.[8] In outdoor applications, the surface properties of any materials particularly polymer deteriorates which influences its service life. Weathering conditions such as light, heat, irradiation, and chemical significantly affects the properties of polymer composites depending on the frequency and intensity of exposure. So it is essential to investigate the aging and thermal stability of EPDM in such conditions, allowing the selection of polymeric materials with superior properties for a specific application.[9,10]

Many studies on the effect of weathering such as heat, oxidative, irradiation, and chemical on the properties of EPDM composites were carried out by other researchers from the past which states the importance of understanding the microstructural destruction of EPDM network upon aging. Bouguedad et al.[11] report the influence of heat aging of EPDM used in insulation of electric cable, revealing the degradation of EPDM due to increased oxidative products on material surface, affecting the physical properties of EPDM. Meanwhile Mitra et al.[12,13] report the changes in surface chemistry of sulphur and peroxide cured EPDM upon exposure to chromo sulphuric acid solution. The effect of oxidative and thermal aging of neat EPDM and EPDM vulcanizate in gelation was reported by Deuri and Bhowmick,[14] who also studied on the network structure and mechanical properties as well as the post-curing reactions and the destruction of crosslinks upon aging.

In the previous study, bentonite (Bt), a type of mineral clay was introduced as a new type of filler in EPDM compounding and experimental study reveals the enhancement of tensile properties, swelling resistance, thermal stability and processability of Bt-filled

Table I. Compounding Formulation (phr)

	Composites						
Materials	Neat EPDM	EPDM/ 10Bt	EPDM/ 30Bt	EPDM/ 50Bt	EPDM/ 70Bt	EPDM/50Bt/ APTES	EPDM/ 50Bt/Si69
EPDM	100	100	100	100	100	100	100
Bt	–	10	30	50	70	50	50
APTES	–	–	–	–	–	3	–
Si69	–	–	–	–	–	–	3
ZnO	5	5	5	5	5	5	5
SA	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBT	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

EPDM composites (EPDM/Bt) as compared to the neat EPDM. Optimum loading of 50 phr Bt is required to achieve the highest properties of the composite whereas, agglomerations of Bt particles occurred at further addition of Bt, that is above 50 phr Bt.[15] On other studies, compatibilization of EPDM/Bt by maleic anhydride grafted EPDM (MAH-g-EPDM) and silane coupling agents (SCAs) showed enhanced tensile, swelling, and thermal properties as compared with uncompatibilized EPDM/Bt composites.[16]

However, in practice, rubbers are normally subjected to various environments particularly EPDM which is mainly used in outdoor application exposed to thermal, radiation, oxidation, or chemical erosion. Deterioration of molecular structure upon exposure subsequently affects the performance and service life of EPDM composites. As reported earlier by Chou et al.,[17] thermal aging had been the main cause of failure of rubber composites in buildings and bridges in Taiwan due to high temperature climate. So it is of our main concern to study the effect of thermal aging on the properties of EPDM/Bt composite and should be taken into account to observe the potential of EPDM/Bt composites as a new composite material in real service environment.

In this research work, the effect of thermal aging on the properties of EPDM/Bt composites was studied as a function of Bt loading. Tensile properties, swelling resistance, and crosslink density of EPDM/Bt composites were measured. Besides, the effect of silane coupling agents (SCAs) addition on the thermal aging of EPDM/Bt composites was also studied.

EXPERIMENTAL

Materials

Ethylene-Propylene-Diene Monomer (EPDM), 778Z with ethylene content of 67%, ethylene norbornene (ENB) of 4.3%, and Mooney viscosity (ML (1+4) 125°C) of 63 MU (Mooney Unit) was purchased from Keltan DSM Elastomers. Bentonite (Bt) was supplied by Ipoh Ceramics (M) Sdn. Bhd. The silane coupling agents i.e., 3-Aminopropyltriethoxysilane (APTES) and Bis-(3-triethoxysilylpropyl) tetrasulphide (Si69) were purchased from Sigma Aldrich Co. (US). Other compounding ingredients; zinc oxide (ZnO), stearic acid (SA), tetramethyl thiuram disulphide (TMTD), 2-mercapto benzothiazole (MBT) and sulphur were all obtained from Bayer (M) Ltd and used as received.

Composite Preparations

Bentonite (Bt) was dried in oven at 100°C for 24 h prior to the compounding to expel absorbed moisture. Series of EPDM/Bt composite containing different Bt loading and with the addition of SCAs were prepared by mixing in laboratory scale (160 mm × 320 mm) two roll mill, model XK-160 based on the compounding formulation as shown in Table I. Curing characteristics were studied using a Monsanto Moving Die Rheometer (MDR 2000) in accordance to ASTM D 2240-93 at 150°C. Vulcanization press was operated at 150°C using a hot press to produce composite sheets of 2 mm thickness based on the respective curing time (t_{90}) obtained from the rheograph.

