Research paper

Experiments and modeling of non-linear viscoelastic responses in natural rubber and chlorobutyl rubber nanocomposites

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ABSTRACT

The filler–filler and rubber–filler interactions in polyisoprene (natural rubber — NR) and chlorine substituted poly isoprene–isobutyl rubber (chlorobutyl rubber — CIIR) were monitored by non-linear viscoelastic measurements (Payne effect). The experimental results have been modeled using the famous Maier–Göritz equation and by the tradition approach of Kraus theory. It was observed that the filler–filler network formation in NR/organoclay nanocomposites was very strong while the interactions in CIIR/organoclay nanocomposites were very poor. The network formation and dispersion of nanoclay platelets were observed using AFM and TEM techniques. Using the DSC technique, the effects of filler–filler and filler–polymer interactions on glass transition temperature (T_g), confinement of polymer chains (χ_i) and the variations in heat capacity (ΔCp) were analyzed. These analyses revealed that the nanofiller loading in rubber matrix developed a rigid amorphous region due to the confinement of polymer chains. The T_g of the natural rubber nanocomposites was increased and then decreased as the filler loading increased from 0 to 10 phr. The mechanical percolation behavior of rubber nanocomposites were estimated using the Huber–Vilgis approach by calculating the excess modulus. The application of this approach pointed out to a cluster–cluster aggregation model (CCA), where space filling clusters were formed. The diffusion of liquids through the nanocomposites was carefully evaluated for explaining the nanofiller interaction with the two rubber matrices. Finally, the Kraus, Lorentz–Parks and Cunneen–Russell models were applied to quantify the degree of reinforcing action of the fillers in both elastomer matrices.

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1. Introduction

A distinctive property to analyze the elastomer–filler interaction and filler–filler interaction is the non-linear viscoelastic response of filled systems, otherwise known as Payne effect (Payne and Whittaker, 1971; Payne, 1962). Many factors can influence the non-linear viscoelastic behavior of rubber nanocomposites. Fröhlich et al. (2005) pointed out that the surface area of the nanofiller; surface modification and activity of the nanofiller are some of the crucial factors that affect the non-linear viscoelastic response. The effect of strain amplitude on the dynamic modulus was observed extensively due to the dynamic deformation of elastomers. i.e., the modulus values of filled elastomers decrease with increasing applied dynamic strain. The higher modulus at lower strains is obtained by the formation of filler–filler networking in filled nanocomposites. Payne (Payne and Whittaker, 1971; Payne, 1962) suggested that the formation of a three dimensional structure was due to the filler (carbon black) incorporated in rubbers and this leads to higher modulus values at lower strains. But, a proper interpretation of the filler–filler interactions and polymer–filler interactions can be made by theoretical modeling of the experimental data. It was Kraus (1984) who proposed a successful model for the first time to make a proper interpretation of the Payne effect. Many researchers have extended this model by considering different aspects of filled elastomers. Some of them are Huber and Vilgis (1999), Klüppel and Heinrich (1995) and Maier and Goritz (1993, 1996, 2000). Kraus (1984) model is based on agglomeration/de-agglomeration mechanism due to the van der Waals interaction between filler particles. The approach by Klüppel and Heinrich (1995) includes diffusion-limited aggregation (DLA) cluster formation and cluster–cluster (CCA) formation by carbon black aggregates. Huber and Vilgis (1999) approach includes the consideration of fractal dimensions and the connectivity of the filler

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network. Maier and Goritz (1993, 1996, 2000) model is based on the adsorption/de-adsorption mechanism and this is made by assuming the additional slope exponent in Kraus model as 1/2. The change in the glass transition temperature (T_g) is one of the most effective ways to interpret the elastomer–filler interactions. The thermal stability of elastomers can vary with the nature of the interaction of nanofillers. This can be understood by evaluating the decomposition pattern of filled elastomers. Many studies have been reported about the nanofiller interactions with elastomers by considering the various above discussed aspects (Ramorino et al., 2007; Rooj et al., 2013). Recently, we have reported on the non-linear viscoelastic effects of natural rubber filled with nano-silica (Meera et al., 2009) and carbon nanotubes (Ponnamma et al., 2013). These composites were made by both two roll mill mixing and latex stage compounding. In the present paper we have examined the rubber–nanofiller and filler–filler interactions by considering two types of rubbers. One is cis-polyisoprene (natural rubber—NR) and the second one is the chlorine substituted poly isoprene–isobutyl rubber (chlorobutyl rubber—CIIR). These rubbers and nanoclay filler system have been chosen specifically in this study because of their applications for the manufacture of automotive inner tubes and inner liners (Zachariah et al., 2014; Zachariah et al., 2012). The nanoclay used for the present study was organically modified and it is reported that the organic modification will reduce the polarity of the nanoclay platelets (Maria et al., 2014; Wu et al., 2004) and this will affect the reinforcing ability of nanoclay. To best of our knowledge, comparative analysis of filler–filler and filler–polymer interactions of CIIR and NR nanocomposites is not reported elsewhere.

2. Experimental

2.1. Materials

Natural rubber was purchased from Rubber Research Institute (RRII), Kottayam, Kerala, India. Chlorobutyl rubber was from EXXON MOBIL (Grade: 1066). The organoclay employed in this study is I.44P (Nanocor, USA), organically modified (OMC) nanoclay having alkyl chain distributions C12—1%, C14—4%, C16—31% and C18—46%. Its cation exchange capacity (CEC) is 70–150 meq/100 g of clay. The organoclay was dried for 16 h at 90 °C before its use. The compounding ingredients used for the preparation of the composites viz. sulfur, stearic acid, zinc oxide and diphenyl guanidine (DPG) purchased locally.

