



Effects of silane coupling agents on the properties of bentonite/nitrile butadiene rubber nanocomposites synthesized by a novel green method



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ABSTRACT

Effects of different silane coupling agents on the mechanical strength, tribological properties, thermal behaviors, swelling properties and rheological properties of bentonite (Bent)/nitrile butadiene rubber (NBR) nanocomposites were explored. The nanocomposites were fabricated with an innovative green method in NBR latex. The composition of the nanocomposites was determined by Fourier transform infrared spectroscopy (FT-IR). The intercalated/exfoliated structure and the dispersion of Bent in rubber matrix were characterized with X-ray diffraction (XRD) and field emission-scanning electron microscopy (FE-SEM). It is revealed that different functional groups from the silanes were effective to the properties of the nanocomposites mainly because of their different interactions with the rubber matrix. Mercaptopropyltrimethoxysilane (MPTMS) showed attractive effects on mechanical modulus, tribological properties and swelling properties. Incorporation of bis-[3-(triethoxysilyl)propyl]tetrasulfide (TESPT) resulted in the highest elongation at break. With octadecyltrimethoxysilane (OTMS), the degradation temperature of the nanocomposite was noticeably elevated due to its “barrier effect”.

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1. Introduction

In recent years, clay has attracted much attention in the development of polymer nanocomposites (Ray and Okamoto, 2003; Karger-Kocsis and Wu, 2004; Azeez et al., 2013), particularly as an alternative to carbon black in the researches of rubbery materials in academic field (Arroyo et al., 2003; Ma et al., 2004). For clay polymer nanocomposites (CPN), predominant performances are attainable including improved mechanical properties, thermal stabilities, chemical resistance and flame retardance (Suin et al., 2014).

As one type of extensively used clay, bentonite (Bent) is a low cost inorganic mineral abundant in nature. In the past few years, Bent has been proved a satisfactory reinforcement for rubber products owing to its laminar structure with high aspect ratio (Gu et al., 2009; Chakraborty et al., 2010). A layer of Bent consists of two silica tetrahedral sheets fused to a central sheet of alumina octahedrons (Bergaya and Lagaly, 2013). However, Bent exhibits hydrophilicity which is detrimental to its compatibility in hydrophobic polymers. The hydrophilic nature of Bent is originated from the abundant ions present in the interlayer spaces, such as Na^+ , Ca^+ , Li^+ as well as the reactive silanol (Si-OH) and aluminol (Al-OH) groups at the surface (Alexandre and Dubois, 2000).

To improve the affinity between Bent and rubber matrix, various modifiers and compatibilizers, including polymers, surfactants, quaternary ammonium salts and silane coupling agents (SCA) have been

employed to lower the surface energy of Bent, thereby enhancing the interactions between Bent and rubber matrix (Pavlidou and Papispyrides, 2008; Das et al., 2011; Bergaya and Lagaly, 2013). Application of modifiers or compatibilizers also facilitates the exfoliation and homogeneous dispersion of the stacked layers of Bent (Kim et al., 2003a; Zheng et al., 2004), which are crucial to the performances of the rubber product. Belonging to the family of organosilanes, SCA normally contain three groups ($\text{CH}_3\text{CH}_2\text{O}-$ or $\text{CH}_3\text{O}-$) which undergo hydrolysis in acidic/basic environment. During the hydrolysis process, silanol groups could be generated which are highly reactive to the hydroxyl groups on the surface of Bent. Meanwhile, SCA always contain a group (e.g., vinyl, amino or mercapto group) which is able to interact with the macromolecules in rubber matrix, forming covalent bonds, ion-molecule interaction or chain entanglement (Manna et al., 1999; Jia et al., 2007; Noriman and Ismail, 2012). Additionally, present in the interlayer spaces or layer edges of Bent, SCA remarkably expand the interlayer spaces, providing a better dispersion state of Bent in the matrix (Bertuoli et al., 2014).

