Polymer Bulletin 49, 473–480 (2003)

Polymer Bulletin

Thermally-cured and e-beam-cured epoxy layered-silicate nanocomposites

Chenggang Chen[1] (✉), David Curliss[2]

[1]University of Dayton Research Institute, 300 College Park, Dayton, OH 45469-0168, USA
[2]Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, OH 45433
E-mail: Chenggang.Chen@wpafb.af.mil, Tel: (937) 255-9066, Fax: (937) 258-8075

Received: 11 October 2002/Revised version: 22 January 2003/ Accepted: 23 January 2003

Summary

Research on nanocomposites attracted a lot of attention because of their unique nanostructure and interesting properties. Layered-silicate epoxy nanocomposites cured by traditional thermal cure processing were prepared, and the morphology was confirmed by the wide-angle x-ray diffraction, small-angle x-ray scattering and transmission electron microscopy. Layered-silicate epoxy nanocomposites could also be cured through e-beam curing. The small-angle x-ray scattering and transmission electron microscopy indicated that the e-beam-cured nanocomposites showed intercalated nanostructure. Dynamic mechanical analysis showed some improvement of the storage modulus for the nanocomposites with high T_g.

Introduction

It has been widely recognized that inorganic/organic nanocomposites, consisting of hard and soft materials synergistically intertwined, are one of the most promising research areas. Among them, the polymer layered-silicate nanocomposites have aroused particular interest in the academic and industrial fields because of the improvement of the properties of the polymeric materials at a low concentration of the layered silicates. The improved properties can include the mechanical properties, thermal stability, heat distortion temperature with reduced thermal expansion coefficient, antiflammability and barrier properties [1-6]. The extremely large surface area and the high aspect ratio of the nanosheets in the layered silicates when dispersed are the main reason for the enhancement of the properties of polymeric materials [1-4]. Polymer layered-silicate nanocomposites consist of two components: a layered silicate and an organic polymer matrix. Montmorillonite is the most often used layered silicate in polymer nanocomposites. Montmorillonite is a 2:1, mica-type layered-silicate clay mineral. It is composed of triple layered structure of an inner alumina octahedral layer sandwiched by two outer silica tetrahedral layers [1,4]. Although the montmorillonite is hydrophilic in nature, the cations in the gallery between these nanosheets can be easily exchanged with ammonium cation to make the layered silicate compatible with the polymer matrix. The dispersion and expansion of the layered silicate in the polymer matrix will determine the morphology of the nanocomposites. Intercalated and exfoliated morphology are two typical morphologies of the polymer layered-silicate nanocomposites. Our research group has successfully made a series of exfoliated organoclay aerospace epoxy nanocomposites with high T_g (~150°C) and an advanced carbon fiber-reinforced composite with aerospace epoxy nanocomposites as matrices [7-9]. The introduction of the organoclay in the aerospace epoxy resin did not increase the viscosity of the resin significantly, and the processing window is still pretty wide. The aerospace epoxy nanocomposites, which exhibited improved static and dynamic modulus, were more resistant to the solvent and reduced diffusion coefficients of the solvent, and improved survivability in extreme environments such as under oxygen plasma. This research showed that the epoxy nanocomposites could be made not only through the traditional thermal curing process with a curing agent, but also through e-beam curing without a curing agent. Radiation curing of the resin and composites by UV or e-beam has been of great interest [10-16]. An e-beam accelerator produces ionic species, free radicals and molecules in excited states. E-beam curing of epoxy resin in the presence of initiators has many advantages over the traditional thermal curing process, such as out-of-autoclave curing for composite manufacturing, much shorter curing time, lower shrinkage, lower tooling cost, improved performance, variable curing temperatures, reduction of volatile organic compounds, and elimination of the typical hazardous and sometimes carcinogenic crosslinking agents [10-13]. This is a very promising and environmentally benign means of curing. It is of great interest to cure the epoxy resin in the presence of the organoclay and to make nanocomposites through e-beam curing. However, it is generally considered that e-beam curing for the epoxy nanocomposite is impossible, because the organoclay generally contains some amount of nucleophilic nitrogen. This paper will report the preparation of the layered-silicate epoxy nanocomposite through e-beam curing.

Experimental

Materials

The resin, cure agent, chemical modifiers, and clay used in this research includes: Shell Epon 862 (a bisphenol F/epichlorohydrin-based liquid epoxy resin) and Epi-Cure curing agent W (diethyltoluenediamine, Shell), *n*-octylamine (Aldrich), hydrochloric acid (Aldrich), DPI-1 (Applied Poleramic, Inc), SNA (Southern Clay Products).

