Mechanical Properties and Structures of Dicyanate–Clay Nanocomposites

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ABSTRACT: Dicyanate–clay nanocomposites comprising a dicyanate resin and a type of organically modified clay were prepared and characterized, and their thermomechanical properties were investigated. The organically modified clay had silicate layers of nanometer size intercalated with an organic modifier, which improved the compatibility between the clay and organic materials, such as dicyanate resins. Dynamic mechanical analysis was performed to investigate the thermomechanical properties of the dicyanate–clay nanocomposites containing various amounts of the clay. The storage modulus of the nanocomposites below their glass-transition temperatures slightly increased with increasing clay content. The glass-transition temperature of the dicyanate–clay nanocomposites increased with increasing clay content. The nanostructures of the dicyanate–clay nanocomposites were characterized by transmission electron microscopy and X-ray diffraction analysis. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2629–2633, 2003

Key words: nanocomposites; clay; mechanical properties

INTRODUCTION

Polymer nanocomposites comprising organic and inorganic materials are a class of composites in which the reinforcing phase dimensions are in the order of nanometers. High-performance organic–inorganic composites can be obtained when the interfacial adhesion between the polymer matrix and the reinforcing material is good enough. Polymer nanocomposites can possess superior properties to conventional polymer microcomposites because their nanometer size characteristics maximize interfacial adhesion.[1,2]

Polymer–clay nanocomposites are the most well known among the various polymer nanocomposites, and they are divided into two classes according to their structures: intercalated nanocomposites and exfoliated nanocomposites.[3,4] Intercalated nanocomposites have polymer chains inserted between silicate layers of clay, which generates ordered lamella with an interlayer distance of a few nanometers. Exfoliated nanocomposites have silicate layers about 1 nm thick that are exfoliated and dispersed in the polymer matrix. Nanostructured composites based on polymers and layered silicates of clay typically exhibit excellent properties, which make them extremely interesting in the field of the design and creation of new construction materials.[5,6] In the last decade, the properties of a variety of elastomers,[7,8] linear[9,10] or crosslinked[11,12]

polymers, have been improved by the incorporation of clay.

Dicyanate resins have excellent mechanical and thermal properties, far exceeding those of many commercial thermosetting resins such as epoxy, unsaturated polyester, and phenol–formaldehyde. Because the viscosity of dicyanate resins is relatively low compared to many thermosetting resins, they have some advantages in reactive polymer processing, including resin-transfer molding and structured reaction injection molding. Three-dimensional crosslinking networks of oxygen-linked triazine rings and bisphenol units, generally termed polycyanurates, are formed by the cyclotrimerization of three cyanate ($-OC\equiv N$) groups. Because no volatile byproducts are formed during polymerization, the cyclotrimerization reaction may be classified as a noncondensation-type step polymerization. Polycyanurates show high glass-transition temperatures (250–290°C) and low water absorption characteristics.[13] Recent studies have focused on their potential matrix applications in advanced polymer composites.[14–17] Introducing a high-performance thermoplastic into a liquid dicyanate resin before curing enhanced fracture toughness, solvent resistance, and other properties of thermoplastic-modified polycyanurates.[18]

In this study, the thermomechanical properties of dicyanate–clay nanocomposite systems composed of a low-viscosity dicyanate resin and a type of organically modified clay were investigated by dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA). The effects of clay content on the thermome-

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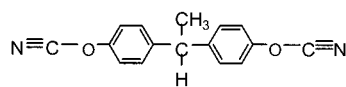
1,1-bis(4-cyanatophenyl) ethane (Arocy L-10)
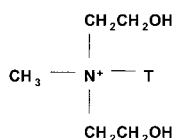
Methyl tallow bis-2-hydroxyethyl quaternary ammonium (the organic modifier)

Figure 1 Chemical structures of the dicyanate resin and the organic modifier contained in the clay (T = tallow).

chanical properties of the nanocomposites were analyzed. The effects of clay content on the glass-transition behavior of the nanocomposites were also investigated by DMA and TMA. The structures of the nanocomposites were investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis.

