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Enhanced morphology and mechanical characteristics of clay/styrene butadiene rubber nanocomposites

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ABSTRACT

Achieving complete exfoliation of clay in their polymer nanocomposite is a matter of interest as it can significantly affect the material properties. Herein, an efficient way of enhancing the interlayer spaces of organically modified clays (OC) containing two types of surfactants, benzyl methyl hydrogenated tallow (Cloisite 10A) and dimethyl dihydrogenated tallow (Cloisite 20A) while mixing with the styrene butadiene rubber (SBR) is reported. The prolonged swelling of the OC in toluene helped the rubber chains to disentangle in the interlayer spaces identifiable from the morphology and the change of the d-value. The small angle X-ray scattering traces for all the Cloisite 20A/SBR composites indicated a very extensive dispersion of the OC and using the Guinier equation from SAXS, radius of gyration was calculated. An optimal size of 6–7 nm for the dispersed clay particles was found for maximizing resistance to abrasion as well as mechanical properties. Finally the enhanced tensile properties were correlated with the vulcanization behavior as well as the filler/polymer interfacial interaction from rheology through the completely exfoliated morphology observed for the swollen clay filled samples. Moreover an exclusive mechanism for curing of the composites was also derived.

1. Introduction

The properties of both synthetic and natural rubbers have been modified to achieve higher performance by incorporating a variety of particles or fillers over the past decade. The Toyota Research Group (Usuki et al., 1993) of Japan pioneered the field of polymer reinforcement, by combining organo-modified clays (OC) in clay-polymer nanocomposites (CPN) and showed that a large increase in physical properties was possible at a low filler loading. Although CPN have been widely studied in the last few years, the quest for the full exploitation of the nanofiller potential for property improvements has not yet achieved its goal (de Paiva et al., 2008; Lambert and Bergaya, 2013; Ray and Okamoto, 2003). A number of issues are still open which require further research; among these one of the most encountered is the large decrease in ductility and impact strength (Causin et al., 2008; Lim et al., 2006; Simons et al., 2011). A decrease in elongation at break and an increase in tensile strength were observed on addition of clay in clay/natural rubber nanocomposites (Jacob et al., 2007). It has also been reported that organo-bentonite at 12 mass% enhanced the tensile strength of styrene butadiene rubber (SBR) about 2.12 times (Sadhu and Bhowmick, 2004), while at the same time increasing the elongation at break.

Among the layered silicates, montmorillonite (Mt) (Gu et al., 2009) is preferred for making CPN since it is hydrophilic and less attuned with polymer matrices. The Na^+ in Mt is replaced with hydrophobic surfactants like alkylated ammonium or phosphonium cations (Mittal, 2008) before processing, to improve compatibility and obtain better layer separation. CPN with a relatively low loading of the filler displayed superior mechanical properties, thermal stability, flame retardancy and gas barrier properties (Alexander et al., 2002; Zhang et al., 2014). They also showed significant improvement in elastic modulus (Hussain et al., 2006), tensile strength and elongation at break (Alexander et al., 2002; Kojima et al., 1993; Mittal, 2008), thermal resistance and reduction in water/gas permeability (Hussain et al., 2006; Varghese et al., 2004) and flammability (Hussain et al., 2006; Mittal, 2008; Zhang et al., 2014; Tiggemann et al., 2015).

The performance of CPN strongly depends on the breaking-up of clay particles in the polymer matrix (Bergaya et al., 2011; Causin et al., 2008). As the degree of interaction between polymer and filler varies, three systems are generally formed: (i) layers may remain stacked in structures called particles, as in the original mineral without any improvement compared to usual microcomposites with low filler loading;

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(ii) polymer chains may penetrate into interlayer spaces, producing an intercalated system where clay layers are more separated; and (iii) an exfoliated structure, with the single clay layers individually dispersed in the matrix (Carrado and Bergaya, 2007). The latter system is the most desirable since nanometric dispersion of clay layers ensures a maximization of the interfacial region between the filler and the polymer matrix, and a consequent improvement in the reinforcement effect (Sadasivuni et al., 2013). If exfoliation occurs, the excellent mechanical properties of the individual clay layers can be effectively exploited and the number of reinforcing components is dramatically increased, since each clay particle contains a very large number of clay layers. The polar or unsaturated matrices (e.g., nitrile rubber and SBR) interact very easily and effectively with such exfoliated OC layers (Fontana et al., 2013; Maria et al., 2014).

Traditionally, the characterization of the structure and morphology of CPN is carried out by transmission electron microcopy (TEM) and wide-angle X-ray diffraction (WAXD). TEM allows an evaluation by direct visualization of the morphology of CPN, but great care must be exercised in the selection of representative images. WAXD is the most frequently used technique, due to its simplicity and wide availability. Here the basal spacing of the stacked Mt layers is determined from which the intercalation and exfoliation could be differentiated. In the case of an intercalation, reflections corresponding to the basal spacing of Mt appear in the low angle range, whereas such reflections disappear in the exfoliated CPN. In exfoliated structures, the inorganic layers dispersed in the polymer have different electron densities with respect to that of the matrix polymer; therefore they still can be detected from the lowest angle fraction of the XRD scattering curve, i.e. by small-angle X-ray scattering (SAXS) (Bergaya et al., 2013; Gelfer et al., 2003; Neppalli et al., 2014; Yoonessi et al., 2005). Thus XRD methods characterize the whole bulk of CPN, thus potentially giving a more generalized picture of its morphology. Literature thrusts the importance of processing conditions also on the mechanical performance and morphology of the clay mineral/SBR nanocomposites (Fang et al., 2013; Maria et al., 2014). For instance, the solvent-free approach using clay/liquid rubber masterbatches resulted in a better clay dispersion and improved tensile strength (4.98 MPa at 10 phr clay) compared with the melt mixed samples (Fang et al., 2013). In short, acquiring better properties and exfoliated structures at higher clay loadings still remains a challenge and designing suitable processing conditions can do much in this regard.