Preparation

Organoclay, SC8, was made using the following procedure. SNA (20g) was added to the mixed aqueous and ethanol solution of *n*-octylamine (2.86 g) and aqueous hydrochloric acid (1N, 22 mL). The mixture suspension was stirred at ~65°C for eight hours. The suspension was filtered, and the solid was washed with a mixture of warm water and ethanol and dried in a vacuum oven overnight. The aerospace epoxy-layered-silicate nanocomposites were prepared as follows. The desired amount of organoclay was added to the epoxy resin. The mixture was stirred at elevated temperature, while stoichiometric curing agent (100:26 Epon 862:curing agent W, wt.) was added to the mixture. The resulting mixture was cast in the mold and cured. The curing cycle for aerospace epoxy resin is as follows: heat the cast in the oven to 121°C over 30 minutes, hold at 121°C for two hours, then heat to 177°C over 30 minutes and hold for another two hours at 177°C, and finally cool to ambient temperature. The e-beam curing was performed at the National Composites Center, Kettering, Ohio. The epoxy resin was placed in a silicone mold and exposed to e-beam radiation.

Characterization

Wide-angle x-ray diffraction was performed in the Rigaku x-ray powder diffractometer. The radiation was Cu K_α with a wavelength of 1.5418 Å. The generator power was 40 kV and 150 mA, and the scan mode was continuous with a scan rate of 0.8°/min. The scan 2θ range is from 2° to 10°. The small-angle x-ray scattering of e-beam-cured nanocomposites was taken using a flat-film Statton camera on a Rigaku RU-200. The radiation was Cu K_α with a wavelength of 1.5418 Å. The power was 50 kV and 150 mA, and the exposure time was ~20 hours. The small-angle x-ray scattering of thermally-cured nanocomposites was performed on a Beamline X27C with a one-dimensional detector at National Synchrotron Light Source at the Brookhaven National Laboratory. Our previous data show that there is no difference in the results from these two different machines [7,9]. The sample for transmission electron microscopy was microtomed in a Reichert-Jung ultracut microtome and mounted on 200-mesh copper grids. Transmission electron microscopy was performed using a Phillips CM200 transmission electron microscope with a LaB_6 filament operating at 200 kV. Differential scanning calorimetry (DSC) was performed on a TA Instruments differential scanning calorimeter 2920 modulated DSC at 4°C/min with air sweep gas. Dynamic mechanical analysis was performed using a Rheometrics ARES dynamic spectrometer using torsion bar geometry at a frequency of 100 rad/sec, a strain of 0.1 percent, and a heating rate of 2°C/min.

Results and Discussion

Thermally-Cured Nanocomposites

Organoclay (SC8) was made from the treatment of sodium montmorillonite with octylammonium chloride through ion-exchange reaction. The wide-angle x-ray diffractions of the SNA and SC8 are shown in Figure 1. The interplanar spacing of SC8 was increased from 11.2 Å (original sodium montmorillonite, SNA) to 13.2 Å when the sodium cation was replaced by the octylammonium cation. SC8 was very compatible with the Epon 862 and curing agent W system. Wide-angle x-ray diffraction of 6% SC8/Epon 862/W nanocomposite shows that there is no peak in the low-angle region (up to 40 Å), Figure 1. This indicates that the interplanar spacing in the layered silicate is at least larger than 40 Å. In order to confirm the nanostructure of this nanocomposite, small-angle x-ray scattering was performed. The small-angle x-ray scattering shows there is a clear weak peak at ~130 Å, Figure 2. This indicates that some ordered structure still existed with the interplanar spacing between the

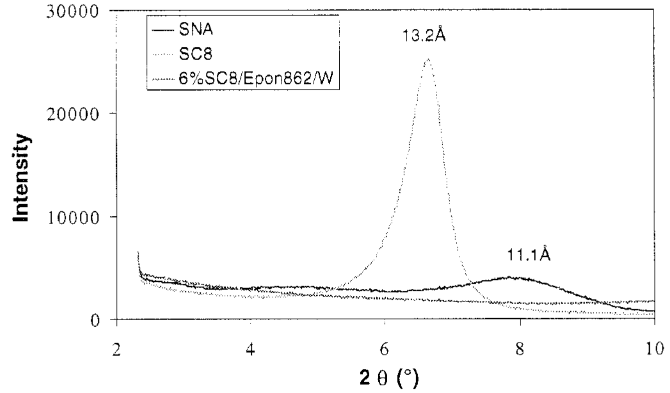

Figure 1. Wide-angle x-ray diffractions of SNA, SC8 and 6% SC8/Epon 862/W nanocomposite.