EXPERIMENTAL

Materials

The dicyanate resin used in this study was 1,1-bis(4-cyanatophenyl) ethane (Arocy L-10, Ciba Specialty Chemicals, Summit, NJ). The viscosity of the resin was 100 cp at room temperature. The resin was used as received without further purification. The nanosize inorganic filler used in this study was a type of organically modified clay named Closite 30B (Southern Clay Products, Inc., Gonzales, TX). The clay was somewhat organophilic because it was treated with an organic modifier, methyl tallow bis-2-hydroxyethyl quaternary ammonium, which was intercalated between silicate layers of clay. The chemical structures of the resin and the organic modifier are shown in Figure 1. The T in Figure 1, which means tallow, was predominantly an octadecyl chain with smaller amounts of lower homologues (approximate composition: 65% C18, 30% C16, and 5% C14). The basal spacing of the organically modified clay was 1.85 nm according to the XRD data obtained from the supplier.

Measurements

DMA

DMA was carried out with a DMA 2940 (TA Instruments, New Castle, DE) in a single cantilever mode to measure the thermomechanical properties of the dicyanate–clay nanocomposites. The frequency of the DMA was fixed to 1 Hz, and the heating rate was

5°C/min. The scanning temperature range was room temperature to 350°C.

At room temperature, the organically modified clay was added to the dicyanate resin, and the mixture was stirred for 1 h to produce a homogeneous mixture. The mixture was degassed in a vacuum oven to remove air bubbles trapped during stirring. By pouring the degassed dicyanate–clay mixture into a mold cavity and then curing the mixture in a hot press, we prepared each sample specimen for DMA measurements. The mold was composed of a silicon rubber spacer (35 × 13 × 3.2 mm) and two steel plates. The curing conditions were 160°C for 1 h, 180°C for 1 h, and then 200°C for 1 h. These cure conditions were determined by referral to previous results on the reaction kinetics of the dicyanate resin.[19] Each sample specimen was postcured at 300°C for 0.5 h to produce fully cured nanocomposites. The amount of the clay in the dicyanate–clay nanocomposite was varied from 0 to 5 phr.

TMA

TMA experiments were performed with a TMA 2940 (TA Instruments) with a standard probe to measure the thermal expansion behaviors and the glass-transition temperatures of the dicyanate–clay nanocomposites. We prepared disk-shaped sample specimens (diameter = 7 mm and height = 3.2 mm) by cutting the cured nanocomposite blocks produced for the DMA experiments. The force applied to fix a specimen was 0.05 N, and the heating rate was 5°C/min. The scanning temperature range was from room temperature to 350°C.

XRD

XRD analysis was performed with a XDS2000 X-ray diffractometer (Scintag, Inc., Cupertino, CA) with Cu Kα radiation (wavelength = 0.15418 nm). The scanning speed was 3°/min, and the step size was 0.02°. The surfaces of the dicyanate–clay nanocomposite specimens were smoothed for the XRD analysis.

TEM

Structural images of the dicyanate–clay nanocomposites were obtained with a Jeol-1020 transmission electron microscope (Jeol, Ltd., Tokyo, Japan). We prepared each TEM specimen by slicing nanocomposite blocks produced for the DMA experiments with an ultramicrotome (LKB 2088 Ultratome V, LKB, Stockholm, Sweden) equipped with a diamond knife (Jumdi; Juniper Ultra Micro, Stockholm, Sweden). Thin film specimens with thicknesses of about 95 nm were prepared for TEM imaging.
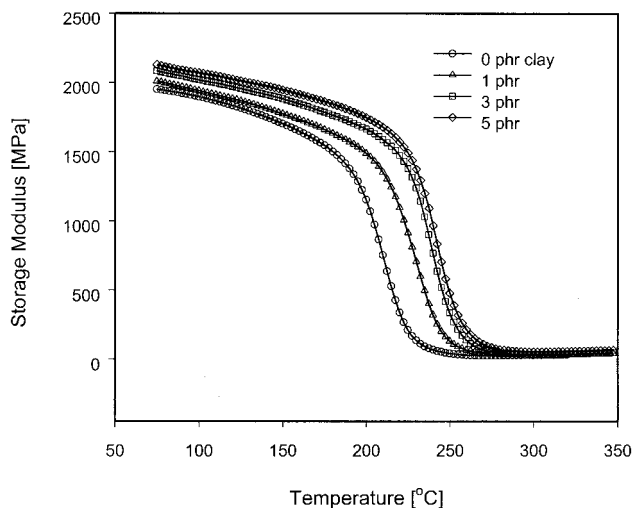
Figure 2 Storage modulus of the dicyanate–clay nanocomposites containing various clay contents.