Hitherto, there have been several technical routes for the utilization of SCA. In the research work of Mathialagan and Ismail (2012), 3-aminopropyltriethoxysilane was added into ethylene-propylene-diene monomer during solid compounding, which could enable reinforced mechanical properties and lower swelling ratio. A solution mixing method was applied by López-Manchado et al. (2004) for the blending of natural rubber and organoclay in toluene. The storage modulus and the crosslinking density of the rubber were apparently increased. This protocol is evidently more effective as compared to solid mixing, however neither economical nor environment-friendly as large amounts of

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organic solvent involved. Melt blending technique is another option which has been utilized in previous works (Kim et al., 2003b; Hasegawa et al., 2005; Liu et al., 2006). Compared with those methods, latex mixing is considered a better choice in the aspects of good dispersion of Bent and low cost for manufacture (Wang et al., 2000; Varghese and Karger-Kocsis, 2003). Conventionally, people treat clay or clay minerals with SCA prior to the mixing step, mainly in alcohol–water cosolvents (Gu et al., 2009; Balakrishnan et al., 2011; Li et al., 2013b), which requires more steps in the fabrication.

In present work, a novel green method for the synthesis of Bent/SCA/NBR nanocomposites was developed. In this method, no organic solvent was involved while the synthesis could be carried out in brief steps. In the preliminary work, the hydrolysis–condensation of (3-mercaptopropyl)trimethoxysilane in the process was identified while the formation of the CPN was discussed (Ge et al., 2015a). In this research, eight SCA were utilized, categorized according to their various groups as follows: (1)alkyl or alkenyl groups: ethyltrimethoxysilane (ETMS), vinylmethoxysilane (VTMS) and octadecyltrimethoxysilane (OTMS); (2)amino or imino groups: 3-aminopropyltriethoxysilane (APTES) and [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTMS); (3)sulfur-containing groups: mercaptopropyltrimethoxysilane (MPTMS) and bis-[3-(triethoxysilyl)propyl]tetrasulfide (TESPT); (4) methacryloyl group: [3-(methacryloyloxy)propyl]trimethoxysilane (MAPTMS). Their effects to the mechanical strength, tribological properties, thermal behaviors, swelling properties and rheological properties of the CPN were evaluated and investigated. Relevant influences of different interactions such as covalent bonds and ion–molecule interaction from various SCA were further explored.

2. Experimental

2.1. Materials

Bentonite (Bent, $\geq 95\%$; water content, $< 3\%$; Na^+ -montmorillonite content, $\geq 95\%$; cation exchange capacity, 0.85 meq/g) was originated in the mountains of Gunma prefecture in Japan and purchased from YAKURI Pure Chem. Acrylonitrile butadiene rubber (NBR) latex (KNB 35 L, 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, $\geq 80\%$), ethyltrimethoxysilane (ETMS, $\geq 97\%$), bis-[3-(triethoxysilyl)propyl]tetrasulfide (TESPT, $\geq 90\%$) and [3-(methacryloyloxy)propyl]trimethoxysilane (MAPTMS, $\geq 98\%$) were purchased from Sigma-Aldrich; 3-aminopropyltriethoxysilane (APTES, $> 98\%$) and octadecyltrimethoxysilane (OTMS, $> 85\%$) were provided by T.C.I.; vinylmethoxysilane (VTMS, $> 98\%$) was supplied by Acros Organics. All other chemicals were of reagent grade and used as received. All the SCA are summarized in Table 1.

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 approximately 500 ml of

NBR latex in a flask, with stirring for 10 min at 400 rpm. Subsequently, 0.051 mol of SCA was added and mixed for 30 min. Thereafter, suspension of Bent (30 g of Bent in 300 ml of water) was blended with the latex, followed by addition of 3.0 ml of ammonia aqueous solution as a catalyst. The reaction was held for 2 h at 25 °C. Finally, the slurry was precipitated with aqueous solution of calcium chloride (1 L, 0.09 mol/L) and then dried in vacuum for 48 h at 70 °C. All the reaction factors were optimized in advance. A series of CPN were prepared with selected SCA. Bent/NBR was prepared following the above procedure in the absence of any SCA. Neat NBR was fabricated by directly precipitating NBR latex in aqueous solution of calcium chloride.

