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Research paper

Study on viscoelastic behaviors of bentonite/nitrile butadiene rubber nanocomposites compatibilized by different silane coupling agents

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ABSTRACT

The influences of bentonite and different silane coupling agents (SCA) on the viscoelastic properties of nitrile butadiene rubber were studied in this work. The silane coupling agents compatibilized bentonite/nitrile butadiene rubber nanocomposites were fabricated by a novel green method. The viscoelastic behaviors of the nanocomposites and their vulcanizates were explored using a rubber processing analyzer (RPA) in the modes of strain sweep and frequency sweep. Storage modulus (G′) and elastic torque (S′) of nitrile butadiene rubber increased significantly with the incorporation of bentonite. In the SCA applied in this work, mercaptopropyltrimethoxysilane (MPTMS) contributed to high storage modulus (G′) of the nanocomposites because of thorough exfoliation of bentonite and short sulfur bonds formed during curing process. Meanwhile, multi-sulfur bonds in bis-[3-(triethoxysilyl)propyl] tetrasulfide (TESPT) and reversible interactions from [3-(2-aminoethylamino) propyl] trimethoxysilane (AEAPTMS) resulted in lower storage modulus of the cured nanocomposites.

1. Introduction

In recent decades, clay has been widely utilized as an alternative of carbon black in the research field of rubbery materials (Arroyo et al., 2003; Ray and Okamoto, 2003; Karger-Kocsis and Wu, 2004; Ma et al., 2004; Azeez et al., 2013). As a species of clay abundant in nature, bentonite (Bent) has been proved a promising reinforcement in the fabrication of clay/polymer nanocomposites (CPN). Its reinforcing effects on the macroscopic properties of CPN are mainly originated from the laminar structure in nano scale and the high aspect ratio of Bent layers (Gu et al., 2009; Chakraborty et al., 2010).

Recent research works about Bent/polymer nanocomposites mainly focused on the reinforcement of Bent/polymer interfaces and uniform dispersion of Bent in the matrixes. In the past few years, a great deal of novel strategies have been developed and applied in the preparation of CPN for the purpose mentioned above (Pavlidou and Papaspyrides, 2008; Das et al., 2011a, 2011b; Bergaya and Lagaly, 2013; Chiu et al., 2014; Zare, 2016). Conventionally, solid mixing, melt blending and solution blending were applied for the preparation of CPN (López-Manchado et al., 2004; Liu et al., 2006; Mathialagan and Ismail, 2012). However, the approach of co-coagulating rubber latex and clay aqueous dispersion was more promising due to its simplicity and superior cost/performance ratio (Wu et al., 2005). For the modification and intercalation of Bent or other clay, organic ammonium salts are most frequently used, which are able to improve the compatibility and dispersion of clay in hydrophobic polymer matrixes (Manitiu et al., 2009; Huskić et al., 2013; Kotal and Bhowmick, 2015). Block copolymers and SCA were also utilized for the modification and intercalation of clay, as well as further exfoliation of organic ammonium salt modified clay (Costache et al., 2006; Carli et al., 2014; Sookyung et al., 2014).

For different applications of CPN, researchers have explored various properties and performances of the materials, in which most of the works focused on mechanical properties (Kim et al., 2010), thermal stability (Tunç and Duman, 2010; Zhang et al., 2014), chemical resistance (Ge et al., 2015), gas barrier properties (Tunç et al., 2016), controlled release of antimicrobial agents (Tunç and Duman, 2011), etc. Some researchers have also made further explorations. As early as in the year 1995, Vaia et al. (1995) investigated the high ion conductivity of polymer electrolyte nanocomposites prepared with montmorillonite/poly(ethylene oxide) and the application in electrochemical devices. Kumar et al. (2010) prepared nanoclay-filled EVA/LDPE composites and evaluated the tribological properties, which are very important when the materials are used in vanes, gears or bearings. In the work of Liang et al. (2009), the gas barrier properties of the rubber/clay

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nanocomposites were examined and related to the polarity of the polymer. Generally, previous research works on the properties and performances of CPN were mainly originated from their potential applications.

Until now, researches on the properties during the processing of CPN are far from sufficient, especially on the viscoelasticity of clay/rubber nanocomposites. The viscoelasticity of clay/rubber nanocomposites and their raw materials is of prime importance for the processability and the performances of rubber products. Investigations on the relationships between moduli and dynamic strain amplitude or frequency are helpful for the understanding of macromolecule motions, crosslinking and filler-rubber interactions (Qiao et al., 2015). This work is also meaningful in rubber industry which could be used as references for the fixing of processing parameters (Zhang et al., 2015). Though very limited, there has been some research works on the viscoelastic behaviors of rubber materials, mainly in three aspects. The first one is about the basic characteristics of rubber. For instance, Gao et al. (2015) and Agrawal et al. (2006) investigated the relationship between rheological behaviors and the molecular structure, such as molecular weight and molecular weight dispersity (MWD). Secondly, researchers investigated the viscoelasticity of novel elastomers or polymer blends, such as epoxidized *trans*-1,4-polyisoprene (Shao et al., 2012) and poly (vinylidene fluoride)/silicone rubber blends (Wang et al., 2013). In their work, the phase interfaces, macromolecular movement and crosslinking during processing were related with the viscoelastic behaviors, which were also influenced by shear rate or shear stress. Finally, considering the importance of polymer composites materials, there have been some researches about polymer composites materials filled with conventional fillers, such as carbon black (Karrabi and Mohammadian-Gezaz, 2010) and novel nano fillers including carbon nanotubes (Feng et al., 2015), regenerated cellulose (Martins et al., 2005), etc. As far as we know, there are only a few reports related to the viscoelastic behaviors of CPN during processing including a series of work from Barick and Tripathy (2010a, 2010b, 2011). Galimberti et al. (2014) explored the influences of delaminated and intercalated montmorillonite modified with dimethyl ditalloyl ammonium cations on the dynamic-mechanical properties of poly(1,4-cis-isoprene) matrix. Until now, there are very few systematically researches about the influences of SCA on the viscoelasticity of CPN.