Measurement of Tensile Properties

Tensile properties were determined according to ASTM D 412 using a model 3366 Instron universal testing machine at crosshead speed of 500 mm/min. The tensile strength, elongation at break (E_b), and tensile modulus at 100% elongation (M100) were measured.

Swelling Properties

Swelling test was conducted using toluene according to ASTM D 471-79. Initial weight (M_i) and swollen weight after 72 h of immersion in toluene (M_s) in grams of the vulcanized specimens were measured using an electronic balance. Swelling percentage indicating the increase in mass due to toluene uptake and the swelling resistance of the vulcanized composites was calculated based on eq. (1).

$$\text{Swelling Percentage} = [(M_s - M_i)/M_i] \times 100 \qquad (1)$$

Crosslink Density

Crosslink density of the specimens were obtained through rapid solvent-swelling measurement using cured specimens with the dimension of 30 x 5 x 2 mm^3 immersed in toluene for 72 h and by applying the Flory-Rehner equation as shown in eq. (2) to eq. (5):

$$M_c = [-\rho_p V_s V_r^{1/3}]/[\ln(1-V_r) + V_r + \chi V_r^2] \qquad (2)$$

$$V_r = 1/(1+Q_m) \qquad (3)$$

Where the M_c is the molar mass, ρ_p is the density of EPDM (0.823 g cm^{-3}), V_s is the molar volume of the solvent i.e., toluene: 107.0 mL/mol, V_r is the volume fraction of the swollen rubber which is calculated by using eq. (3), Q_m is the swelling weight of the EPDM/

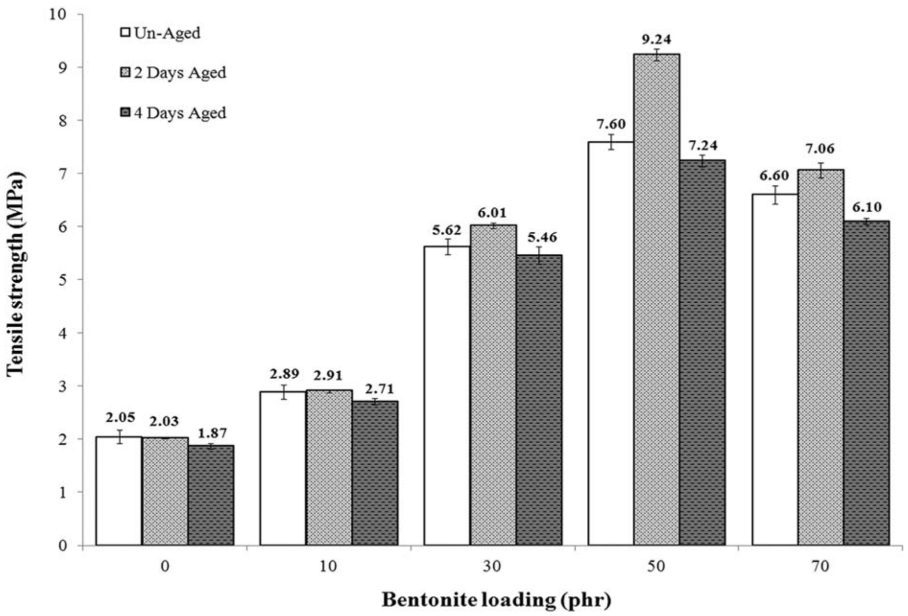

Figure 1. Effect of Bt loading on the tensile strength of unaged and aged EPDM/Bt composites.

Bt composites in toluene and χ is the interaction coefficient between the solvent and the rubber network (0.49) which is calculated by using eq. (4) where δ_s and δ_r are the solubility parameters of the solvent and rubber network, respectively, R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature. The degree of crosslink density (V) is calculated by using eq. (5):

$$\chi=(\delta_s-\delta_r)\,V_O/RT \tag{4}$$

$$V=1/(2M_c) \tag{5}$$

Thermal Aging Test

Thermal aging test was carried out in accordance to ASTM D 573 in an air-circulating oven operating at 100°C for interval time of 2 and 4 days. Aging test of EPDM was conducted at 100°C (2–4 days) instead of 70°C (1–2 weeks) which is normally used for rubbers due to high thermal stability of EPDM as compared to natural or other synthetic rubber. The specimens were conditioned at room temperature for 24 h upon the removal from oven. Tensile properties, swelling resistance and crosslink density of EPDM/Bt composites as a function of aging period were determined based on the procedures mentioned earlier. The deterioration of properties of the composites was determined by comparing the properties of aged composite with that of unaged composite.

