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Preparation and characterization of Si_3N_4/SBR nanocomposites with high performance

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ABSTRACT

In this work, native silicon nitride (Si_3N_4) nanoparticles were modified by macromolecular coupling agent (LMPB-g-MAH) which was designed and synthesized according to the chain structure of styrene butadiene rubber (SBR), and Si_3N_4/SBR nanocomposites were prepared by two-segment mixing process. The structure and surface properties of modified Si_3N_4 nanoparticles were characterized by Transmission Electron Microscope (TEM), Fourier Transform Infrared Spectroscopy (FTIR), size distribution analyzer, and contact angle measuring instrument. The effect of different dosage of nano-Si_3N_4 on Si_3N_4/SBR nanocomposites was also systematically studied. It can be got that LMPB-g-MAH can effectively inhibit the agglomeration and improve the hydrophobic property of Si_3N_4 nanoparticles. It also can be found that modified Si_3N_4 nanoparticles brings well physical and dynamic mechanical properties, aging resistance, oil resistance, wear resistance, and low rolling resistance to SBR, especially, when the dosage is 0.5–1.5 phr, the best overall performance of Si_3N_4/SBR nanocomposites can be achieved.

1. Introduction

Recently, polymer nanocomposites have attracted worldwide attention because of their high performance [1–5]. But there still exist many difficulties to get a wide range of applications in rubber, plastic, adhesive, coatings, etc. For example, nanoparticles have a strong tendency to reunite due to its high surface energy, so it is hard to disperse in polymer matrix well; Nanoparticles have weak combination with the polymer matrix because of badly consistent interface. Therefore, surface modification of nanoparticles is necessary and the coating layer on the surface of nanoparticles must be thicker enough to bring more strong electrostatic, steric stabilization and forceful interaction between particles and polymer matrix.

Up to now, there are mainly three ways to modify nanoparticles, small molecular coupling agent (SMCA) [6,7], macromolecular coupling agent (MCA) by one step [8,9] and surface grafting modification (SGM) by two steps [10,11]. From the comparison in Fig. 1A and B, MCA can bring more thicker coating layer than SMCA, especially when MCA has well intermiscible with polymer matrix and the chain of MCA can unfold fully, as shown in Fig. 1C. Moreover, due to the lower grafting efficiency of SGM, surface modification by MCA has more advantages. So, the key to prepare polymer nanocomposites with high performance is how to design and synthesize MCAs.

In our previous work, many MCAs were designed and synthesized by radical polymerization, like tercopolymer butyl acrylate (BA)-D-methacrylic acid (MAA)-acrylonitrile (AN) [12] and tercopolymer butyl acrylate (BA)-methyl methacrylate (MMA)-vinyl triethoxy silane (VTES) [13], etc., which were used to modify Si_3N_4 nanoparticles and prepare Si_3N_4/NBR nanocomposites. Due to the strong interface action, this nanocomposites we prepared exhibit unique hybrid properties including good heat-resistance, good wear-resistance, good dynamic mechanical properties, etc.

In this study, Si_3N_4/SBR nanocomposites with high performance were prepared and characterized. Firstly, Si_3N_4 nanoparticles were chose as an effective filler due to its high strength, high fracture toughness, low coefficient of thermal expansion, and good resistance to abrasive and erosive wear [14–16]. Secondly, a new MCA (LMPB-g-MAH) which was designed according to the chain structure of SBR and synthesized by graft copolymerization was used to modify Si_3N_4 nanoparticles; On one hand, maleic anhydride group (—(C=O)$_2$—O—), which can react with imine groups (—NH—), amidocyanogen groups (—NH_2) and hydroxy group (—OH) on the surface of Si_3N_4 nanoparticles, is chose as anchor groups; On the other hand, low-molecular-weight polybutadiene

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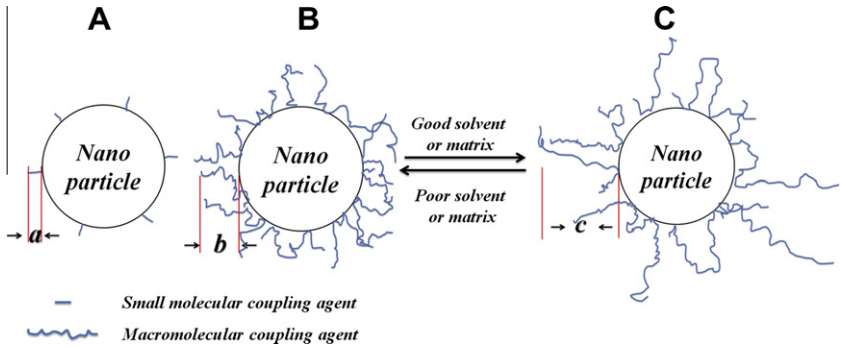

