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Nitrile butadiene rubber/hindered phenol nanocomposites with improved strength and high damping performance

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Abstract

A hindered phenol (AO-80) was studied to prepare rubber nanocomposites with nitrile butadiene rubber (NBR). The NBR/AO-80 rubber nanocomposites were successfully developed by applying the adopted preparation procedure/conditions, especially by introducing mechanical kneading of the NBR/AO-80 composites at a temperature higher than the melting point of AO-80, followed by the crosslinking of NBR molecules during the subsequent hot-pressing/vulcanization process. The nanocomposites consisted of two phases: (1) the AO-80 enriched phase (nanoparticles with the average size of approximately 20 nm) and (2) the NBR enriched phase (matrix). The generation and uniform distribution of the nanoparticles were attributed to the high temperature mechanical kneading process, the strong intermolecular interactions between AO-80 and NBR molecules, and the formation of a three-dimensional NBR network. The morphological, structural and mechanical properties of the composites were systematically investigated in each preparation step using SEM, TEM, DSC, XRD, FT-IR, DMTA and a tensile tester. The results indicated that the prepared NBR/AO-80 rubber nanocomposites had single relaxation transitions, improved tensile strengths, high dynamic mechanical loss values, and reasonably good stabilities. The NBR/AO-80 rubber nanocomposites are expected to have important applications as a high performance damping material.

Keywords: Nanocomposites; NBR; Hindered phenol

1. Introduction

The research on rubber nanocomposites can be both fundamental and applied, and has attracted growing attentions. Numerous studies have demonstrated that the uniform distribution of nano-scaled filler particles into a rubber matrix, with reasonably good interfacial bonding strength, could lead to a rubber nanocomposite with significantly improved properties [1–5]. For example, by distributing 10 phr (parts per hundred of rubber by mass) of organically modified montmorillonite into styrene butadiene rubber (SBR), the tensile strength of the resulting rubber nanocomposite could exceed 18 MPa, which was 9 times higher than that of the neat SBR [2]. It was also reported that when the particle size of magnesium hydroxide ($Mg(OH)_2$) was reduced from micron-level to nano-level, both the mechanical and the fire retardation properties of its filled ethylene propylene diene monomer (EPDM) rubber could be substantially improved [6]. Theoretical analyses have suggested that properties of nanofiller particles, interfacial bonding strength of filler/matrix, and uniform distribution of nanofiller particles were the most important factors on the properties of rubber nanocomposites [7–9].

Nanofillers can be generally classified as inorganic and organic ones. Inorganic nanofillers (including nano-scaled

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carbon black, silica/silicate and metal oxide/hydroxide) have been extensively researched for decades, while organic nanofillers have been of increasing interests recently, particularly in the development of rubber nanocomposites. Unlike inorganic nanofillers that often require additional surface treatments to improve the filler/matrix interfacial properties, organic nanofillers usually possess favorable surface functional groups that can form strong intermolecular interactions (hydrogen bonding and/or van der Waals' forces) with the rubber molecules in the matrices. On the other hand, unlike most inorganic nanofillers that pre-exist as nano-scaled particles, organic nanofillers usually must be transformed into nano-scaled particles during the preparation of rubber nanocomposites. Therefore, effectively generating organic nanofiller particles and uniformly distributing them into rubber matrices are two major challenges during the preparation of rubber nanocomposites.