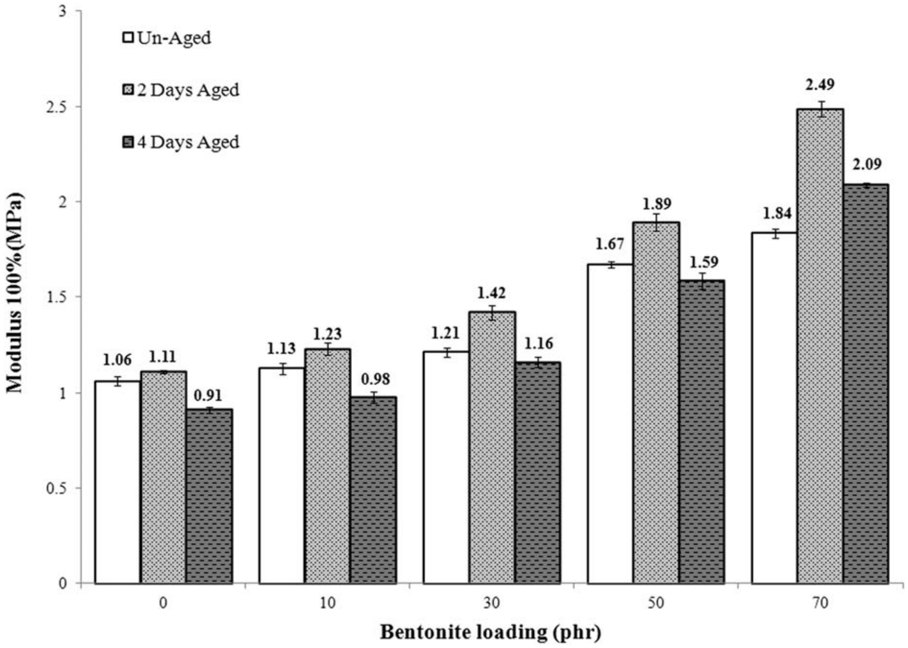

Figure 2. Effect of Bt loading on the M100 of unaged and aged EPDM/Bt composites.

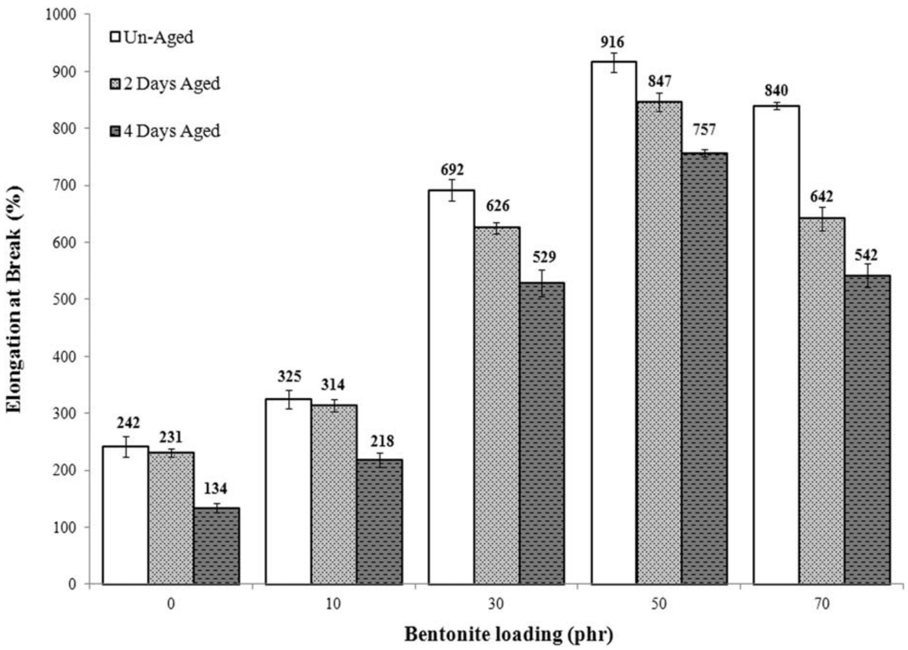

Figure 3. Effect of Bt loading on the elongation at break of unaged and aged EPDM/Bt composites.

Scanning Electron Microscopic (SEM)

Morphological observations of the tensile fractured surface of the composites were examined under a ZEISS SUPRA-35VP SEM with GEMINI field emission column. Sample surface were sputter coated with a thin layer of gold-palladium prior to the examination to prevent the electrostatic charging effects.

RESULTS AND DISCUSSION

Effect of Thermal Aging of EPDM/Bt Composite as a Function of Bt Loading

Tensile Properties. The effect of thermal aging on the tensile properties i.e., tensile strength, tensile modulus at 100% elongation (M100) and elongation at break (E_b) of EPDM/Bt composites as a function of Bt loading are shown in Figures 1–3 respectively. Tensile properties of EPDM were enhanced with the addition of Bt as compared with the neat EPDM and with the increasing Bt loading. Optimum tensile strength and Eb were obtained with the addition of 50 phr Bt meanwhile M100 gradually increases with the increasing Bt loading.

From Figure 1, it can be seen that the tensile strength of neat EPDM gradually deteriorates with the prolonged aging period. Meanwhile the tensile strength of EPDM/Bt composites was increased initially with 2 days of aging and decreases slightly at 4 days of aging. Similarly, M100 of EPDM/Bt composites were also initially increased at 2 days of aging which then reduced slightly as the aging prolonged to 4 days (Figure 2). On the other hand, as can be seen from Figure 3, the Eb of neat EPDM and EPDM/Bt composites was gradually reduced with increasing aging period at similar Bt loading.