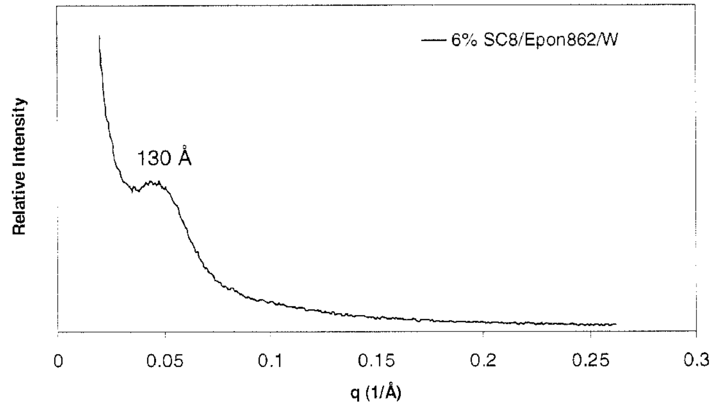

Figure 2. Small-angle x-ray scattering of 6% SC8/Epon 862/W nanocomposite.

nanosheets at ~130 Å. The interplanar spacing between the nanosheets in the gallery of the organoclay is 130 Å from the original 13.2 Å (SC8). This huge expansion of the gallery of the layered silicate is due to the compatibility of organoclay (SC8) with the epoxy resin and the penetration of the epoxy resin into the gallery of the organoclay. So, the nanosheets of the layered silicate are well dispersed in the polymer matrix. This also demonstrates that the eight-carbon chain from the organic pendent group in the organoclay is enough for wetting the surface of the silicate nanosheet to be compatible with epoxy resin. Transmission electron microscopy clearly showed the morphology of these thermally-cured polymer layered-silicate nanocomposites. The TEM image of 6% SC8/Epon 862/W is shown in Figure 3. The dark lines are cross sections of the silicate sheets of nanometer-sized thickness. The original aggregates of the silicate sheets were disrupted, and each individual sheet with nanometer-thickness was well dispersed in the epoxy resin. Some sheets are

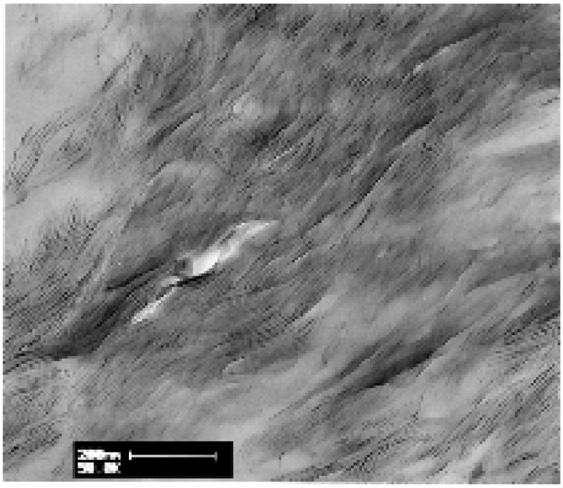

Figure 3. Transmission electron microscopy of 6% SC8/Epon 862/W nanocomposite.

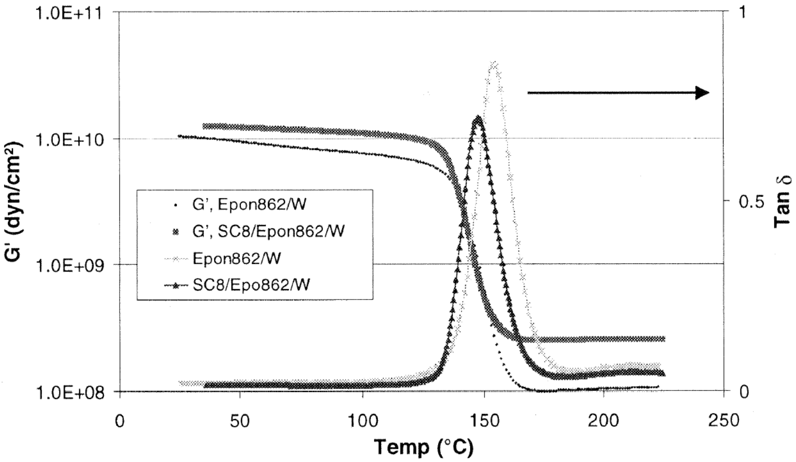

Figure 4. The storage modulus and tan δ curve of pure Epon862/W and 6% SC8/Epon862/W nanocomposite.

disordered, while others still preserve the ordered structure with more than 10 nm separations between the nanosheets, which is consistent with the SAXS results in Figure 2. Although the ideal exfoliated morphology is that the individual silicate layers are completely separated and dispersed in a continuous polymer matrix, this nanocomposite can be considered as exfoliated nanocomposite because of the well-dispersed layered-silicate in the epoxy matrix. The dynamic mechanical analysis is shown in Figure 4 and indicated that the storage modulus of the 6% SC8/Epon 862/W thermally-cured nanocomposite is increased about 25% in the glass state. Based on the tan δ curve, the glass transition temperature of the nanocomposite is decreased to 148°C compared with 153°C of the pure Epon 862/W resin.

