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THERMAL AND MORPHOLOGY STUDIES OF SILICONIZED EPOXIDIZED ETHYLENE-PROPYLENE-DIENE TERPOLYMER

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ABSTRACT

Siliconized epoxidized ethylene-propylene-diene terpolymer was developed by ethylene-propylene-diene terpolymer (EPDM) was epoxidized with an *in situ* formed per formic acd to prepare epoxidized EPDM (eEPDM) with hydroxyl terminated polydimethysiloxane (silicone) modifier using 3-aminopropyltriethoxysilane (APTES) crosslinker and dibutyltindilaurate (DBTDL) as catalyst. The chemical structure of Siliconized epoxidized ethylene-propylene-diene terpolymer was confirmed by FT-IR spectroscopy. The thermal properties and morpholiges of the EPDM, eEPDM and Siliconized epoxidized ethylene-propylene-diene terpolymer were investigated. Siliconized epoxidized ethylene-propylene-diene terpolymer is observed that the improves their thermal stability due to the partial ionic nature, high bond energy and thermal stability of –Si-O-Si- linkage. Siliconized epoxidized ethylene-propylene-diene terpolymer systems show heterogeneous morphology.

Key words: eEPDM, Dibutyltindilaurate, Thermal properties, Morphology.

INTRODUCTION

It has been reported that ethylene-propylene-diene terpolymer (EPDM) has superior resistances to light, heat, ozone and oxygen because it has little contents of the nonconjugated diene component[1-4]. Epoxidation is the easy and efficient method for

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introducing a novel reactive group into polyolefins, leading to innovative and useful properties and broad use in an assortment of applications[5-8]. Epoxidation of olefinic compounds using organic peracids has been widely studied since oxiranes were prepared by reacting ethylenic compounds with perbenzoic acid. Oxiranes are generally prepared using perbenzoic acid[9], chlorperbenzoic acid[10] and monoperphalic acid[11]. Performic acid is an extremely active organic peracid[12-16] used for the epoxidation, but, owing to its instability[17], it has to be prepared in situ. In recent years, silicone compounds are considered to be among the finest modifies owing to their better thermal and thermo-oxidative stability, outstanding moisture resistance, partial ionic nature, low surface energy, superior flame retardancy and the probable free rotation of chains about the Si-O bonds contribution unique flexibility, as well as the excellent hydrophobicity and compressivity[18]. Silicone rubbers, particularly poly(dimetylsiloxane) (PDMS), exhibited a number of good-looking properties including soaring chain flexibility, elevated thermal and oxidative stability, low temperature flexiblility and excellent hydrophobic behavior[19,20]. This combination of excellent features provided the essential conditions for the application of PDMS as an elastomeric modifier to build the modified epoxy resin with enhanced properties[21-23]. However, pure PDMS had extremely little use as a toughening agent because of the deprived compatibility between soft segments of PDMS and polar hard segments in epoxy, which principally resulted from the lack of hydrogen bonding. These materials, which typically exhibited separate T_g values due to thermodynamic inaptness, were either macroscopically immiscible or exuded from the cross-liked matrix during curing procedure in the conservative introduction of siloxane into polymers during blending methods[24,25], ensuing in deprived thermo-mechanical properties and compositional heterogeneity ensuing from poor segmental compatability, this partial the use of larger silicone concentrations[26,27]. To conquer this limitation and improve the interface between PDMS and epoxy matrices with enhanced thermo-mechanical properties and toughness, numerous techniques were reported in the literature, counting using silane coupling agents[28,29].

In our study, the EPDM was first epoxidized with *in situ* formed per formic acid, which induced functional epoxy groups into the EPDM macromolecular backbone. Further, 3-aminopropyltriethoxysilane and poly dimethlsiloxane on epoxidized ethylene-propylene-diene terpolymer has been synthesized in toluene. The structural, thermal and morphological properties were investigated using FTIR, TGA and SEM.