In the present paper, prolonged swelling of OC in toluene was designed as an effective method to fabricate its SBR nanocomposite in order to achieve complete rate of dispersion in the elastomer. Solution casting cum mill mixing was also employed to study the CPN properties and for deriving the influence of processing conditions. A complementary set of techniques, i.e. SAXS, WAXD, and TEM, were used for the full characterization of the clay mineral dispersion in the OC/SBR nanocomposites. Guinier equation was applied to the SAXS patterns of the samples to assess the size of the clay particles, their radius of gyration and thereby the extent of dispersion. The filler/polymer interaction was addressed using the rheology and curing behavior. Importantly, effort has been taken to establish a possible correlation between the mechanical properties and the mechanism of curing with interlayer space expansion of the clay layers and its particle size.

2. Experimental section

2.1. Materials

SBR (1502), [with a styrene content 23.5%, Mooney viscosity (ML_1) 52 and density $\rho = 0.935$ g/cm^3] was supplied by Apollo Tyres, Kalamassery, Kerala. OC (Cloisite 10A and Cloisite 20A) were obtained from Southern Chemicals, USA. Toluene AR grade, rubber curing ingredients and all minor reagents of 99% purity were procured from Merck, India. The rubber compounding ingredients of commercial grade used are shown in Table 1 and the characteristics of the OC in Table 2.

2.2. Preparation of OC/SBR nanocomposites

Clay dispersions in toluene were made by magnetically stirring (3 h) the specific quantities of clay mineral (1, 3 and 5 phr) pre-soaked in toluene for 10 h (1 g/50 ml). A part of the polymer (SBR) from the specific matrix composition required, was dissolved in toluene (1 g polymer/100 ml toluene), added to the clay–toluene mix and mechanically stirred for 10 h. The resultant clay/SBR mixture was placed in a vacuum oven maintained at a temperature of 100 °C to remove the excess solvent. This 'master OC/SBR nanocomposite' was then mixed with the remaining quantity of the rubber followed by the curing ingredients (Table 1) for 20 min in the two roll mill. By following this method of developing individual masterbatches of OC concentrations, all samples containing 1, 3 and 5 phr OC were prepared. In addition, a gum sample was prepared without adding the OC. Separately 5 phr clay was swelled in toluene for 72 h and a corresponding SBR sample was prepared as per the above protocol. This was done to find out whether there was any enhancement of properties due to the exposure of clay in toluene for an extended period. The maximum time was found to be 72 h as per the swelling index data given in the Supporting Information (Figure S1).

After obtaining the cure time using an oscillating disc rheometer (Monsanto R-100), the CPN were compression molded on a two platen lab press at 160 °C using a hydraulic press under a pressure of about 120 bar for the respective cure times. The vulcanized sheets obtained were cooled to room temperature and left to be conditioned for 48 h.

The sample codes are shown in Table 3 by *Cxx-y*, where *xx* denotes the type of Cloisite used, whereas *y* denotes the quantity (in phr) of added Cloisite. In addition to the mill mixed 'casted-masterbatches', another set of samples with the same formulation was also prepared by the traditional mill mixing (without an additional solution process) alone. This was done only for the comparison of the mechanical properties and have been indicated as 'mill mixed' where necessary.

2.3. Characterizing the morphology

2.3.1. Wide angle X-ray diffraction studies (WAXD)

The change in basal spacing of the OCs was measured with X-ray diffraction. The specimens were cut from the solution processed vulcanizate sheets in the perpendicular direction to its surface. Measurements were made in transmission geometry using a Rigaku X-ray diffractometer at room temperature. The X-ray beam was nickel-filtered CuKα radiation (source) with 0.02° 2θ step size; 0.066 mm slit width and 2 s count time generated at operating conditions of 50 kV and 150 mA. The X-ray data obtained was between 1.5° and 10° (2θ) at a scan rate of 0.5°/min.

The WAXD measurements in reflection mode were recorded in the diffraction angular range by a Philips X'Pert PRO diffractometer, equipped with a graphite monochromator on the diffracted beam (CuK$_\alpha$ radiation) with the same parameters described for the transmission mode. To

Table 1
Formulations used for the preparation of samples.

Sl. no	Ingredients	Mass (phr)
1	Styrene butadiene rubber (SBR)	100
2	Zinc oxide	5
3	Stearic acid	2
4	1,2-Dihydro-2,2,4-trimethyl quinoline (TDQ) (antioxidant)	1
5	Clay-Cloisite 10A or Cloisite 20A	1, 3 and 5
6	Sulfur (vulcanizing agent)	2.2
7	N-cyclohexyl benzothiazol-2- sulfenamide (CBS) (accelerator for vulcanization)	1

Phr-per hundred rubber.