A hindered phenol of 3,9-bis[1,1-dimethyl-2-{β-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy}ethyl]-2,4,8,10-tetraoxaspiro-[5,5]-undecane (AO-80) was investigated to prepare the rubber nanocomposites in this study. The chemical structure of AO-80 is shown in Fig. 1. The AO-80 molecule has a relatively high molecular weight, and AO-80 can be crystalline or amorphous, depending upon the processing procedures/conditions [10]. Nano-scaled particles containing amorphous AO-80 can be generated in the rubber matrices by mechanically kneading AO-80 with a polar rubber such as nitrile butadiene rubber (NBR) at a temperature higher than the AO-80 melting point of 122.5 °C, followed by hot-pressing/vulcanization. Additionally, since the AO-80 molecule has numerous polar functional groups (hydroxyl, carbonyl and others) that can form strong intermolecular interactions with NBR, the NBR/AO-80 rubber nanocomposites are likely to possess good filler/matrix interfacial properties. Wu and co-workers reported that AO-80 was used to prepare composites with chlorinated polyethylene (CPE) [11–13]. The preparation method that was adopted in their studies included: (1) adding various amounts of AO-80 (crystalline powder) into the pre-kneaded CPE, followed by kneading the mixtures at room temperature for 10 min; (2) heating the samples to a temperature higher than the melting point of AO-80 for 3 min, then hot-pressing the samples at 160 °C for 7 min at a pressure of 18 MPa; and (3) quenching the samples using an ice water bath to obtain the CPE/AO-80 composites. In their prepared composites, a small portion of the AO-80 existed as nanoparticles with sizes smaller than 100 nm, but the majority existed as particles with sizes of 0.4–0.5 μm. Such composites exhibited two distinct relaxation transitions: (1) the glass transition associated with CPE in the matrix and (2) the hydrogen bonding dissociation associated with AO-80 in the particles. While the authors discovered that hot-pressing was crucial for the formation of uniformly distributed AO-80 particles, the prepared composites could not be considered to be ''nanocomposites''. They also reported that the composites possessed a much higher dynamic mechanical loss property when compared to the neat CPE. This was attributed to the strong intermolecular interactions between the AO-80 and the CPE molecules, since such interactions would enhance the intermolecular friction and result in a large consumption of energy during dynamic deformations.

The aim of this study was to prepare, characterize and evaluate NBR/AO-80 composites with particle sizes that are smaller than 100 nm (nanocomposites). NBR is easier to crosslink/vulcanize than CPE since NBR contains butadiene units. More importantly, NBR can form stronger intermolecular interactions with AO-80 since the nitrile group in NBR has a higher polarity than the chlorine/carbon and α-hydrogen/carbon bonds in CPE. Unlike Wu and co-workers, we introduced two important steps into the preparation procedure: (1) high temperature (135 °C) kneading of NBR/AO-80 composites (note that Wu and co-workers simply heated their composites before conducting hot-pressing), and (2) molecularly crosslinking of NBR molecules during the subsequent hot-pressing/vulcanization process. Our hypotheses were that: (1) the mechanical kneading at a temperature higher than the melting point of AO-80 could molecularly disperse AO-80 into NBR. This was because the extensive shearing involved in the high temperature kneading process could greatly enhance the intermolecular interactions between the liquid state AO-80 and the rubbery state NBR molecules; and (2) the subsequent hot-pressing/vulcanization and its resulting formation of a three-dimensional NBR network could compress and aggregate the molecularly dispersed AO-80 into nano-scaled particles. The NBR network could also partially block the generated nanoparticles and effectively prevent them from over aggregation into large particles, thus could lead to the formation of NBR/AO-80 rubber nanocomposites. We adopted the following preparation method: (1) adding various amounts of AO-80 (crystalline powder) into the pre-kneaded NBR by applying a room temperature kneading process; (2) kneading the prepared NBR/AO-80 composites at a temperature higher than the melting point of AO-80; (3) after the high temperature kneaded samples being gradually cooled to room temperature, adding the compounding and crosslinking agents into the samples by applying a room temperature kneading process; (4) hot-pressing the samples at 160 °C to allow the NBR molecules to crosslink/vulcanize into three-dimensional rubbery networks; and (5) gradually cooling the hot-pressed/vulcanized samples to room temperature to prepare the final NBR/AO-80 composites (rubber nanocomposites). The

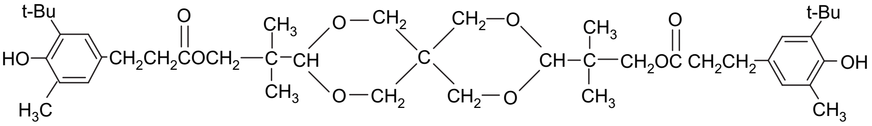

Fig. 1. Molecular structure of AO-80.