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Reinforcement and migration of nanoclay in polychloroprene/ethylene–propylene–diene-monomer rubber blends

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ABSTRACT

This communication demonstrates, an approach of compatibilization between polychloroprene (CR) and ethylene propylene diene monomer rubber (EPDM) by using nanoclay as a compatibilizer and, simultaneously, as a very strong reinforcing nano-filler. With the incorporation of less than 9 wt.% nanoclay, the dynamic storage modulus above the glass transition region of such a blend increases from ~2 MPa to ~54 MPa. This tremendous reinforcing as well as the compatibilization effect of the nanoclay was understood by thermodynamically driven preferential framework-like accumulation of exfoliated nanoclay platelets in the phase border of CR and EPDM, as observed i.e. from transmission electron microscopy. The extra-ordinary improvement of dynamic modulus can also be understood by a very strong filler–filler networking that we observed in strain sweep experiments. Moreover, we found that the compatibilized blends exhibit an extra dynamic-mechanical relaxation process at higher temperatures ($\sim T_g + 130$ K). The suggested method for compatibilization of incompatible rubber blends offers routes to the design of new rubber based technical products for diversified applications.

1. Introduction

The fundamental justification for blending two or more elastomers is acquisition of different features exhibited by vulcanizates of the component elastomers in a single composite. Unfortunately and most commonly, however, it has been found that co-vulcanization leads to reduction in the mechanical strength of the vulcanizate compared with its expected values. Homogeneity of mixing and retention of the compatibility during the vulcanization are the most relevant issues although micro-heterogeneity is usually desirable to retain the individual properties of the respective elastomer components remaining in a blend.

It is well established that the presence of certain polymeric species, usually block or graft copolymers with special chemical structure, can indeed result in compatibilization of an immiscible elastomer blend because of their ability to alter the interfacial adhesion [1]. It is also a proven fact that certain type of multifunctional organic compounds can act as a compatibilizer and these type of compounds are frequently known as ‘multifunctional rubber additives’. These additives generally offer a chemical linking between two different rubber phases during the vulcanization reactions [2,3].

It is described that nanoclays are an attractive alternative to traditional compatibilizers because they can be compounded quite easily. They have also been known to stabilize different crystalline phases of polymers, and to posses the ability of improving mechanical and thermal properties. For example, Vo and Giannelis [4] reported the compatibility and phase separation behaviour of poly(vinylidine fluoride)/Nylon-6 blends by the use of organically modified nanoclay. Addition of 5 wt.% organoclay and maleic anhydride grafted polyethylene was found to be effective in reducing the ethylene–octene copolymer phase size in low density polyethylene/ethylene–octene copolymer blends [5]. Poly(ε-caprolactone)/poly(ethylene oxide) blends were prepared in the presence of nanoclay, and it was found that exfoliated silicate platelets were preferentially located at the interface between the two phases [6]. The effect of organically modified clay on the morphology and properties of poly(propylene)/poly(butylene succinate)-co-adipate blends is studied and enhancement of physical properties, thermal stability and rheological behaviour are reported [7].

Blending of rubbers is a very common practice and incorporation of nanoclay to reinforce the rubber blend is obviously a common approach to get a rubber compounds with superior physical properties. As a result, the outcomes of such efforts were appeared in several publications. Most of the reports [8–14] focused to evaluate the reinforcement effect of the clay on rubber-blend matrixes. As for example, Arroyo et al. [11] reported the effect of nanoclay on the morphological behaviour of the blends comprised with natural

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rubber (NR) and epoxidized natural rubber (ENR). In this work ENR was used as a compatibilizer between NR and clay to get intercalated and exfoliated clay particles in NR matrix. Due to the polar nature of ENR the exfoliation of the clay layers was becoming easier and the exfoliated clay particles were found to be located at the NR/ENR interface. Similar type of work also could be found where a particular amount of organically modified clay was used in different NR/ENR blends with varying proportions of ENR [12]. Besides the reinforcement effect, the vulcanizing acceleration effect of organoclay was found to be very prominent in this NR/ENR system. The worthy of ENR as a compatibilizer has also been proved in nanoclay filled nitrile rubber [13] and nanoclay filled styrene butadiene rubber [14]. The compatibilizing action of the pristine montmorillonite clay was also investigated and the presence of clay was detected at the interface on nitrile rubber and styrene butadiene rubber blends [15]. The preferential confinement of layered silicate in the polyurethane phase was noticed while studying the morphology and mechanical properties of layered silicate reinforced natural and polyurethane rubber blends produced by latex compounding [16]. It was also reported that organically modified clay was found to behave like an anti-reversion agent in natural rubber/polychloroprene rubber blends [17]. Very recently, the effect of sodium bentonite, calcium bentonite, and kaolin fillers on the macrostructure and microstructure of acrylonitrile butadiene rubber/ethylene propylene diene rubber blends was studied through electrical and mechanical measurements, as well as with positron annihilation lifetime spectroscopy [18]. In this study it was found that the reinforcement effect of sodium bentonite is better as compared with other two fillers and the free volume holes are rather unaffected by the types of fillers.

To further explore the idea about the compatibility effect of nanoclay in between two rubbers with a large polarity and glass transition temperature difference polychloroprene (CR) and ethylene propylene diene monomer rubber (EPDM) blends were taken into consideration in our present study.