E-beam cured nanocomposite

The initiator used for this research is DPI-1, which is diaryliodonium salt. This research found that the epoxy nanocomposite could be cured with low e-beam dosage. Three samples, Epon 862/SC8/DPI-1 (96/4/3 by wt.) (epoxy/clay/e-beam catalyst), Epon 862/DPI-1 (96/3 by wt.), and Epon 862/SC8 (96/4 by wt.), were radiated with a first e-beam dosage of 1.26 MR and continued with a second e-beam dosage to yield a total dosage of 1.45 MR. After the first e-beam radiation, both Epon 862/SC8/DPI-1 and Epon 862/DPI-1 were solidified and cured, while Epon 862/SC8 without DPI-1 was not cured at all. There was no change in the appearance of all three samples after the first e-beam radiation and after the second e-beam radiation. DSC studies show that both Epon 862/SC8/DPI-1 and Epon 862/DPI-1 have almost the same curing degree. Small-angle x-ray scattering of the e-beam-cured sample of Epon 862/SC8/DPI-1 showed that the nanocomposite has an intercalated nanostructure with an interplanar spacing of 36 Å, Figure 5.

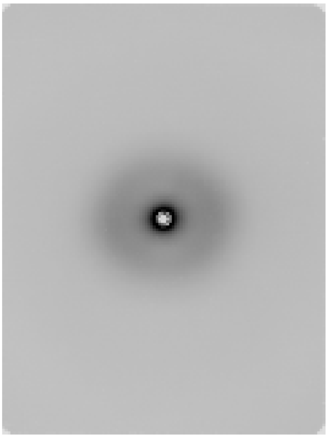

Figure 5. Small-angle x-ray scattering of SC8/Epon 862/DPI-1 (4/100/3, wt.) nanocomposite.

A TEM image of SC8/Epon 862/DPI-1 is shown in Figure 6. The dark lines are nanometer-thickness layered silicates. The TEM image shows the ordered nanolaminated structural morphology clearly and provides direct evidence of the intercalated nanostructural morphology of the e-beam-cured nanocomposite. The interplanar spacing between the nanosheets is around 4 nm, which is consistent with the data from SAXS (36 Å). The original interplanar spacing for the organoclay is 13.2 Å, and, therefore, a lot of the epoxy resin still penetrates inside the gallery of the nanoclay and expands the gallery to 36 Å. The reason why an intercalated nanocomposite is obtained instead of the exfoliated nanostructure for the e-beam curing processing is related to the kinetics of e-beam curing. The exfoliation generally took place during the curing for the thermally-cured epoxy nanocomposite [9]. However for the e-beam curing, the Epon 862 outside the gallery and inside the

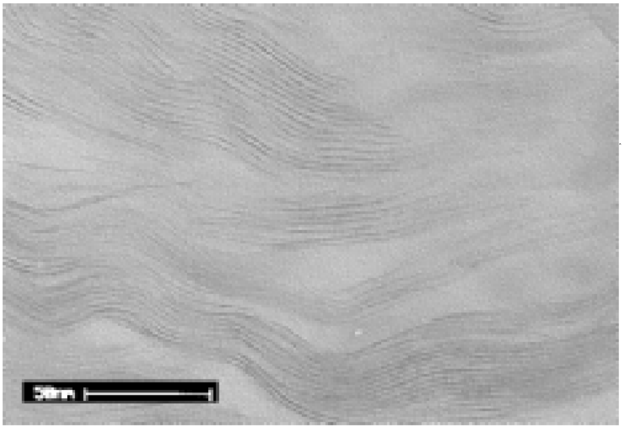

Figure 6. Transmission electron microscopy of SC8/Epon 862/DPI-1 nanocomposite.