EXPERIMENTAL

Materials

The EPDM (ENB) elastomer used in this study was a commercial grade Nordel IP

4770P (ethylene/propylene/5-ethylidene-2-norborane = 70/25/5 by wt. %, Mooney viscosity, $MIL_{(1+4)}$ at 125°C is 70 and density of 0.87 g/cc) of DuPont Dow elastomer, USA. Hydroxl-terminated polydimethylsiloxane (HTPDMS) as modifier, 3-aminopropyltriethoxysilane (APTES), was procured from Aldrich Chemicals, USA. Dibutyltindilauarate (DBTDL) was purchased from Merck, Germany. Analytical grade formic acid (88%), hydrogen peroxide (30%), toluene-hexane were used as received.

In situ epoxidation of ethylene-propylene-diene terpolymer

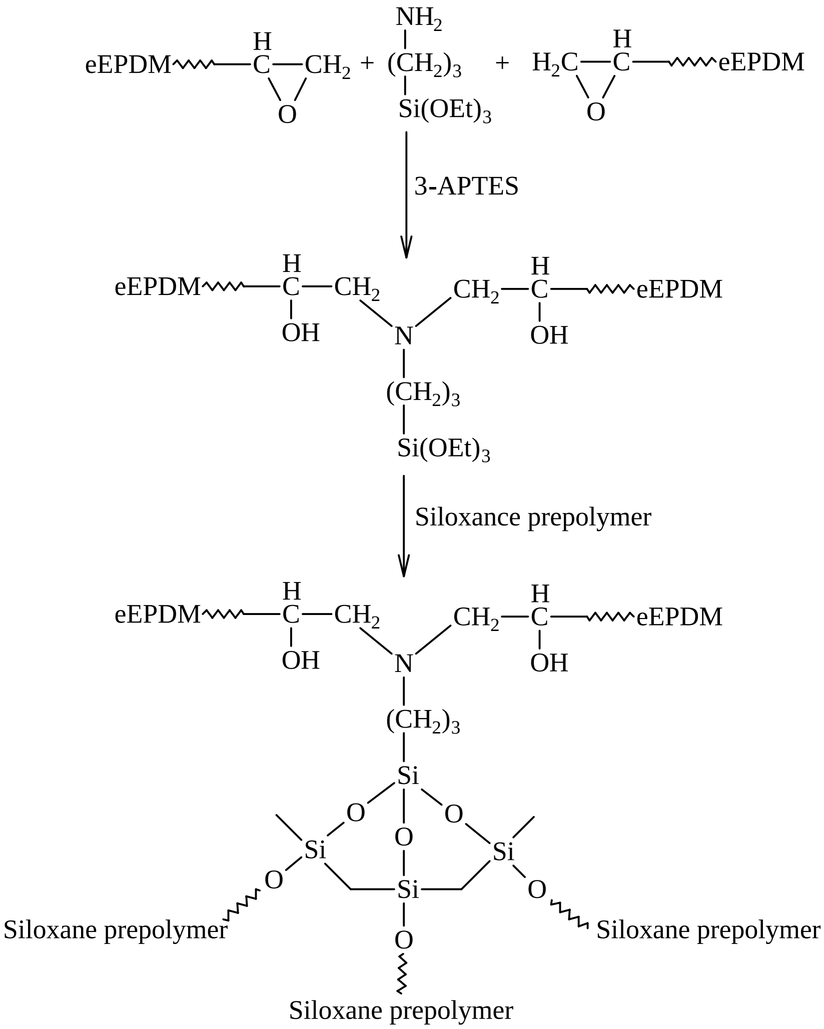
The EPDM was first dissolved in toluene in a three necked flask equipped with a mechanical stirrer and thermometer and maintained at 50°C in water bath. Under continuous stirring, the EPDM solution was acidified stepwise with 88% formic acid to pH 2-3. The epoxidation was performed by dropping the required amount of H_2O_2 (30%) for 30 min. A rapid introduction of this reagent is not recommended, because it causes excessive development of oxygen due to the decomposition of hydrogen peroxide at high temperature. The reaction was continued for 7 hr at 50°C. After epoxidation, the rubber was coagulated in acetone, thoroughly washed with distilled water, soaked in 1% w/v Na_2CO_3 solution for 24 hr and finally rinsed with distilled water. The rubber prepared was dried in a vacuum oven at 40°C to a constant weight.