Fig. 1. Schematic drawing of the possible structure of modified nanoparticles.

liquid rubber (LMPB) is chose as a solvent chain, because it not only has quite similar chain structure and polarity with SBR chain, but also has unsaturated bonds which can join in the process of rubber vulcanization, which can be seen from Fig. 2. So it brings functional modification to Si_3N_4 nanoparticles, and solves out the problem that it is hard to control the chain structure and molecule weight by former methods. Thirdly, the preparation process of Si_3N_4/SBR nanocomposites is also adjusted to improve the dispersion of Si_3N_4 nanoparticles in SBR matrix from one-segment mixing (just by an internal mixer) to two-segment mixing (by an internal mixer and an open mill).

Additionally, this paper will attempt to characterize the performances of the Si_3N_4/SBR nanocomposites, discuss the effect of nano-Si_3N_4 with different dosage on oil resistance, aging resistance, wear resistance, rolling resistance and dynamic mechanic thermal analysis (DMTA), and further analyze the potential application of the Si_3N_4/SBR nanocomposites to tire, and conveyor belt, etc.

2. Experimental

2.1. Materials

LMPB-g-MAH (Mn = 3000–5000) was synthesized in laboratory, which has been described previously [17]. Nano-Si_3N_4 was purchased from Hefei Kiln Nanometer Technology Inc. of China (average particle diameter 40–60 nm, specific surface area 115 $m^2\ g^{-1}$). SBR(1502), carbon black N330, calcium carbonate, sulfur, accelerator TMTD and CZ, stearic acid, antioxidant RD and 4010NA, heavy aromatic oil, etc., were supplied by AnHui Zhongding Holding Group Co., Ltd. Other reagents were of analytical grade and used as received.

2.2. Surface modification of Si_3N_4 nanoparticles with LMPB-g-MAH

The native Si_3N_4 nanoparticles (3 g), a certain amount of LMPB-g-MAH, and dimethylbenzene (50 ml) were added into the flask, mixing round with high speed at 60 °C for 3.5 h, then vacuum drying for 10 h.

2.3. Preparation of Si_3N_4/SBR nanocomposites

The nanocomposites in our experiments were prepared by two-segment mixing process. For the first segment mixing, two rubber master batches (RMB), RN-0 and RN-6, were prepared by an internal mixer at 147 °C for 8 min (within this time period torque was stabilized) at a rotor speed of 60 rpm. For the second segment mixing, the residual rubber batches from RN-1 to RN-5 were gotten from RN-0 and RN-6 by different proportions through an open mill. The details can be seen from Table 1. The Si_3N_4/SBR nanocomposites were cured at 147 °C for optimum cure time (t_{90}).

2.4. Characterization methods

Native nano-Si_3N_4 and modified nano-Si_3N_4 suspensions in dimethylbenzene, which was got by the ultrasonic vibrating method, were investigated by Transmission Electron Microscope (TEM, JEM-100SX, JEOL, Japan), size distribution analyzer (3000HS, Malvern, England) and Fourier Transform Infrared Spectroscopy (FTIR, Neuxs-830, Nicolet, USA); Surface hydrophilicity of Si_3N_4 nanoparticles was investigated by Contact Angle Measuring Instrument (KRUSS GmbH, Germany) at the temperature of 25 °C, methanol and water were dropped on the sample surface at ten different sites separately, then the average values for a sample was taken as its contact angle.

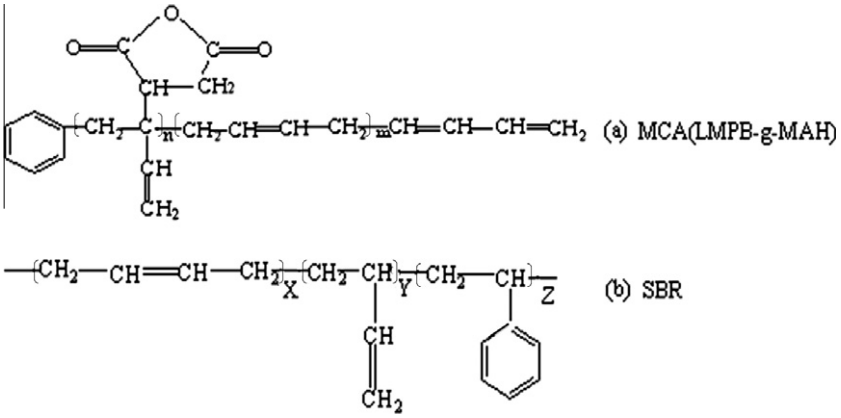

Fig. 2. The contrast of molecule structure between macromolecular coupling agent (LMPB-g-MAH) and SBR.