



Macromolecular Nanotechnology

Tube-like natural halloysite/fluoroelastomer nanocomposites with simultaneous enhanced mechanical, dynamic mechanical and thermal properties

Sandip Rooj^a, Amit Das^{a,*}, Gert Heinrich^{a,b}

^a Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, D-01069 Dresden, Germany

^b Technische Universität Dresden, Institut für Werkstoffwissenschaft, Helmholtzstrasse 7, D-01069 Dresden, Germany

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ABSTRACT

A novel kind of fluoroelastomer nanocomposites based on tube-like halloysite clay mineral were successfully prepared using a bis-phenol curing system, which resulted in prominent improvements in mechanical and dynamic mechanical properties and in the elevation as high as 30 K of the thermal decomposition temperature. Wide-angle X-ray scattering and transmission electron microscopy techniques were employed to assess the morphology developed in the nanocomposites, while stress strain diagrams were used to evaluate the mechanical properties. These nanocomposites were further characterized by moving die rheometer, dynamic mechanical properties and thermo-gravimetric analysis. Structure-properties relationship and the improvement of the mechanical, dynamic mechanical and thermal properties of fluoroelastomers are reported in the present study. Increasing amount of the filler reduced the curing efficiency of the bis-phenol curing system, which was evident from the rheometric and physical properties of the resulting composites. A sort of filler–filler interaction was perceived during the strain sweep analysis of the composites. The polymer–filler interaction was reflected in the improved mechanical and thermal properties which were the consequence of proper dispersion of the nanotubes in the polymer matrix; whereas the intercalation of macromolecular chains into the nanotubes was not reflected in the X-ray diffraction analysis.

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1. Introduction

Incorporation of a small amount of nano-fillers into the polymer matrix has drawn considerable attention during the last decade [1–6]. Significant improvements of physical properties of polymer can be achieved through this technique. This improvement mainly depends on certain factors such as the aspect ratio, degree of dispersion, orientation of the filler. It is also well known that fibrous or rod-like nanoparticles are a very promising class of reinforcement materials owing to their large surface areas and high aspect ratios [7–10]. For instance, carbon nanotubes (CNTs)

have been incorporated in many polymer matrices in order to achieve nanocomposites with enhanced tensile strength and modulus [11,12]. Regardless of providing exciting performance improvements, relatively high price, inconvenience in large-scale production and environmental issues of CNTs still confine their practical implementation. Recently, halloysite nanotube (HNTs), a kind of naturally occurring silicate with tubular structures were revealed to reinforce polymers and offer unique reinforcing effects to different polymers [13–15].

However, the applications of this material in rubber matrices are still largely unexplored. Being an economically viable material, halloysite is now treated as nano clay mineral for technological applications starting from porcelain manufacture to control release drug delivery [16].

* Corresponding author.

E-mail address: das@ipfdd.de (A. Das).

Basically, it exists in hollow tubular form in earth deposits. This can be excavated from the consequent deposit as a raw mineral. Mismatch in the two-layered alignment of the tetrahedral sheet of silica bonded to the octahedral or gibbsite sheet of alumina causes the wall to curve into the cylindrical shape as explained by Bates et al. [17]. Intercalated water molecules may be presents between the repetitive two-layered sheets, can be irreversibly removed during processing. As for most natural materials, the size of HNT particles varies within 1–15 μm of length and 10–150 nm of inner diameter. Due to its high aspect ratio (L/D), it gives a large amount of filler–polymer interactions compared to other nano-fillers. Over the past fifty years, fluoroelastomers (FKM) have benefited the world in several ways. Fluoroelastomer products are a family of specialty materials appreciated for their elastic behaviour under comparatively harsh conditions [18]. These elastomers are largely used in seals and other fabricated components to afford barriers against a broad range of fluids under severe conditions. Majority of the fluoroelastomers products are utilized in automotive applications, mainly in fuel and high pressure sealing application. Amounts of fluoroelastomers consumed per vehicle are small compared to natural and synthetic rubber within the tires of a vehicle, but the fluoroelastomer parts are extreme crucial for safety reason, reliable operation and environmental protection. Other fluoroelastomers applications are in number of areas like aerospace appliances, fluid power, chemical industry, oil field, semiconductor application/fabrication and high pressure seals for plasma coating [19]. On the other hand, it is a common tradition to incorporate some filler into the rubber matrix in order to obtain the ultimate properties out of it, and fluoroelastomers are also not exception of that. To improve their performance, various fillers have been examined, including carbon black [20], and recently nanofillers like layered silicates [21,22], carbon nanotube [23], polyhedral oligomeric silsesquioxane (POSS) [24], etc.

