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Material Properties

The fabrication and properties of natural rubber-clay nanocomposites

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ABSTRACT

Natural rubber-clay (NR-clay) nanocomposites were prepared by blending on a two roll mill. Organo-modified Cloisite clay was used in this study. The effect of concentration of clay, type of clay and vulcanizing systems on the mechanical properties of nanocomposites were studied in detail. NR-clay nanocomposites were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM) and atomic force microscopy (AFM) analysis. X-ray results suggest that the intergallery distance is increased in all samples studied. There is good improvement in properties like tensile strength, elongation at break and modulus on incorporation of nanoclay in NR. TEM photographs show that exfoliation of the clay occurred at a concentration of 5 phr of cloisite 20A.

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1. Introduction

The properties of elastomers are improved by reinforcing with various fillers such as carbon black, silica, clay etc. For the past few decades a new type of filler known as nanofiller was developed and introduced in the polymeric matrices for overall improvement in properties. Nanofillers tremendously improve the various properties of polymeric products and thus new materials were formed. Nanofillers consist of nanoclays, nanotubes, nanoparticles etc. Nanocalys belong to the category of montmorillonite types of clay. The clay is used as such or modified before introducing in the polymer matrix. The selection of clay depends on the interaction between the clay and the polymeric matrix. NR based nanocomposites with 10 wt% natural and synthetic layered silicates were prepared by the latex compounding method [1]. Layered silicates outperformed the reference material (commercial clay) in all aspects due to the intercalation/exfoliation of the silicates and to the formation of a skeleton silicate network in the NR matrix.

Nanocomposites containing natural rubber (NR) as matrix, epoxidized natural rubber (ENR) as compatibilizer and organophilic layered clay (organoclay) as filler were produced in an internal mixer [2]. The effects of ENR with 25 and 50 mol% epoxidation were compared at different rubber concentrations. Incorporation of ENR and organoclay strongly affected the cure characteristics of the composites. The organoclay was mostly intercalated according to X-ray diffraction (XRD) and transmission electron microscopic (TEM) results. The NR/clay nanocomposites were prepared by melt mixing to produce NR/Na-MMT, NR/DDA-MMT and NR/ODA-MMT composites [3]. An optimum electron beam dose of 250 kGy for crosslinking of NR, NR/DDA-MMT and NR/ODA-MMT was determined by gel content and tensile strength measurements. Upon electron beam irradiation, the tensile modulus of the nanocomposites keeps increasing with the increase of clay content up to 10 phr. However, the tensile strength and gel content of the nanocomposites show optimum values at a range of 3.0—5.0 phr clay content. Natural rubber (NR)/rectorite nanocomposite was prepared by co-coagulating NR latex and rectorite aqueous suspension [4]. Nanocomposite exhibited a higher glass transition temperature, lower tan δ peak value and slightly broader glass transition region compared with pure NR. The nanocomposites have a unique stress—strain behavior due to the reinforcement and the hindrance of rectorite layers to the tensile crystallization of NR.

Styrene butadiene rubber (SBR)/natural rubber (NR)/organo-bentonite nanocomposites were prepared from emulsions [5]. The effect of organo-bentonite on the mechanical properties, thermal stability and swelling behavior was investigated. TEM and XRD analysis showed that rubber chains were intercalated into the

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organo-montmorillonite particles. The addition of a small amount of OMMT greatly improved thermal stability and swelling behavior, which was attributed to the good barrier properties of the dispersed and partially exfoliated organo-montmorillonite particles. Single-walled carbon nanotubes (SWNTs) and SiC nanoparticles in natural rubber solution and subsequently evaporated the solvent to prepare NR nanocomposites [6]. The influence of nano-fillers on the mechanical properties of the resulting nanocomposites show an increase in the initial modulus with nanoscale reinforcements for up to 50% strain compared to pure NR. The modulus and strength of natural rubber with 1.5% SiC nanoparticles appear to be superior to those of SWNTs with the same filler content. In addition to mechanical testing, these nanocomposites were studied using the SEM and Raman spectroscopy techniques in order to understand the morphology of the resulting system and the load transfer mechanism, respectively.

Natural rubber (NR)/Na$^+$—montmorillonite (MMT) nanocomposite was prepared using poly(ethylene glycol) (PEG) [7] as dispersing agent. The influence of PEG on the network structure has been evaluated by static proton double-quantum nuclear magnetic resonance spectroscopy at low-field. Silicate nanoparticles with a high aspect ratio (clay tactoids) and a more crosslinked rubber network have been obtained for an optimum PEG/MMT ratio. Cellulosic nanoparticles were used as reinforcing phase to prepare nanocomposite films in natural rubber latex [8]. The stiffness of the natural rubber was significantly increased above its glass—rubber transition temperature upon nanoparticles addition. The reinforcing effect was shown to be higher for nanocomposites with MFC compared to whiskers. It was ascribed to the higher aspect ratio and possibility of entanglements of the former. The mechanical properties of non-vulcanized natural rubber and dialyzed natural rubber-clay nanocomposites have been studied by uniaxial deformations [9]. It was found that non-rubber molecules contribute to auto-reinforcement and the removal of this molecule improves significantly the performance of clay as reinforcement agent. The nanocomposites prepared by latex-mixing with aqueous dispersions of clay are found to contain completely exfoliated clay lamellae in co-existence with tactoids. At high deformations, strain-induced alignment of the clay exhibits anisotropic scattering and anisotropy increasing with clay concentration and stretching.

The technical feasibility of natural rubber nanocomposites with Cloisite 15A to substitute for conventionally used silica (SiO$_2$) as filler [10]. Thus intercalation of OC by the rubber chains in the CPN reduced the enthalpy of the curing process and indicated a lower crosslink density. The TEM analysis indicated that the OC was homogeneously dispersed in the CPN. The set of results for the mechanical properties indicated that 50 phr silica can be replaced by 4 phr OC without affecting the properties of the final material even after aging. Octadecylammonium montmorillonite/natural rubber/ cis-1,4-polybutadiene (OMMT/NR/BR) nanocomposites were prepared by direct mechanical blending [11]. The structure of these nanocomposites and the dispersion state of OMMT particles were evaluated by transmission electron microscopy (TEM) and X-ray diffraction (XRD). TEM confirmed that the majority of the OMMT particles were dispersed uniformly in the NR matrix. The XRD patterns revealed that the clay mineral particles were completely exfoliated when the OMMT content was <6 mass%. Tribological characteristics of natural rubber nanocomposites for wear resistant applications have been studied by sliding against a steel blade, in a specially designed abrader [12]. Among the various parameters, nanofiller loading have the most significant influence on wear characteristics. Analysis of the micrographs of the abraded surface and the corresponding debris reveals that the specific wear rate of both the nanocomposites (sepiolite and carbon nanofiber filled) is found to increase with increasing structural complexity of the

debris formed. Natural rubber/silica (NR/SiO$_2$) nanocomposite is developed by combining self-assembly and latex-compounding techniques [13]. The results show that the SiO$_2$ nanoparticles are homogenously distributed throughout NR matrix as nano-clusters and as well as core shell structure depends on the amount of SiO$_2$. When more SiO$_2$ is loaded, secondary aggregations of SiO$_2$ nanoparticles are gradually generated, and the size of SiO$_2$ cluster dramatically increases.

Magnetic and microwave absorbing properties of thermoplastic natural rubber (TPNR) filled magnetite (Fe$_3$O$_4$) nanocomposites were investigated [14]. The TPNR matrix was prepared from polypropylene (PP), natural rubber (NR) and liquid natural rubber (LNR) in the ratio of 70:20:10 with the LNR as the compatibilizer by melt blending method. XRD reveals the presence of cubic spinal structure of Fe$_3$O$_4$ with the lattice parameter of $a = 8.395$ Å and TEM micrograph shows that the Fe$_3$O$_4$ nanoparticles are almost spherical with the size ranging 20—50 nm. The values of saturation magnetization, remanence, initial magnetic susceptibility, and initial permeability increase, while the coercively decreases with increasing filler content for all compositions. However a detailed investigation of the properties of natural rubber-nanoclay based on the influence of vulcanizing systems, nature and concentration of modified MMT was not reported so far.

The main objective of the work is to investigate the influence of vulcanizing systems such as conventional, efficient and peroxide on the mechanical properties of the clay reinforced natural rubber. This study is also trying to find the relation between clay and the nature of vulcanizing systems for improving the mechanical properties of the elastomers. Moreover this study uniquely focused to find the effect of different types of modified organoclay on the properties of the natural rubber. In addition to this, organomodified clay composite is compared with carbon black and silica filled elastomeric composites. Characterization of clay-nanocomposites was carried out by XRD, TEM and AFM analysis. Bearing, roughness and power spectral density (PSD) analysis were also carried out as a function of concentration of clay to characterize the nanocomposites.

2. Experimental details

2.1. Materials

The natural rubber used was ISNR-5 obtained from Rubber Research Institute of India. Organo modified nanoclays viz; (Cloisite 10 A, 15 A, 20 A, 25 A, 30 B and 93 B) were supplied by Southern Chemicals U.S.A used in this study. The properties of clay used were given in Table 1. Carbon black (Semi reinforcing furnace, SRF) and Silica (Precipitated Silica).

All other rubber ingredients used were of laboratory reagent grade. Table 1.

2.2. Preparation of natural rubber—clay composites

Compounding of Natural rubber and clay was done on a two-roll mixing mill (friction ratio1:1.4) according to ASTM D 15-627 using the formulation given in Table 2. Uncured rubber compound was analyzed by Monsantorheometer R$_{100.}$ All curing was carried out between the electrically heated platens of hydraulic press at 150 °C for the optimum cure time. In order to study the effect of vulcanizing systems on the role of nanoclays, NR was differently vulcanized with conventional (CV), efficient (EV) and peroxide (DCP) systems (D, E & F respectively) along with nanoclay (cloisite 10A-10 phr) and it was compared with corresponding pure vulcanizing systems (A, B, C respectively). In order to study the effect of concentration of modified nanoclays, NR was conventionally