

Preparation and Properties of Bio-Based Epoxy Montmorillonite Nanocomposites Derived from Polyglycerol Polyglycidyl Ether and ϵ -Polylysine

Yoshiro Takada, Kiyomi Shinbo, Yoshihiro Someya, Mitsuhiro Shibata

Department of Life and Environmental Sciences, Faculty of Engineering, Chiba Institute of Technology, Narashino, Chiba 275-0016, Japan

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ABSTRACT: Glycerol polyglycidyl ether (GPE) and polyglycerol polyglycidyl ether (PGPE) were cured with ϵ -poly(L-lysine) (PL) using epoxy/amine ratios of 1 : 1 and 2 : 1 to create bio-based epoxy cross-linked resins. When PGPE was used as an epoxy resin and the epoxy/amine ratio was 1 : 1, the cured neat resin showed the greatest glass transition temperature (T_g), as measured by differential scanning calorimetry. Next, the mixture of PGPE, PL, and montmorillonite (MMT) at an epoxy/amine ratio of 1 : 1 in water was dried and cured finally at 110°C to create PGPE-PL/MMT composites. The X-ray diffraction and transmission electron microscopy measurements revealed that the composites with MMT content 7–15 wt % were exfoliated nanocomposites and the composite with MMT content 20 wt % was an intercalated nanocomposite. The

T_g and storage modulus at 50–100°C for the PGPE-PL/MMT composites measured by DMA increased with increasing MMT content until 15 wt % and decreased at 20 wt %. The tensile strength and modulus of the PGPE-PL/MMT composites (MMT content 15 wt %: 42 and 5300 MPa) were much greater than those of the cured PGPE-PL resin (4 and 6 MPa). Aerobic biodegradability of the PGPE-PL in an aqueous medium was \sim 4% after 90 days, and the PGPE-PL/MMT nanocomposites with MMT content 7–15 wt % showed lower biodegradability. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 479–484, 2009

Key words: nanocomposites; thermosets; renewable resources; polylysine; polyglycerol polyglycidyl ether

INTRODUCTION

Bio-based polymer products derived from annually renewable agricultural and biomass feedstock have become increasingly important as sustainable and eco-efficient products that can replace the products based exclusively on petroleum feedstock.^{1,2} As bio-based epoxy resins, epoxidized vegetable oils (EVOs) such as epoxidized soybean oil and linseed oil are industrially available in large volumes at a reasonable cost.^{3–5} EVOs currently are used as plasticizers, stabilizers, and reactive modifiers to modify the properties of other resins. Much effort had been made to improve the thermal and mechanical properties of the cured EVO resins.^{6–17} The incorporation of bio-based polymers into clay nanoplatelets would be one of the best combinations for developing environmentally benign high-performance bio-based materials. For example, the high-performance nanocomposites of EVO and alkylammonium-modified montmorillonite (MMT) had been already reported by some groups.^{8,12}

Glycerol is also an important bio-based raw material that is a triol component of triglyceride vegetable oils. Recently, glycerol also has gained much attention as a 10% byproduct of biodiesel production via the transesterification of vegetable oils.¹⁸ Glycerol-based epoxy resins such as glycerol polyglycidyl ether (GPE) and polyglycerol polyglycidyl ether (PGPE) also are industrially available and inexpensive epoxy resins that have been used in textile and paper-processing agents and as reactive diluents. However, there have been few investigations on the improvement of the thermal and mechanical properties of the glycerol-based epoxy resins.

The present study describes a bio-based nanocomposite composed of glycerol-based epoxy resins and MMT. Our attention was focused on the use of bio-based curing reagent for the bio-based epoxy resin, the formation of exfoliated nanocomposite by use of natural unmodified MMT, and the use of water as a solvent from the environmental point of view. In this study, as bio-based curing reagent, ϵ -poly(L-lysine) (PL), which is produced by aerobic bacterial fermentation using *Streptomyces albulus* in a culture medium-containing glucose, citric acid, and ammonium sulfate, was used.^{19,20} PL has been used as a food preservative,²¹ although it has not yet been

Correspondence to: M. Shibata (shibata@sky.it-chiba.ac.jp).

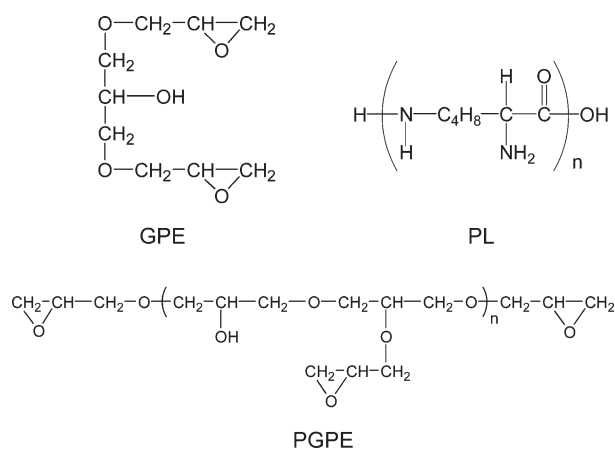


Figure 1 Structure of the reagents used in this study.

applied to the industrial polymeric materials. The chemical structure of PL is shown in Figure 1. PL differs from usual proteins in that the amide linkage is not between the α -amino and carboxylic groups in typical of peptide bonds but between the ϵ -amino and carboxyl group. The pendant α -amino groups are expected to react with epoxy groups. Because both the PL and glycerol-based epoxy resins are soluble in water and MMT is hydrophilic, environmentally benign water can be used as a mixing solvent.

EXPERIMENTAL

Materials

Figure 1 shows the structure of main components of the reagents used in this study. Glycerol polyglycidyl ether (GPE, DENACOL EX-313, total Cl 9.0 wt %) and polyglycerol polyglycidyl ether (PGPE, DENACOL EX-512, total Cl 6.5 wt %) were supplied from Nagase ChemteX, