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ORIGINAL PAPER

EPDM/vinyl triethoxysilane modified phenol formaldehyde resin composite

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Abstract In the present study, attempts have been made to modify a phenolic resin (PF) with vinyl triethoxysilane (VTES) in order to compatibilize it with EPDM. It was proved by Fourier transform infrared spectrometer (FTIR) that vinyl-silicon group had been successfully introduced to the structure of PF. Dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM) were used to characterize the structure of EPDM/PF composite. Glass transition of PF disappeared and the diameter of PF phase reduced from 44 to 86 μm to approximately 600 nm when modified PF was used. The compatibility mechanism of EPDM and modified PF is also suggested as follows: modified PF was transformed into semi cross-linked particles by condensation reaction in the presence of water and shear force of two-roll mill, and the particles were fully cured and grafted to the network of EPDM during vulcanization, respectively.

Keywords Vinyl triethoxysilane · PF · EPDM · Compatibilize · Composite

Introduction

Polymer blending is an economic strategy to design new materials from existing polymers to develop new properties or to improve the existing ones to meet specific customer needs or reduce material cost without substantial loss in properties. Even though more than 400 miscible polymer pairs have been reported [1], most mixed

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polymer systems are not miscible on a molecular scale and tend to phase separate during mixing into individual components domains.

EPDM is a copolymer of ethylene, propylene, and a non-conjugated diene which is largely unaffected by weather with very good resistance to ozone and has good low temperature flexibility. Studies on EPDM blends have been emphasized on blending EPDM with other rubbers to improve their heat and ozone resistance [2–6], as well as on blending EPDM with thermoplastics as an impact modifier [7–11].

When EPDM is blended with other polymers, compatibilizers are widely used to improve the compatibility. Polymers and grafted polymers are widely used as compatibilizers to improve the compatibility of EPDM and other polymer blends. Many polymers such as aminated epoxidized EPDM, chlorinated polyethylene (CM), chlorosulphonated polyethylene (CSM), maleated ethylene–propylene diene monomer rubber (MAH-g-EPDM), EPDM rubber grafted with poly[2-dimethyl-amino ethylmethacrylate] [DMAEMA] (EPDM-g-PDMAEMA), mercapto-modified ethylene–vinyl acetate copolymer (EVASH) are used as compatibilizers [12–16]. All those compatibilizers are polymers which have both non-polar backbones and polar side chains.

Physical blending requires an additional step for the synthesis and the design of the compatibilizing agent. In contrast, reactive blending is a very cost-effective process that allows the formulation of new multiphase polymeric materials. The in situ formed compatibilizing agent (block or graft copolymer, cross-linked species, ionic associations, etc.) reduces the interfacial tension between the immiscible blend components, enhances the adhesion between the phases and, as a consequence, imparts to the blend acceptable mechanical properties [17–19].

This paper reports a unique EPDM/PF composite prepared by EPDM and VTES modified PF novolac by reactive compatibility.

Experimental

Materials

The characteristics of EPDM (4045, Mitsui Chemical, Japan) used in the present investigation are as follows: Mooney viscosity ML(1 + 4) at 100 °C 45, E/P ratio 52/48, ENB content 5% by weight Sp. Gr.0.86. Analytical grade phenol, formaldehyde, oxalic acid, VTES, hexamethylenetetramine were used. Zinc oxide, stearic acid, sulfur, and accelerators were commercial grade.

Preparation of VTES modified PF novolac

188 g of phenol, 138 g of 37% by weight formaldehyde, 3.7 g of oxalic acid were added to a boiling flask equipped with a stirrer, a backflow condenser, and a thermometer. When oxalic acid was completely dissolved at room temperature, the solution was heated to 100 °C in an hour and kept boiled for 3 h under reflux, and then 0.094 g of sodium hydroxide was added. Subsequently the reaction mixture was dehydrated under a reduced pressure for 60 min, thereafter; the temperature was

stepwise raised from 100 to 150 °C. Then, 19 g of VTES was added in an hour and the mixture was stirred until the temperature reduced to 120 °C. The by-product alcohol was removed under a reduced pressure for 30 min until the system was stepwise heated to 150 °C. An amber opaque resin and about 7 g of alcohol were obtained.

Preparation of EPDM/PF composite

Zinc oxide and stearic acid were mixed with EPDM by a two-roll mill at room temperature. Then the mill was heated to 90 °C and PF (modified or unmodified) was added and mixed for 1 h. When the mill was cooled to room temperature, sulfur, accelerators, and hexamethylenetetramine were added and mixed. 24 h later, the compound was vulcanized by a plat vulcanizing machine at 170 °C for 8 min. Formula of EPDM/PF composite is shown as Table 1.

Fourier transform infrared spectrometer

Fourier transform infrared spectroscopy (FTIR) was recorded on an FTIR spectrometer (Nicolet 380, Nicolet Analytical Instruments, USA) using compression-molded thin film samples. Sample of modified PF was purified according to the following steps for FTIR test: toluene was dropped into alcohol solution of modified PF, and then the precipitation was washed by toluene at room temperature for three times and dried in a vacuum drying oven at the temperature of 50 °C for 24 h.

Scanning electron microscope

The morphology observation was conducted with a scanning electron microscope (LEO, LEO-L530VP). All samples were immersed in liquid nitrogen for 5 min and broken, and the cryogenically fractured surfaces were sputter-coated with gold before examination.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out on a Rheometric Scientific Dynamic Mechanical Analyzer (DMTA-V). All measurements were performed

Table 1 Formula of EPDM/PF composite

	EPDM/ unmodified PF	EPDM/ modified PF
EPDM	100	100
ZnO	5	5
SA	2	2
PF	50	–
Modified PF	–	50
Hexamethylenetetramine	5	5
Sulfur	1.2	1.2
Accelerator	3.5	3.5

at a fixed frequency of 1 Hz and strain amplitude of 5% in tension mode. The temperature's range studied was from −70 to 150 °C with a heating rate of 10 °C/min.

Results and discussion

FTIR of modified phenol formaldehyde novolac

Figure 1 shows the FTIR spectra of modified PF novolac and unmodified PF novolac. The absorption at 950 cm^{-1} (attributed to Vi–Si), 1020 cm^{-1} (attributed to Vi–Si), and 1050 cm^{-1}(attributed to Ph–O) appears in the spectrum of modified PF, which are absent in the spectrum of unmodified PF. These results provide a substantial evidence of reaction of VTES and PF novolac. Water was not completely removed from PF, so some of the vinyltriethoxy silane was transformed into a silsesquioxane mixture with the formation of Si–O–Si bonds. These resonances were hidden in the IR spectrum under the broad peak around 1100 cm^{-1}. As 7 g of by-product alcohol (0.152 mol) was obtained when 0.1 mol of VTES was used, it is assumed that vinyl triethoxysilane was linked to a series of linear silsesquioxane and possible mechanism is shown as Scheme 1.

Morphology of EPDM/PF composite

When unmodified PF was used to prepare an EPDM/PF composite, a smooth fracture can be observed from Fig. 2, and the connected holes are the domains of PF phase with a diameter of 44–86 μm. The section exhibited ductile fracture and the domain of PF phase reduced to approximately 600 nm (Fig. 3) when modified PF was used.

During the preparation of EPDM/PF composite, the temperature was higher than the melt point of PF, and PF phase tended to aggregate and formed a large

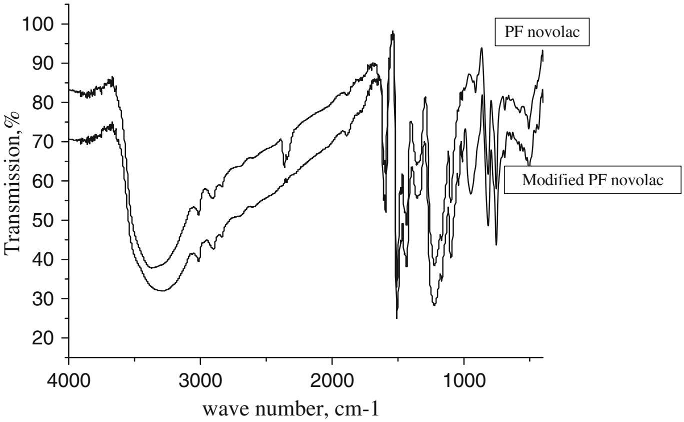
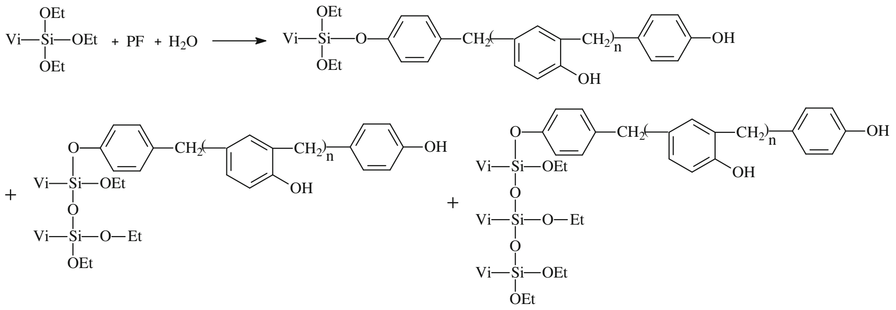


Fig. 1 FTIR of modified and unmodified phenol formaldehyde novolac



Scheme 1 Possible reaction mechanism of VTES and PF

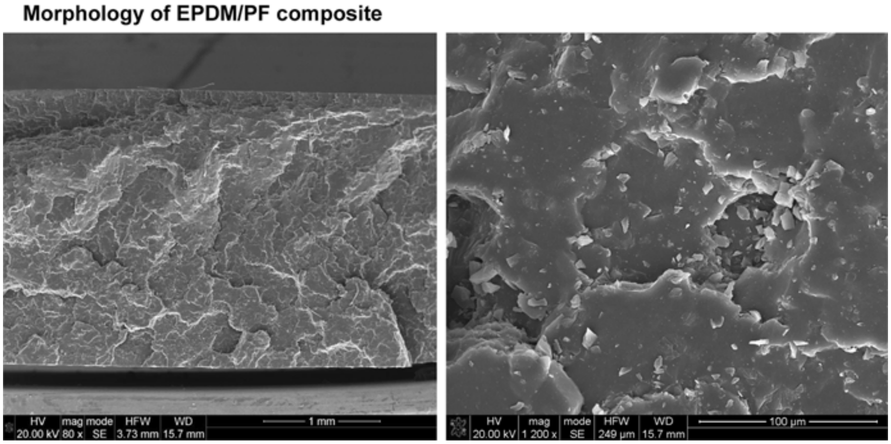


Fig. 2 SEM images of EPDM/PF composite (×80 *left*, ×1200 *right*)

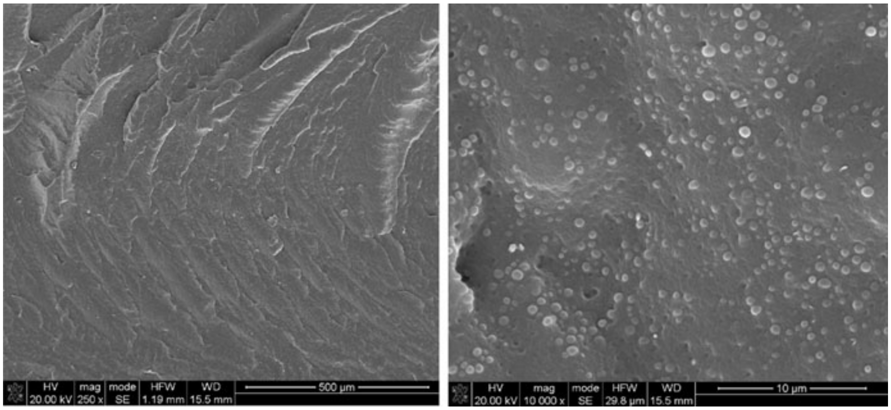
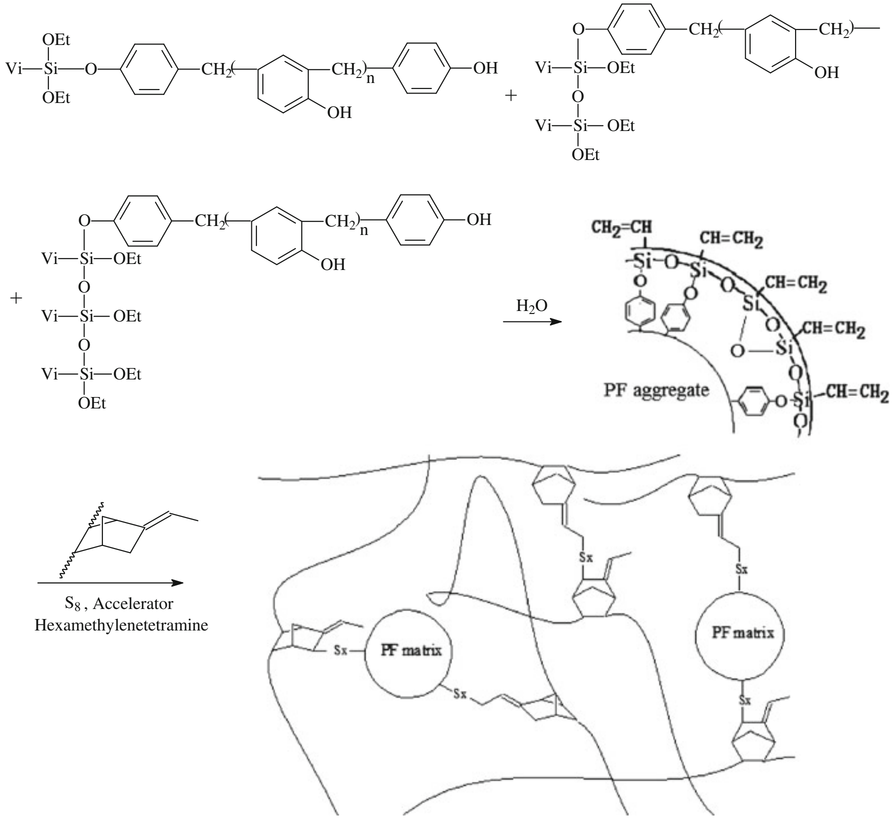