Preparation of Siliconized epoxidized EPDM

The reactions are carried out in 500 mL three necked, round bottom flask equipped with a reflux condenser, a Teflon-coated mechanical stirring and a nitrogen inlet. 10 g of eEPDM was dissolved in 2900 mL toluene and refluxed untill complete dissolution of eEPDM. Further, 0.25 wt.% APTES and 0.75 wt.% dissolved in 50 mL of toluene were added to eEPDM, using dibutyl tindilaurate catalyst, with continuous stirring for 2 hr at 50°C. After the completion of reaction, the products were precipitated with methanol, filtered and dried in vacuum.

Measurments

EPDM, eEPDM and Siliconized epoxidized EPDM were characterized with the help of IR spectra obtained from Shimadzu-1800S, using solvent casted thin films. Thermo gravimetric analysis (TGA) were carried using a NETZSCA TG 209 instrument under nitrogen atmosphere at a heating rate of 10°C/min. Scanning electron micrographs were performed on a Quanta-200, FEG (SEM, Netherland) at accelerating voltages of 20.00 kV. The surface of samples was sputtered with a thin layer of gold.



Scheme 1: Schematic representation of Siliconized epoxidized EPDM

RESULTS AND DISCUSSION

Fourier-transform infrared spectroscopy

Fig. 1 shows the FTIR spectra of EPDM, eEPDM and Siliconized epoxidized EPDM. The IR spectra of EPDM (Fig. 1(a)) shows the C-H stretching vibration (aliphatic) at 2911 cm^{-1}, $-CH_2$ rocking vibration at 1451 cm^{-1}, CH_3 symmetric bending vibration at 1367 cm^{-1} due to the presence of propylene group, $-(CH2)_n-$ wagging vibration at 721 cm^{-1} due to the presence of polyethylene chain, C-C stretching vibration at 2851 cm^{-1} and the unsaturation band (>C=CH-) at 811 cm^{-1} due to the presence of ENB content. The FTIR spectrum of EPDM (Fig. 1 (b)) was characterized by the presence of an epoxides band at 870 cm^{-1} due to asymmetric epoxides ring stretching. Furthermore, the intensity of the >C=CH- band at 811 cm^{-1} decreases because o the expoxidation of EPDM, which demonstrates that the C=C double bond in EPDM was converted to the epoxy functional group in eEPDM. The conversion of double bond to epoxides was obtained as 50% (ca.2.4 mol %). To take advantage of relative change of absorbance at 811 and 870 cm^{-1}, a quantitative analysis was performed by area measurement of methyl deformation band at 1369 cm^{-1} as internal standard[30].

Fig. 1 (c) illustrates the IR spectra of Siliconized epoxidized EPDM, which reveals; absorption peak appeared at 2900 cm^{-1} and between 1140 cm^{-1} to 960 cm^{-1} confirms the presence of –Si-$(CH_2)_3$- and residual –Si-OH, respectively. Absence of peak at 2850 cm^{-1} of –Si-OCH_2CH_3 and formation of Si-O-Si at 1143 cm^{-1} confirms the completion of reaction between HTPDMS and APTES coupled epoxidized EPDM.