Figure 3 Tan δ of the dicyanate–clay nanocomposites containing various clay contents.

RESULTS AND DISCUSSION

In general, DMA is performed to measure the viscoelastic properties of polymeric materials under the application of a periodic (sinusoidal) stress or strain. DMA is also valuable in the determination of the glass-transition and melting-transition temperatures of polymers. Information on the miscibility of polymer blends can be also obtained from DMA by the measurement and analysis of the glass-transition behavior of the blends.

Figure 2 shows the storage modulus of the dicyanate–clay nanocomposites containing various amounts of the clay. The storage (elastic) modulus of the nanocomposites below their glass-transition temperatures increased with increasing clay content. The glass-transition temperatures of the dicyanate–clay nanocomposites corresponded to the temperatures showing the sharpest decrease in the storage modulus curves. The glass-transition temperatures determined from the sharpest decreasing region in the storage modulus curves increased as the content of the clay was increased.

Figure 3 shows the damping factors (tan δ) of the dicyanate–clay nanocomposites containing various amounts of the clay. The damping factor increased with increasing temperature up to the glass-transition temperature and showed maximum value near the glass-transition temperature. The damping peaks shifted to a high-temperature region as the clay content was increased because the glass-transition temperature increased with increasing clay content. The height of the damping peak for the nanocomposites decreased with increasing clay content because the elastic characteristics of the nanocomposites increased with increasing clay content.
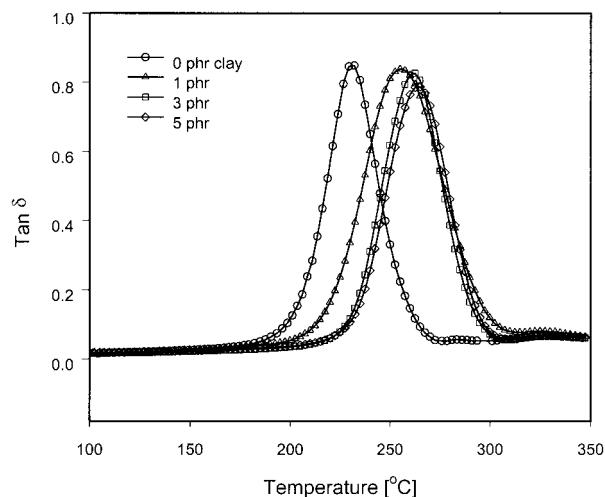
TMA was carried out to investigate the thermal expansion behavior of the dicyanate–clay nanocomposites as a function of temperature at a constant heating rate of 5°C/min. Figure 4 shows the one-dimensional (linear) dimension change of the dicyanate–clay nanocomposites as a function of temperature for various clay contents. We believe that the dimensional stability of the nanocomposites improved with increasing clay content because the slope of the TMA curves below the glass-transition temperatures decreased slightly with increasing clay content. The glass-transition temperatures of the nanocomposites could be obtained from the TMA curves because the linear (or volumetric) thermal expansion coefficient of a polymer in glassy region is smaller than that of the polymer in rubbery region. The glass-transition tem-
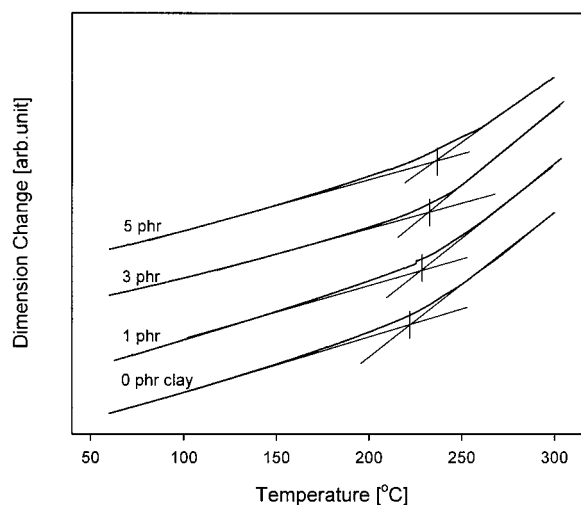

Figure 4 Dimension changes of the dicyanate–clay nanocomposites containing various clay contents.

perature of the polymer is defined as the temperature showing inflection (curves up) in the TMA curve. The inflection point is usually determined as the crossing point of the two tangent lines, one originating from below the glass-transition temperature region and the other originating from above the glass-transition temperature region. The glass-transition temperature increased with increasing clay content, and this result coincided well with the results of the glass transition behavior of the nanaocomposites obtained by DMA.