In our earlier study, efforts have been paid to develop natural nanocomposites based on natural rubber (NR) and natural halloysite nanotube [25], and the effect of HNT on the properties of NR have been investigated. In the present study, novel FKM–HNT nanocomposites were prepared for the first time based on tube-like naturally occurring halloysite nanotube. We explore the effect of HNT loading on the mechanical and dynamic mechanical properties of the FKM nanocomposites. XRD and TEM were also carried out to visualize the dispersion of HNT particles in the fluoroelastomers matrix. A magnificent influence of thermal stability was observed at 5 phr HNT loading, and further increase in HNT content tends to deviate in negative direction.

2. Experimental

2.1. Materials

LEVATHERM F6625 (a copolymer of vinylidene fluoride (VF_2), hexafluoropropylene (HFP), fluorine content 66–67 wt%, specific gravity 1.83, Mooney viscosity

ML(1 + 10)@121 = 50) was kindly supplied by Lanxess, Germany. Halloysite nanotubes were procured from Sigma–Aldrich, Germany. This material had an average tube diameter of 50 nm and inner lumen diameter of 15 nm. Typical specific surface area of this halloysite was 65 m^2/g ; pore volume of $\sim 1.25 \text{ mL/g}$; refractive index 1.54; and specific gravity 2.53 g/cm^3 . 4,4'-(Hexafluoroisopropylidene)diphenol and Benzyltriphenylphosphonium Chloride were purchased from Sigma–Aldrich and Acros respectively. Calcium hydroxide and magnesium hydroxide were used of rubber industrial grade.

2.2. Preparation of nanocomposites

The compounding of FKM with HNT including other ingredients such as calcium hydroxide, magnesium oxide (MgO), bisphenol A and phosphonium chloride was done on a laboratory-sized two-roll mill (Polymix110L, friction ratio = 1:1.25, roll temperature = 60 $^\circ\text{C}$). Table 1 depicts the compositions of HNT filled FKM rubber nanocomposites. This compounded rubber was then subjected to rheometric study to obtain the optimum cure time of the compounded rubber. The rubber samples were then cured until their optimum curing time (t_{90}) by a hot press at 180 $^\circ\text{C}$, cooled to room temperature and kept 8 h for post cure at 230 $^\circ\text{C}$.

2.3. Characterization techniques

Curing studies were performed using Scarabaeus SIS V50 in an isothermal time sweep mode for all the samples at 180 $^\circ\text{C}$ for 60 min.

X-ray diffraction (XRD) measurements were carried out with a Rigaku D/Max β -diffractometer, using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$) at 40 kV and 30 mA. The d -spacing of the layered particles was then calculated from Bragg's equation $n\lambda = 2d\sin\theta$, where λ is the wavelength of the X-ray, d is the interlayer distance and θ is the angle of incident X-ray radiation.

Tensile tests of cured samples were carried out using Zwick 1456 (Z010, Ulm, Germany) with crosshead speed 200 mm/min (DIN 53504/S2). E-modulus is calculated in between 0.5% and 1.0% of strain. For each compound three specimens were tested.

Dynamic mechanical analysis was performed on cutted strips with 10 mm width and 35 mm in length using a dynamic mechanical thermal spectrometer (Gabo Qualimeter, Germany, model Eplexor-2000N) in the tension mode. The isochronal frequency employed was 10 Hz and the heating rate was 2 $^\circ\text{C}/\text{min}$.

The thermo-gravimetric analysis was done using a TA Q 500 instrument (USA) with a heating rate of 20 $^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

The state of dispersion of the clay particles in the nanocomposites was investigated using transmission electron microscopy (TEM) with the microscope JEM 2010 model. The ultra-thin sections of the samples were prepared by ultramicrotomy (Leica Ultracut UCT) at -120°C with a thickness of a section 100 nm.

In order to analyze the network structure of the FKM–HNT nanocomposites, the swelling experiment was

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