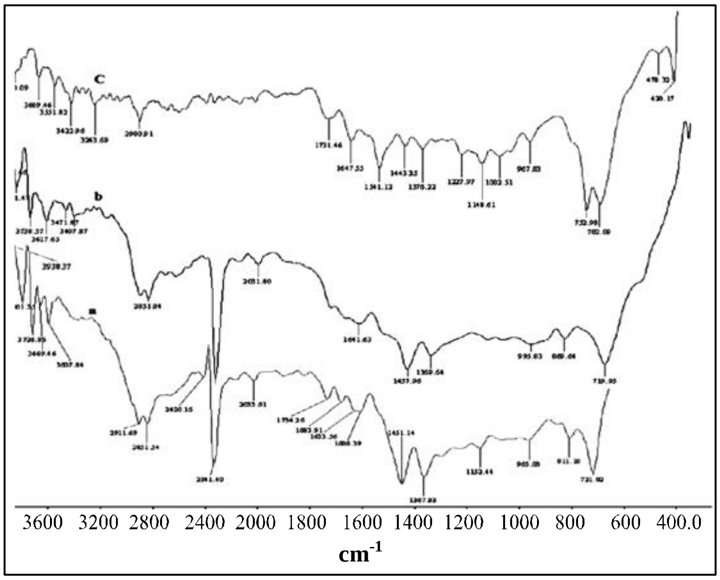


Fig. 1: FTIR spectra of (a) EPDM (b) eEPDM and (c) Siliconized epoxidized EPDM

Thermal properties

Thermogravimetric analysis

Thermograms of EPDM, eEPDM and siliconized epoxidized EPDM are given in Fig. 2. The inception decomposition temperature of EPDM, eEPDM and siliconized epoxidized EPDM are 440, 444 and 453°C, respectively. Similarly the final decomposition temperatures of EPDM, eEPDM and Siliconized epoxidized EPDM are 482, 486 and 494°C, respectively. The higher thermal stability of eEPDM compared to EPDM can be explained by the substitution of the double bond on the EPDM side chain with the epoxy rings[31]. Siliconized epoxidized EPDM also increases both inception and final decomposition temperatures because of the delay in degradation caused by silicone moiety may be attributed to its, high bond energy and thermal partial ionic nature and thermal stability of -Si-O-Si- linkage.

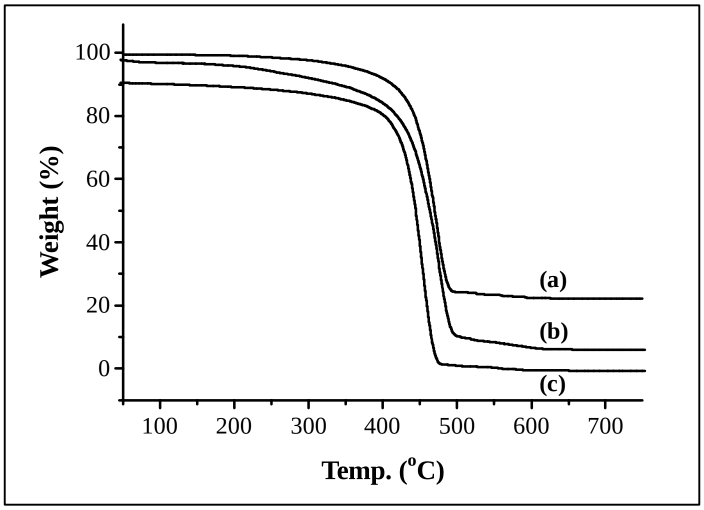


Fig. 2: TGA curves of (a) EPDM (b) eEPDM (c) Siliconized epoxidized EPDM

Differential scanning calorimetry

The glass transition behavior of the hybrid material is associated with cooperative motion of large chain segment. The DSC results of EPDM, eEPDM and Siliconized epoxided EPDM are shown in Fig. 3. The midpoints of the transition temperature curve in the DSC curve are recorded as T_g values. The T_g values EPDM, eEPDM and Siliconized epoxided EPDM are 43, -40 and -36°C. The glass transition temperatures T_g, increased due epoxidation. The increase in T_g as a result of epoxidation may be caused by the presence o the polar epoxides group, which gives more backbone than the unsaturated group[32,33]. The results also indicate that the T_g value for Siliconized EPDM is higher than eEPDM and EPDM, due to the silane content. Similar behavior was obtained for PMMA-MSMA hybrid system[34].