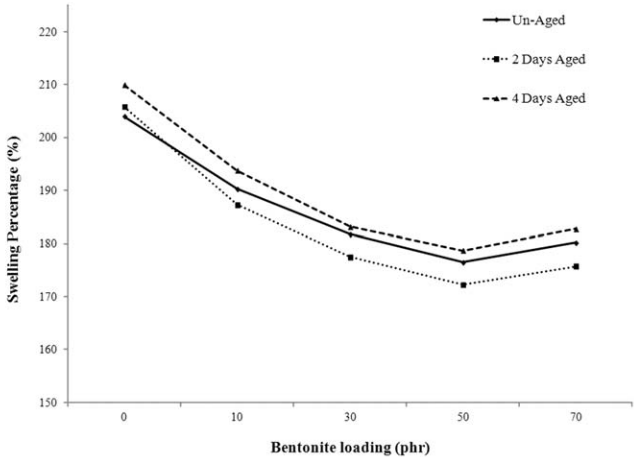

Figure 4. Effect of Bt loading on the swelling percentage of unaged and aged EPDM/Bt composites.

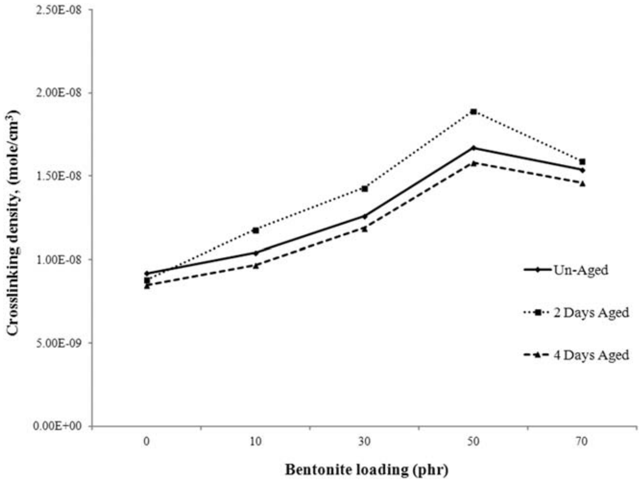

Figure 5. Effect of Bt loading on the crosslink density of unaged and aged EPDM/Bt composites.

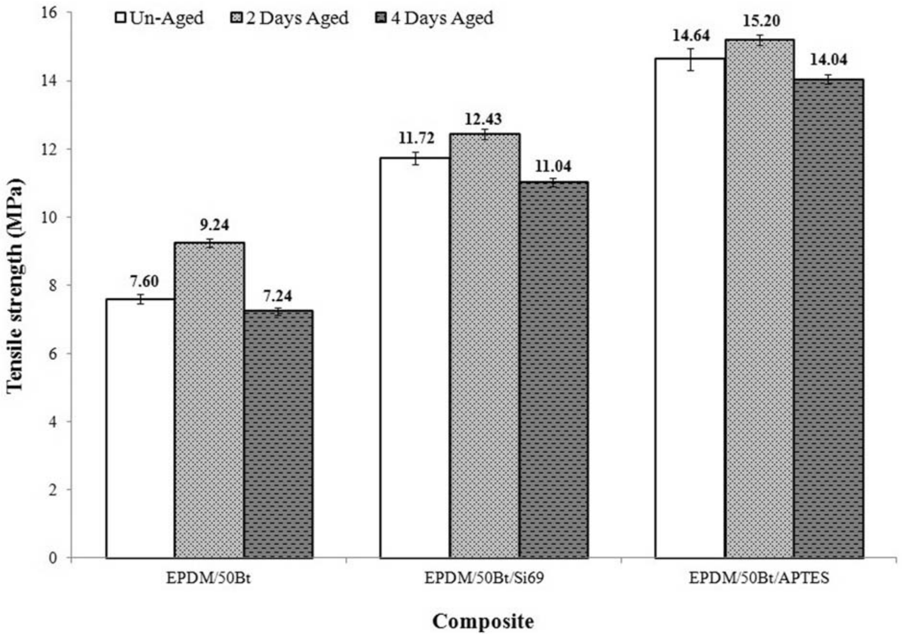

Figure 6. Tensile strength of EPDM/50Bt, EPDM/50Bt/Si69 and EPDM/50Bt/APTES before and after aging for 2 and 4 days.

Ismail et al.[18] reported similar observation on the effect of thermal aging of rattan-filled natural rubber composites, who suggested that the deterioration of tensile properties upon aging indicate the degradation of rubber which is independent of filler loading. The increase in tensile strength of EPDM/Bt composites after 2 days of aging is attributed to the presence of free, unreacted sulphur in the composite which leads to the crosslink formation upon thermal exposure known as post-curing. The composite's stiffness increases with the formation of additional crosslinks upon aging process. This results in reduced E_b and increased M100 which indicates the deformability and stiffness of the composite materials, respectively.