In the present work, bentonite/nitrile butadiene rubber nanocomposites compatibilized with three different SCA were prepared with a novel green method reported previously (Ge et al., 2015). Various interactions between Bent and the rubber matrix were introduced by different SCA, which led to various viscoelastic behaviors of the raw materials and cured vulcanizates during strain amplitude sweep and frequency sweep. The viscoelastic behaviors were investigated in detail. Their relationships with the dispersion of Bent and the interactions between Bent and the matrix were also explored, which are beneficial for better understanding of the filler-rubber system.

2. Experimental

2.1. Materials

Bentonite (Bent, ≥95%; water content, < 3%; Na^+-montmorillonite content, ≥95%) was supplied by YAKURI Pure Chem. Acrylonitrile butadiene rubber (NBR) latex (KNB 35L, solid content: 20.3%, w/v; acrylonitrile content: 34%) was supplied by Korea Kumho Petrochemical. (3-Mercaptopropyl)trimethoxysilane (MPTMS, 95%), [3-(2-aminoethylamino)propyl]triethoxysilane (AEAPTMS, ≥80%) and bis[3-(triethoxysilyl) propyl]tetrasulfide (TESPT, ≥90%) were purchased from Sigma-Aldrich. All the other chemicals were of reagent grade and used as received.

2.2. Synthesis and vulcanization of the CPN

Aqueous solution of dodecylbenzenesulfonic acid, sodium salt (DBS-Na, 0.2 g in 50 ml of water) was added into 500 ml of NBR latex, with mechanical stirring for 10 min. Subsequently, 0.05 mol of SCA was added into the mixture and stirred for 30 min, continuously. Dispersion of Bent (30 g of Bent in 300 ml of water) was then blended with the latex with 3.0 ml of ammonia aqueous solution added as a catalyst. Catalyzed by ammonia, the alcoholic groups in SCA were hydrolyzed. Then the generated silanol groups condensed with each other or with the hydroxyl groups on Bent, as we reported previously (Ge et al., 2015). The reaction was held for 2 h at room temperature.

At the end of the reaction, the obtained slurry was precipitated with aqueous solution of calcium chloride (1000 ml, 0.09×10^{-3} mol/ml) and then dehydrated in vacuum oven for 48 h at 70 °C. Bent/SCA/NBR nanocomposites were prepared using MPTMS, AEAPTMS and TESPT, respectively. Bent/NBR was prepared in the absence of SCA. The sample of neat NBR was fabricated by directly precipitating NBR latex in calcium chloride aqueous solution.

The prepared CPN were compounded with other additives on a two-roll mill. The formulations for synthesis and compounding were all summarized in Table 1. For further evaluation of the mechanical properties, the CPN were vulcanized under a pressure of 10 MPa in a heating press (Auto hydraulic press type, Ocean Science) at 160 °C. Optimum cure time (t_{90}) was obtained from rubber process analysis in advance. The final vulcanizates had a thickness of 2 mm. As for the abbreviations, letter “B” stands for bentonite. “M”, “A” and “T” stand for MPTMS, AEAPTMS and TESPT, respectively. “N” stands for nitrile butadiene rubber. The uncured CPN prepared with MPTMS, AEAPTMS and TESPT were designated as “BMN”, “BAN” and “BTN”, respectively. Bent filled NBR nanocomposites are termed as “BN” while neat NBR is marked as “nN”. The cured CPN were marked as “BMNc”, “BANc”, etc.

2.3. Characterization

2.3.1. Structure and morphology of the CPN

After compounded with other additives, the uncured CPN samples were analyzed with X-ray diffraction (XRD). XRD analysis was performed at 25 °C with a X-ray diffractometer (Empyrean, Malvern Panalytical B.V., Netherlands) using Cu-Kα radiation (λ = 0.154 nm) at 40 kV and 40 mA. The data were collected over the range 2° to 10° (2θ) at a step size of 0.02° and a scan rate of 2°/min (divergence slit size: 0.6°). The fractured surface of the cured CPN coated with a thin film of gold was examined using field emission scanning electron microscopy (FE-SEM) with a model number of JSM-7500 (JEOL, Japan).

2.3.2. Viscoelasticity of the CPN

In this work, the viscoelastic properties and the curing characteristics were determined with a rubber process analyzer (RPA-V1, U-Can Dynatex Inc., Taiwan).

Table 1
The formulation of the CPN nanocomposites.

Ingredients	Bent/SCA/NBR
NBR (phr[a])	100
Bent (phr)	30
SCA (mol)	0.051[b]
DBS-Na (phr)	2
ZnO (phr)	5
Stearic acid (phr)	1.5
2,2′-Dibenzothiazolyl disulfide (phr)	1
N-Cyclohexyl-2-benzothiazolylsulfenamide (phr)	3
Sulfur powder (phr)	1.5

[a] phr, parts per hundreds of rubber.
[b] 0.0255 mol for TESPT.

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