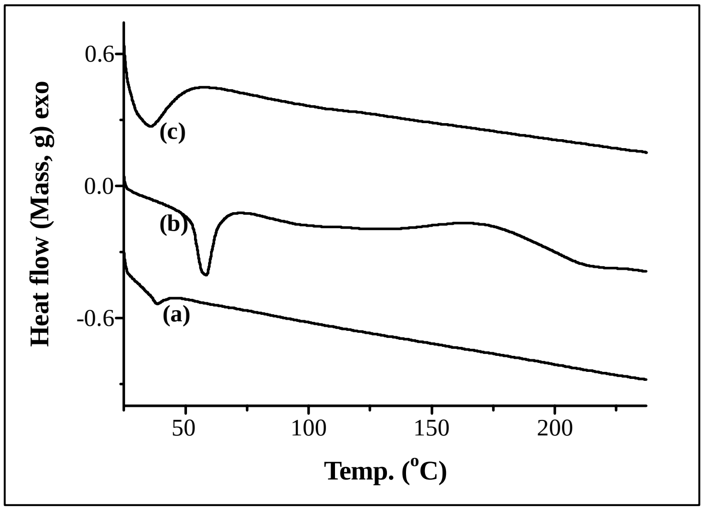


Fig. 3: DSC curves of (a) EPDM (b) eEPDM (c) Siliconized epoxidized EPDM

SEM Analysis

The morphological characterization of the films was carried out through SEM analysis. Fig. 4, 5 show the SEM photographs of EPDM and eEPDM, which indicates a plane and smooth surface with some bigger particles. However, the surface of Siliconized epoxidized EPDM is some orientations as seen in Fig. 6. The optimal network structure appears on the surface of Siliconized epoxidized EPDM can be probably due to –Si-O-Si- linkage.

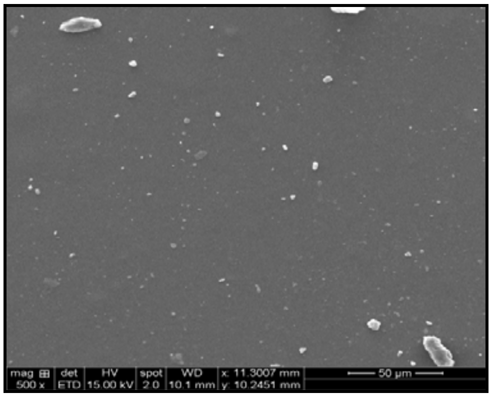


Fig. 4: SEM photograph of EPDM

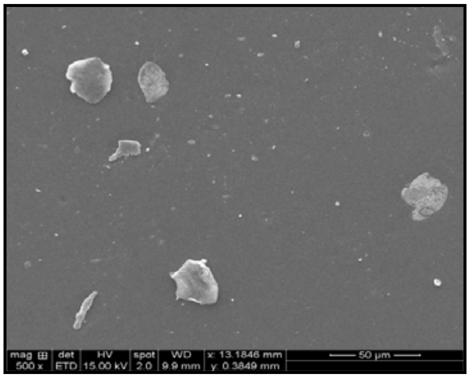


Fig. 5: SEM photograph of eEPDM

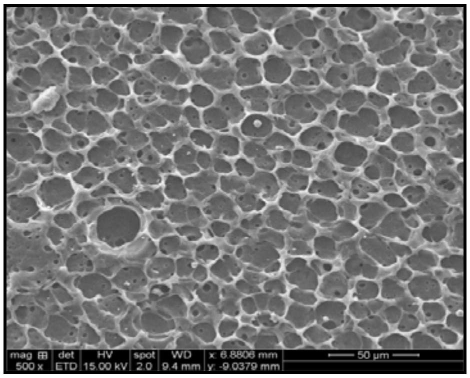


Fig. 6: SEM photograph of Siliconized epoxidized EPDM

CONCLUSION

Siliconized epoxidized EPDM was synthesized in toluene. The following conclusions were made based on the data resulted from different experimental studies. The completion of reaction between HTPDMS and APTES coupled, which has been confirmed from FTIR spectra. Siliconized epoxidized EPDM also increaseas both inception and final decomposition temperatures because of the delay in degradation due to their inherent flexibility and free rotation about bond. The SEM micrograph of the Siliconized epoxidized EPDM system reveals that the optimal network structure appears on the surface can be probably due to –Si-O-Si- linkage.

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