However, tensile properties drops as the aging prolonged to 4 days due to the scissioning of EPDM chains and the destruction of sulphur crosslinks. Some other fundamental studies report that the sulphur cured rubber compounds undergoes crosslinking on the initiation of aging process resulting in the formation of new crosslinks which enhances the tensile properties of the

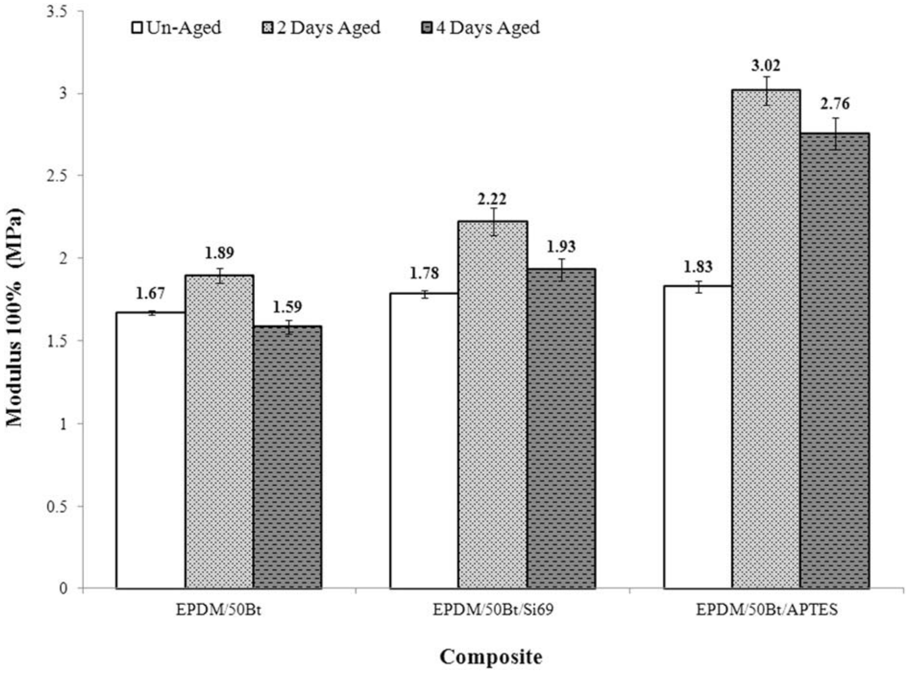

Figure 7. M100 of EPDM/50Bt, EPDM/50Bt/Si69, and EPDM/50Bt/APTES before and after aging for 2 and 4 days.

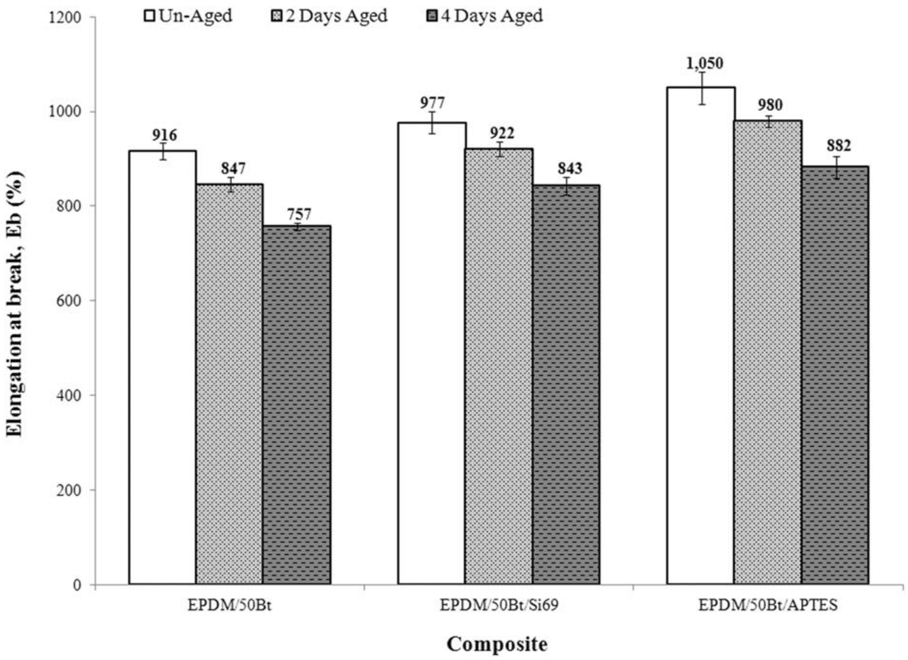

Figure 8. Eb of EPDM/50Bt, EPDM/50Bt/Si69, and EPDM/50Bt/APTES before and after aging for 2 and 4 days.

compound. As aging prolonged, scissioning of rubber chains and the destruction of crosslinks takes place lead to deterioration of physical and mechanical properties of the material.[19–21] Besides, it was also obtained that the tensile properties of EPDM/Bt composites were always higher than that of the neat EPDM even after 4 days of aging suggesting greater potential of Bt to improve and retain the properties of EPDM in the real service environment.