2.2. Preparation of nanocomposites

The rubber–clay nanocomposites were prepared by the method reported elsewhere (Zachariah et al., 2014). The cure time of these nanocomposites was determined using a Rubber Processor Analyzer at 160 °C. Composites are named as; NR series — NRN0 (0 phr nanoclay), NRN2 (2.5 phr nanoclay), NRN5 (5 phr nanoclay), NRN7 (7.5 phr nanoclay) and NRN10 (10 phr nanoclay) and CIIR series — CIIRN0 (0 phr nanoclay), CIIRN2 (2.5 phr nanoclay), CIIRN5 (5 phr nanoclay), CIIRN7 (7.5 phr nanoclay) and CIIRN10 (10 phr nanoclay).

2.3. Characterizations

The shear strain scans were done by using the Perkin Elmer DMA 805 at 25 °C at a frequency of 1 Hz from 0.1 to 10%. The loss modulus values, storage values are obtained for each strain value. Differential Scanning Calorimetry (DSC) studies were done using Mettler Toledo DSC 822e differential scanning calorimetry from −80 to 20 °C at a scan rate of 10 °C/min. The DSC scans were taken from second heating. The tensile specimens were punched out from molded sheets (2 mm thick) with ASTM Die C. The stress–strain properties were determined using a universal testing machine, Zwick UTM 1445 from M/s Zwick, Ulm, Germany, in accordance with ASTM D412 at a crosshead speed of 500 mm/min at 25 °C. For measuring the diffusion properties, 2 mm

thick circular disks with 20 mm diameter were immersed in toluene. The swelling ratio was determined by weighing the polymer sample prior to the immersion in toluene (denoted as m_1). The samples were kept in diffusion bottles at room temperature. The samples were removed from the diffusion bottles periodically and weighed immediately (m_2). The experimental procedure was continued until the equilibrium swelling was attained. The samples were immersed for 24 h in the solvent which was enough to reach the equilibrium state. The uptake solvent percentage, $Q(t)$ was calculated as follows:

$$Q(t) = \frac{(m_2 - m_1)}{m_2} \times 100. \tag{1}$$

The scanning and analysis of the samples were done using the tapping mode (TM) tip in a Multi Mode Atomic Force Microscopy with a Nanoscope IIIa controller by Digital Instruments Inc. (Veeco Metrology Group), Santa Barbara, CA, USA. We have done the AFM images of five different regions of the samples. For transmission electron microscopy (TEM) measurements, 100 nm sections were microtomed at −70 °C using Leica ultramicrotome with a diamond knife. Measurements were carried out with a JEOL JIM 200 TEM at an acceleration voltage of 200 kV.

3. Results and discussion

3.1. Non-linear viscoelastic studies

The dynamic shear storage modulus and loss modulus of NR and CIIR nanocomposites are given in Fig. 1(a) to (d) as a function of strain amplitude. These figures are similar to the trend reported by many workers (Ramorino et al., 2007; Rooj et al., 2013) about rubber–nanoclay composites. From these figures, it is clear that as the nanoclay loading in NR matrix increases the modulus values at lower strains show significantly high value. This is true for all the loadings. In the case of CIIR nanocomposites, this enhancement in modulus values upon the addition of nanoclay loading is observed predominantly up on 10 phr loading. This kind of higher modulus values at lower strains are due to the formation of filler–filler and filler–polymer networks. These networks could break at higher strains and these results in the reduction of the modulus to lower values as shown in Fig. 2(a). Usually, a competition between filler–filler and polymer–filler interactions takes place in filled elastomers. If filler–filler interaction predominates, the Payne effect is more pronounced in elastomers. Similar trend is observed with different kinds of fillers such as carbon black (Yurekli et al., 2001) silica (Cassagnau, 2008) and carbon nanotubes (Bokobza, 2012). These effects have been reported by many authors including our research group (Meera et al., 2009; Ponnamma et al., 2013). According to Meera et al. (2009), this depends upon the thermodynamics of the system and kinetics of sample preparation. In NR nanocomposites, the non-polar nanoclay form higher extent of filler–filler interaction at lower strains. But in CIIR nanocomposites, such kind of the filler–filler networks is observed only at CIIRN10 system (Fig. 2(b)). Actually, it is expected that the Payne effect could be more pronounced in CIIR nanocomposites due to incorporation of non-polar nanofiller into it and this could prefer more filler–filler network than filler–polymer interactions. But, in reality, the behavior is very different from normal expectation. This is due to the formation of agglomerates of clay in the CIIR matrix and therefore the formation of the network is not possible due to these agglomerates as shown in Fig. 2(c). More interpretations can be made by considering the non-linear viscoelastic models. But, it is not possible to provide an exact mechanism for the formation of filler–filler networks in elastomer nanocomposites. Fröhlich et al. (2005) suggested that filler–filler contacts have occurred through a very thin polymer layer separated by thickness in the nanometer range. Also they pointed out that there are three distinct regions in nanofiller loaded elastomer matrices. One is the area of polymer shell with low mobility (associated with the