Fig. 3 SEM images of EPDM/modified PF composite (×280 *left*, ×10,000 *right*)



Scheme 2 Mechanism of graft reaction between modified PF and EPDM

domain because of the interfacial tension between EPDM and PF. When modified PF was mixed with stearic acid, zinc oxide, and EPDM in a two-roll mill, the temperature was approximately 90 °C and water was the product of the reaction of stearic acid and zinc oxide, consequently Et–O–Si in the structure of modified PF hydrolyzed and was transformed into a formation of Si–O–Si gradually. Partly cross-linked modified PF particles were formed by shear force and dispersed in EPDM phase. When the compound was vulcanized, PF particles were completely cured by hexamethylenetetramine and were chemically bonded to EPDM matrix in the presence of sulfur and accelerators. Based on the chemical structure of accelerated-sulfur-vulcanized EPDM [20], the mechanism is shown as Scheme 2.

Dynamic mechanical analysis of EPDM/PF composite

Figure 4 shows the plot of loss tangent (tanδ) against temperature obtained from the DMA of EPDM/modified PF and EPDM/unmodified PF composite. The glass transition occurs at −39 °C in the case of EPDM/modified PF, while two glass transitions can be found when EPDM/unmodified PF was tested (−39 and 77.8 °C).

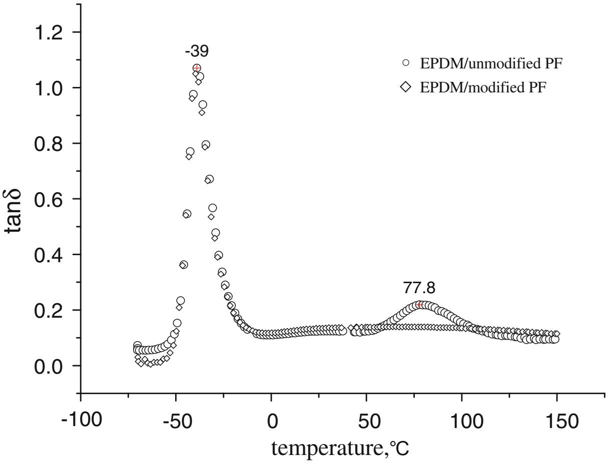


Fig. 4 Effects of PF on temperature dependence of tanδ at 1 Hz

The peak at the temperature of 77.8 °C is attributed to the glass transition of PF and the one at −39 °C is attributed to EPDM, which shows that the compatibility of modified PF and EPDM was so greatly improved that the glass transition of PF phase disappeared.

When the temperature is higher than 0 °C, the loss tangent of EPDM/modified PF is higher than that of EPDM/unmodified PF except the range of glass transition of PF. Based on the mechanism shown in Scheme 2, modified PF particles were chemically bonded to the sulfur cross-linked network of EPDM, which blocked the internal rotation of molecular chains. Hence the composite appeared a higher energy loss (tanδ).

Conclusion

Vinyl-silicon group was introduced to the structure of PF novolac by the reaction of VTES and PF novolac. The compatibility of modified PF and EPDM was greatly improved, which was supported by DMA and SEM. The mechanism of compatibility is suggested as follows: modified PF was transformed into semi cross-linked PF particles by condensation reaction in the presence of water and shear force of two-roll mill, and the particles were fully cured and grafted to the network of EPDM during vulcanization, respectively.

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