Swelling Resistance and Crosslink Density. The swelling percentage indicating the swelling resistance of neat EPDM and EPDM/Bt composites before and after thermal aging as a function of Bt loading is presented in Figure 4. Reduction in swelling percentage indicates the enhancement of swelling resistance and can be used as a direct measure of crosslink density in the case of rubber composites. It can be clearly seen that the swelling percentage of the unaged composite decrease with increasing Bt loading up to 50 phr and increased slightly at 70 phr Bt. Result indicate the enhancement of swelling resistance of EPDM with the addition of Bt, attributed by the better wettability of Bt by EPDM and good dispersion of Bt in EPDM matrix, preventing solvent diffusion and higher swelling resistance of the composite.

Figure 4 also illustrates the effect of thermal aging on the swelling percentage i.e., swelling resistance of EPDM/Bt composites. The swelling percentage of neat EPDM increases gradually with the increasing aging days meanwhile EPDM/Bt composites showed an initial decrease of swelling percentage at 2 days aging and increasing swelling percentage when the aging prolonged to 4 days at similar Bt loading. The occurrence of post-curing with the initiation of aging lead to the formation of additional crosslinks in EPDM-Bt network, disrupting solvent diffusion path subsequently reduces the percentage toluene diffusing into the composite. However, the swelling percentage was increased after 4 days of aging indicating the breaking of crosslinks and scissioning of EPDM chains allowing rapid toluene diffusion and lower swelling resistance of EPDM/Bt composites as compared to unaged composite.

Figure 5 illustrate the changes in the crosslink density of neat EPDM and EPDM/Bt composites, before and after aging at various Bt loading. The crosslink density of EPDM/Bt composites increases with the increasing Bt loading up to an optimum value at 50 phr Bt loading. The increase in crosslink density with increasing Bt loading indicates good dispersion of Bt in EPDM and improved processability of EPDM in the presence of Bt. Good dispersion of Bt in EPDM facilitates the dispersion of other curatives, subsequently promoting the curing process and an increase in crosslink density. However, the free volume for the mobility of EPDM chains decreases with the addition of Bt which further reduce at higher Bt loading causing chains to move closer, amplifying the crosslink formation. Upon 2 days of aging, the crosslink density of EPDM/Bt composites increases as a result of post-curing and the formation of new crosslinks which is in good agreement with the tensile properties and swelling resistance of EPDM/Bt composites. And a slight reduction in crosslink density was attained with the prolonged aging of 4 days proving the destruction of crosslink density and the reduction of tensile properties and swelling resistance.

Effect of Thermal Aging of Silane Coupling Agents Added EPDM/Bt Composite

Tensile Properties. Silane coupling agents (SCAs) namely 3-Aminopropyltriethoxysilane (APTES) and Bis-(3-triethoxysilylpropyl) tetrasulphide (Si69) were added in-situ to enhance the properties of EPDM/Bt composite. The effect of SCA addition and thermal aging on the tensile properties of