Polychloroprene is an extremely versatile synthetic rubber with more than 75 years of proven performance in a broad industrial spectrum due to its unique combination of properties: ozone resistance, oil resistance, toughness, dynamic flex life, good adhesion to other materials and heat resistance up to 100 °C. This rubber has been the material of choice for mouldings and extrudates of versatile types, for example, reinforced hoses, roll covers, conveyor belts, air spring bellows, cables, sponge rubber, corrosion-resistant linings, sheeting, fabric proofing and footwear, power belts, boots, water suit and water sealant, and various other numerous applications. To meet these emerging needs and for new material development for more demanding applications, improvement in heat, ozone, and cut growth resistance of CR products are very desirable. The above requirement for chloroprene product could be satisfied by blending with polyolefin elastomers such as ethylene/propylene rubber (EPR) or ethylene/propylene/diene terpolymer (EPDM) which have better heat/ozone and cut growth resistance [19]. As such, however, these chloroprene/EPR or EPDM blends are incompatible.

However, till now no such report has been found which aims to establish the compatibility effect of nanoclay by showing direct evidence of compatibility. In the present study, quaternary ammonium modified montmorillonite has been taken as an alternative means to control the phase compatibility between CR and EPDM. In our earlier work [20] we reported that extra amount of stearic acid in the rubber curing recipe improved the reinforcing efficiency of nanoclay in acrylonitrile butadiene rubber. Thus, in the present study a higher amount of stearic acid has also been considered in the vulcanization recipe in order to get a sufficient number of intercalated and exfoliated silicate platelets in the rubber matrix.

2. Experimental part

Ethylene propylene diene monomer rubber (EPDM, BUNA EP G 6850, Mooney ML(1 + 4)125 °C: 60 ± 5, ethylene content 51 wt.% and ENB content 7.7 wt.%) and polychloroprene rubber (CR, Bayprene 216, Mooney ML(1 + 4)100 °C: 46–48) was supplied by Lanxess Germany. The clay (Nanofil-15) was collected form Süd-Chemie AG, Moosburg, Germany. The accelerator (zinc dimethyl dithocarbamate) was industrial grade (ZDMC-80) supplied by Rhein Chemie Corp, Germany. Stearic acid (97-% purity, Acrös Organics, Belgium), soluble sulfur, zinc oxide (ZnO), (99.5-%, Acrös Organics, Belgium) were used in this study as received.

A typical mixing procedure was followed to get the CR/EPDM blend compounds. At first the clay was treated with stearic acid in a mortar and placed in the oven at 100 °C for 30 min. After heating the mass was thoroughly grinded with a pestle in hot condition and again the vessel was kept at 100 °C. This hot material was cooled at room temperature and again it was grinded. This compound, thus prepared, was used as a filler. The EPDM rubber was mixed with ZnO and the stearic acid modified clay was incorporated into it in a two-roll mixing mill for 5 min. This mix, thus obtained, was added with pre-masticated CR and finally the curatives (accelerator and sulfur) were incorporated to the rubber compounds. For gum compounds (without any clay) the stearic acid was added after the addition of ZnO to the EPDM. Finally the rubber compound was compression moulded at 160 °C to prepare samples with ~2 mm thickness. The curing time used in preparation of the vulcanizates was calculated previously with the help of a moving die rheometer (Scarabeaus-SIS-V50). It should be mentioned here that the curing retardation or curing problem due to adsorption of stearic acid by the organoclay have not been detected during the rheometric characterisation. A detail investigation on the sulfur curing activity of stearic acid modified clay has been done and reported to elsewhere [21,22].

Dynamic mechanical analysis was performed using a dynamic mechanical analyser (Gabo Qualimeter, Germany, model Eplexor-2000N) in the tension mode. Measurements of loss tangent and storage modulus were done at frequency 10 Hz with a static load at 1% strain and the dynamic load at 0.5% strain. Tests were performed between −80 and +80 °C with a heating rate 2 K/min. A strain sweep experiment was also carried out with the Eplexor-2000N (Gabo qualimeter, Germany) for the variation of the strain from 0.01% to 40% at 10 Hz frequency. A pre-strain of magnitude 40% was chosen to hold the sample with the size of $10 \times 2 \times 35\ \mathrm{mm}^3$.

Wetting experiments (Wilhelmy method, and capillary penetration method) were taken out, using the dynamic contact angle meter and tensiometer DCAT 21, DataPhysics Instruments GmbH, Filderstadt, Germany. For further details, the work of Stöckelhuber et al. could be consulted [23,24].

3. Results and discussion

X-ray diffraction patterns of stearic acid organoclay and organoclay-stearic acid mixture are presented in Fig. 1. X-ray diffraction shows that the long spacing for stearic acid C form is 3.95 nm. The length of the *c* axis of the unit cell of stearic acid C form is 4.66 nm, which is equal to the length of two molecules. That means stearic acid remains in the dimmer form. The organoclay has a gallery height of 2.98 nm, and after modification by stearic acid it increases to 3.94 nm. The X-ray diffractograms of the organoclay-stearic acid mixture do not show any new reflection as compared to those from stearic acid and organoclay. However, some close reflections from stearic acid and stearic acid-organoclay mixture merge and show single peak in the mixture. It clearly indicates that gallery height of the clay layers increases to the same extent as that