The XRD curves for the organically modified clay and the dicyanate–clay nanocomposites with various clay contents are shown in Figure 5. The strong peak at $2\theta = 4.76°$ represents the diffraction from the (001) surfaces of the silicate layers of the clay. The corresponding interlayer spacing for the peak was calculated to be 1.86 nm according to Bragg's equation.[20] This result was almost the same as that of the data (1.85 nm by XRD analysis) supplied by the supplier of the clay. No peaks were observed in the range $2\theta = 3–18°$ for the dicyanate–clay nanocomposites. This result indicates that silicate layers of the clay were either intercalated to a distance of over 3 nm or exfoliated in the dicyanate–clay nanocomposites.

A TEM micrograph of the dicyanate–clay nanocomposite containing 5 phr clay is shown in Figure 6. The dark lines correspond to each silicate layer of the clay. The micrograph shows that the interlayer spacing of silicate layers was over 3 nm. These interlayer spacings were larger than the original interlayer spacing (1.85 nm) between the silicate layers in the clay. Some individual silicate layers were well dispersed in the polycyanurate matrix. This result was almost the same to the result obtained from the XRD analysis on the interlayer spacing of the silicate layers in the dicyanate–clay nanocomposite. Along with the XRD results, Figure 6 provides additional evidence for the
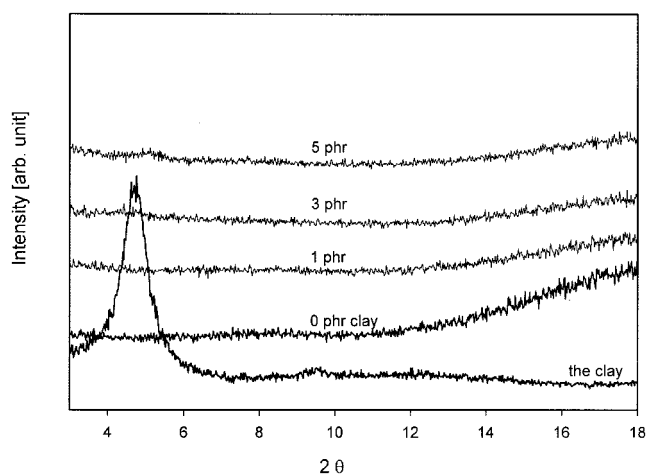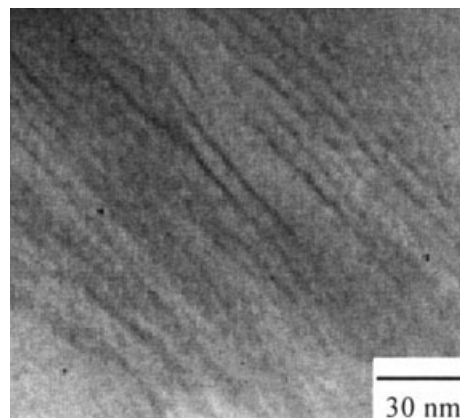

Figure 6 TEM micrographs of the dicyanate–clay nanocomposites containing 5 phr clay.

nanostructures of the dicyanate–clay nanocomposites. From both the XRD and TEM results, we believe that silicate layers of the clay were either intercalated to a distance of more than 3 nm or exfoliated in the dicyanate–clay nanocomposites.

CONCLUSIONS

The thermomechanical properties and nanostructures of the dicyanate–clay nanocomposites containing various amounts of organically modified clay were investigated. The storage moduli of the nanocomposites below their glass-transition temperatures slightly increased with increasing clay content. The height of the damping peak for the nanocomposites decreased with increasing clay content. Dimensional stability of the nanocomposites was believed to increase with increasing clay content because the slope of TMA curves decreased slightly with increasing clay content. According to the DMA and TMA results, the glass-transition temperature of the dicyanate–clay nanocomposites increased with increasing clay content. From the XRD analysis and the TEM micrograph, we showed that the silicate layers of the clay were either intercalated to a distance of more than 3 nm or exfoliated in the dicyanate–clay nanocomposites

Figure 5 XRD patterns of the clay and the dicyanate–clay nanocomposites containing various clay contents.

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