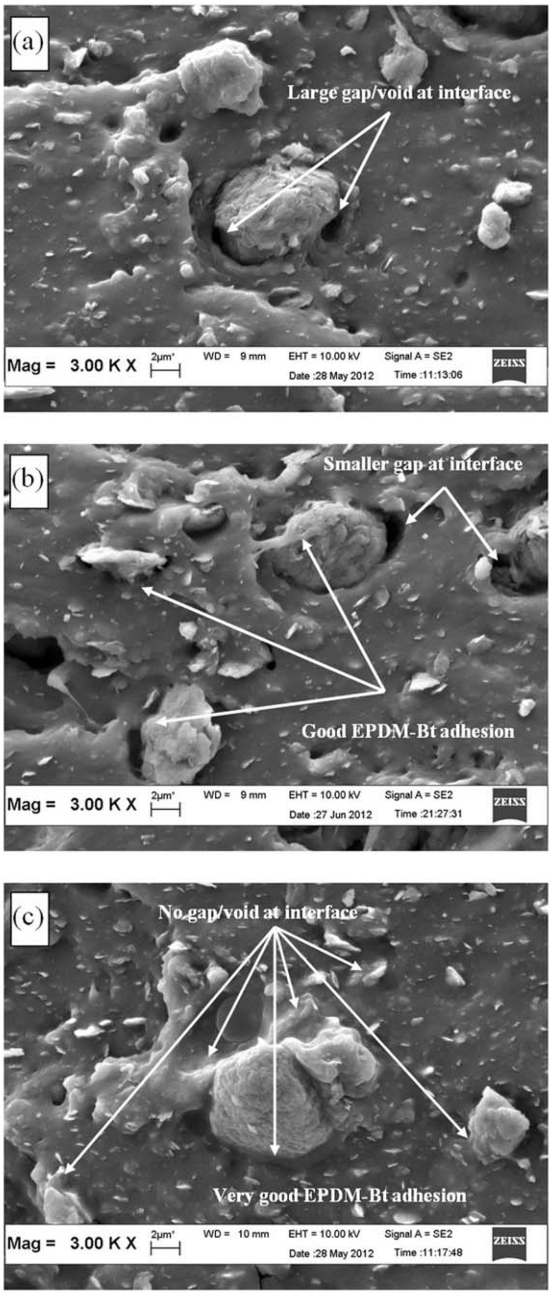

Figure 9. SEM micrographs of: (a) EPDM/50Bt, (b) EPDM/50Bt/Si69 and (c) EPDM/50Bt/APTES composites.

EPDM/Bt composite at optimum loading of 50 phr Bt are compiled in Figures 6–8. It can be clearly seen from Figures 6 to 8 that the tensile strength, M100 and Eb of EPDM/Bt composites were all improved with the addition of APTES or Si69. In the presence of SCA, greater interfacial interaction between EPDM and Bt occurs attributing to the coupling reactions of the APTES or Si69 resulting in the higher tensile properties as compared to the EPDM/Bt composite without SCA.[22]

However, EPDM/50Bt/APTES composite was greatly enhanced and possess higher tensile properties as compared to EPDM/50Bt/Si69 composite. The amino groups of APTES capable of accelerating the curing process of EPDM/Bt composites, switching the vulcanization system from semi efficient vulcanization (SEV) to efficient vulcanization (EV) system (higher crosslink density). Whereas, the tetrasulphide groups of Si69 generates additional sulphur which switches the vulcanization system of EPDM/50Bt/Si69 composite from semi efficient vulcanization (SEV) to conventional vulcanization (CV) system (moderate crosslink density). On the other hand, the triethoxysilylpropyl group of Si69 is larger and bulky which inhibits the crosslink formation, producing much flexible interaction at Bt vicinity as compared with shorter and smaller APTES molecules.[23] The formation of high crosslinks and greater interfacial interaction of EPDM/Bt composite in the presence of APTES as compared to Si69 reveals the stronger coupling effect of APTES resulting in higher tensile properties of EPDM/50Bt/APTES composites.

Besides, both tensile strength and M100 of EPDM/Bt composites, with and without SCA, increases initially with the thermal aging at 2 days which then decreases with the prolonged aging at 4 days. Meanwhile, E_b of the composites was gradually decreased with the thermal aging for 2 and 4 days. As of the similar reason, the increment of tensile properties of EPDM/Bt composites with or without APTES or Si69 was attributed by the post-curing of EPDM chains upon initiation of aging.

However, EPDM/50Bt/APTES composite showed the highest tensile strength, M100 and Eb as compared to EPDM/50Bt or EPDM/50Bt/Si69 composites even after 2 days and 4 days of aging. It was reported earlier in our previous study that APTES shows higher coupling effect to EPDM and Bt as compared to Si69, which may restrict the oxidation of EPDM chains in EPDM/50Bt/APTES composite.[22] Hence, the newly formed crosslink upon the initiation of aging may retain due to high thermal stability of SCA added EPDM/Bt composites resulting in high stiffness composite with lower Eb value.

Figures 9(a–c) is the scanning electron microscopic (SEM) images of EPDM/50Bt composites with and without SCA, proving the enhancement of interfacial interaction between EPDM matrix and Bt particles in the presence of SCAs. The large gaps or void at the interface indicates the poor interfacial adhesion between EPDM and Bt particles in the absence of SCAs [Figure 9(a)]. However, smaller gap or void and the presence of matrix tearing at Bt surface reveals the enhanced interfacial adhesion between EPDM and Bt particle in the presence of Si69 [Figure 9(b)]. Whereas, no gaps or voids were seen at EPDM-Bt interface indicating a better enhancement of interfacial adhesion between EPDM and Bt particle in the presence of APTES [Figure 9(c)] as compared with Si69.

Swelling Resistance and Crosslink Density. The swelling percentage and crosslink density of EPDM/50Bt, with or without APTES or Si69, before and after aging at 2 and 4 days are shown in Figures 10 and 11, respectively. For unaged composite sample, the swelling percentage of EPDM/50Bt was decreased by 7.4% and 27.4% respectively with the addition of Si69 and APTES. Reduction of swelling percentage indicates the enhanced swelling resistance of EPDM/50Bt in the presence of SCAs. The