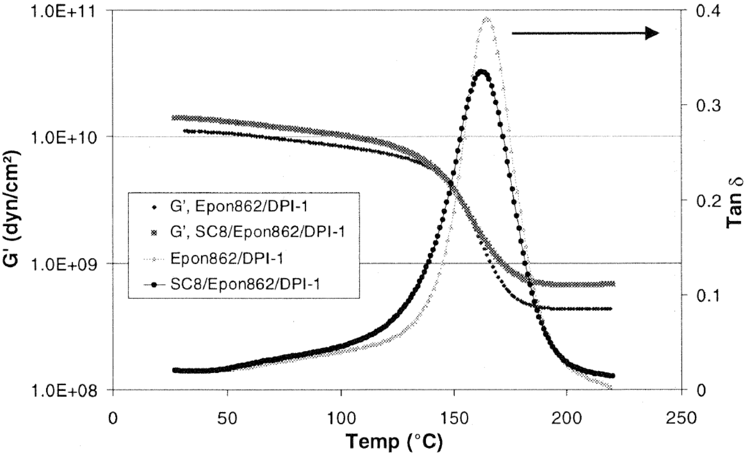

Figure 7. The storage modulus and tan δ curve of pure Epon 862/DPI-1 (control, 100:3, wt.) and SC8/Epon 862/DPI-1 (4/100/3, wt.) nanocomposite.

gallery was cured simultaneously, and the curing was so fast that the epoxy resin surrounding the nanosheets was crosslinked and rigidly fixed immediately. So there is no large expansion of the interplanar spacing of the nanosheets for the e-beam-cured nanocomposite during the e-beam curing. Differential scanning calorimetry data show a similar curing degree of the e-beam-cured Epon 862 with and without the organoclay. The dynamic mechanical analysis study for the e-beam-cured nanocomposite is shown in Figure 7. It showed that the Tg is 162°C for cured Epon 862/SC8/DPI-1 and 163°C for cured pure Epon 862/DPI-1 based on tan δ curve. The storage modulus of cured Epon 862/SC8/DPI-1 nanocomposite has increased by 30 percent in the glass state compared with cured pure Epon 862/DPI-1. The e-beam-cured nanocomposites have increased the storage modulus with almost no decrease in the glass transition temperature. More detailed research will be continued.

Conclusions

The mixture of Epon 862/curing agent W with SC8 organoclay was cured to make nanocomposites by traditional thermal curing. The eight-carbon alkyl chain in the organic pendent group attached to the nanosheet backbone appears to be enough to make the layered silicate compatible with aerospace epoxy resin. The characterization from wide-angle x-ray diffraction, small-angle x-ray scattering and transmission electron microscopy indicated an exfoliated nanostructure of SC8/Epon 862/W nanocomposites. This research also demonstrated that the layered-silicate epoxy nanocomposite could also be cured through e-beam curing, which is inspiring and promising in the field of nanocomposite and e-beam curing technology. The characterization from the small-angle x-ray scattering and transmission electron micrography showed the intercalated nanostructure of this e-beam-cured nanocomposite. Dynamic mechanical analysis showed improvement of the modulus without decrease of the glass transition temperature for the e-beam cured nanocomposite.

Acknowledgements.

This material is based in part upon the work supported by the Air Force Research Laboratory, Materials & Manufacturing Directorate (Contract No. F33615-00-D-5006), and the Air Force Office of Scientific Research

References

1. Giannelis EP (1996) Advanced Materials 8(1):29
2. LeBaron PC, Wang Z, Pinnavaia TJ (1999) Applied Clay Science 15:11
3. Alexandre M, Dubois P (2000) Materials Science and Engineering 28:1
4. Pinnavaia TJ and Beall GW (2002) Polymer-Clay Nanocomposites. John Wiley & Sons, Ltd., Chichester, UK
5. Vaia RA, Giannelis EP (2001) MRS Bull 26:394
6. Krishnamoorti R, Vaia RA (2002) Polymer Nanocomposites: Synthesis, Characterization and Modeling. ACS Symposium Series 804, American Chemical Society, Washington, DC
7. Chen C, Curliss D (2001) SAMPE J 37(5):11
8. Rice BP, Chen C, Cloos L, Curliss D (2001) SAMPE J 37(5):7
9. Chen C, Curliss D (2002) 47th International SAMPE Symposium 1074
10. Seidel JR Radiation Curing of Polymers, Randell DR ed. (1987) The Royal Society of Chemistry, London, 12
11. Lopata V, Sunders C, Singh A, Janke C, Wrenn G, Havens S (1999) Radiation Physics and Chemistry 56:405
12. Sunders C, Lopata V, Barnard J, Stepanik T (2000) Radiation Physics and Chemistry 57:441
13. Korrenev S (2001) Vacuum 62:233
14. Dabestani R, Ivanov IN, Sands JM (2002) 47th International SAMPE Symposium 51
15. Crivello JV (2002) Radiation Physics and Chemistry 63:21
16. Berejka AJ, Eberle C (2002) Radiation Physics and Chemistry 63:551