The CPN were compounded with other ingredients on a laboratory-scale two-roll mill at 40 °C. The formulations for the synthesis and compounding are all tabularly summarized in Table 2. 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 recorded with rheometer in advance. The final vulcanizates had a thickness of 2 mm.

2.3. Characterization

2.3.1. Structure and morphology of the CPN

Infrared spectra were recorded with Fourier transform infrared spectroscopy (FT-IR) (Perkin Elmer Spectrum 100) in the region of 650–4000 cm^{-1} with a resolution of 4 cm^{-1} . Each sample was scanned for 5 times. X-ray diffraction (XRD) was performed at 25 °C with Empyrean (manufactured by PANalytical) X-ray diffractometer with copper as the source for the generation of X-ray (wavelength: 1.54 nm). X-ray diffraction data were collected over the range 4° to 11° (2θ) at a step size of 0.013° and a scan rate of 2°/min (divergence slit size: 0.44°). The tensile fractured surfaces of the vulcanizates were coated with a thin layer of gold and examined using field emission scanning electron microscopy (FE-SEM) with a model number of JSM-7500 (JEOL) under accelerating voltage of 10.0 kV.

2.3.2. Performances of the CPN

Vulcanization characteristics of the CPN, expressed in terms of scorch time (t_{s2}), optimum cure time (t_{90}), minimum torque (M_L) and maximum torque (M_H) were determined with rheometer (MDR 2020) at a cure temperature of 160 °C.

Tensile, tear and hysteresis tests were performed on a universal testing machine (Tinius Olsen H5KT-0401) following ASTM D412 and ASTM D624 standards. For tensile test, specimens in standard dumb-bell shape were cut from the vulcanizate sheets with dimensions 25 mm \times 6 mm \times 2 mm while specimens for tear strength test were with a 90° angle on one side and tab ends (102 mm \times 19 mm \times 2 mm). Hysteresis test was performed till 100% strain and the hysteresis loss ratio (h_r) was calculated by dividing loop area with the area of work performed by extension deformation (Chattopadhyay et al., 2011). Shore A hardness of the specimens was obtained with Shore Durometer Type A according to ASTM D2240.

Concerning tribological properties, static friction coefficient (μ_s) of the vulcanized CPN was measured with Test One friction testing

Table 1
List of the silane coupling agents and relevant physical properties.

Silane coupling agents	Functional groups	Molecular weight	Density (g/cm^3 , 25 °C)
Mercaptopropyltrimethoxysilane (MPTMS)	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$	196.3	1.06
3-Aminopropyltriethoxysilane (APTES)	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	221.4	0.95
[3-(2-Aminoethylamino)propyl]triethoxysilane (AEAPTMS)	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$	222.4	1.03
Octadecyltrimethoxysilane (OTMS)	$-\text{CH}_2(\text{CH}_2)_{16}\text{CH}_3$	374.7	0.89
Ethyltrimethoxysilane (ETMS)	$-\text{CH}_2\text{CH}_3$	150.3	0.94
Vinylmethoxysilane (VTMS)	$-\text{CH}=\text{CH}_2$	148.2	0.97
Bis-[3-(triethoxysilyl)propyl]tetrasulfide (TESPT)	$-\text{CH}_2\text{CH}_2\text{CH}_2-\text{S}-\text{S}-\text{S}-\text{S}-\text{CH}_2\text{CH}_2\text{CH}_2-$	539.0	1.08
[3-(Methacryloyloxy)propyl]trimethoxysilane (MAPTMS)	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{OOC}(\text{CH}_2)\text{CH}_3$	248.4	1.05

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