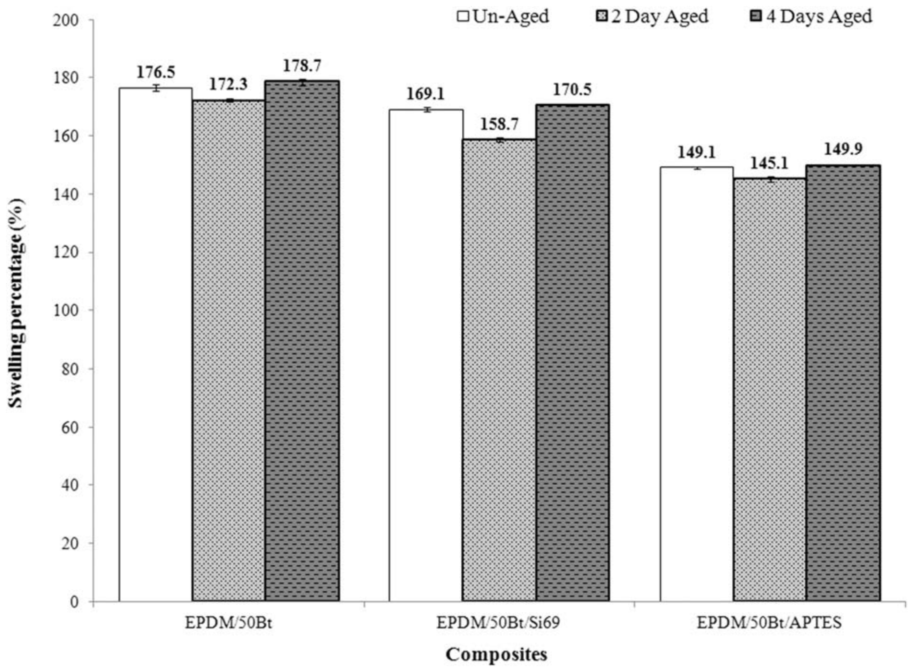

Figure 10. Swelling percentage of EPDM/50Bt, EPDM/50Bt/Si69, and EPDM/50Bt/APTES before and after aging for 2 and 4 days.

greater coupling reaction between EPDM and Bt in the presence of SCAs forms a stronger interfacial interaction, preventing the toluene diffusion into EPDM-Bt network. However, EPDM/50Bt/Si69 composite shows slightly higher swelling percentage as compared with EPDM/50Bt/APTES which is attributed by the longer macromolecular chains of Si69 as compared with APTES. Bulky and longer molecules of Si69 forms large interface which prone to toluene diffusion causing slightly higher swelling percentage.

Thermal aging shows very small changes in the swelling resistance of EPDM/50Bt composite in the presence of SCAs. Swelling percentage was initially decreased for all the composites and increased again with the prolonged aging time. The formation of new crosslinks upon post-curing attributes to the lower toluene uptake of 2 days aged composites which were proved as shown in Figure 11. Crosslink density of EPDM/50Bt, EPDM/50Bt/Si69 and EPDM/50Bt/APTES composite were all increased initially after 2 days aging and drops after 4 days of aging. EPDM/50Bt/APTES composite possess the highest swelling resistance as compared to EPDM/50Bt or EPDM/50Bt/Si69 composites even after 4 days of aging. And this may be attributed to the stronger coupling effect and thermally stable interface present in between EPDM and Bt in the presence of APTES.

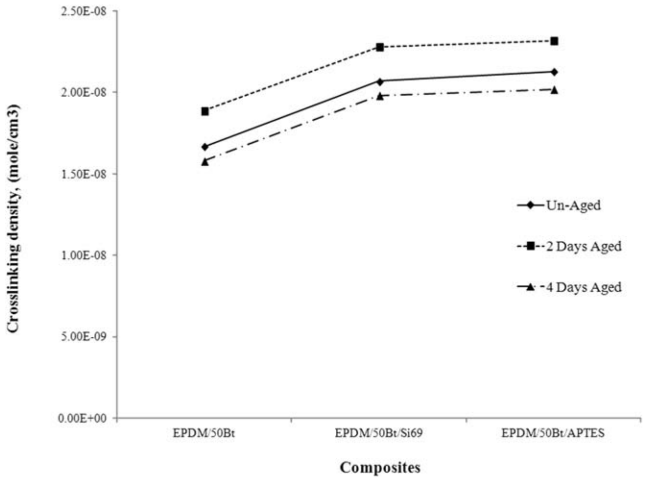

Figure 11. Crosslink density of EPDM/50Bt, EPDM/50Bt/Si69, and EPDM/50Bt/APTES before and after aging for 2 and 4 days.

CONCLUSIONS

Tensile strength, tensile modulus at 100% elongation (M100), swelling resistance, and crosslink density were all increased with the initial aging for 2 days attributed by the post-curing and the formation on new crosslinks. The properties were then decreased with prolonged aging for 4 days due to the destruction of crosslinks and scissioning of EPDM chains due to aging.

Tensile properties and swelling resistance of EPDM/Bt composite were enhanced with the addition of SCAs. Upon aging, tensile strength, M100, swelling resistance, and crosslink density were all increased initially after 2 days ageing and decreased after 4 days ageing. Both EPDM/50Bt/APTES and EPDM/50Bt/Si69 composites showed remarkably higher tensile properties and swelling resistance as compared to EPDM/50Bt composites upon aging.

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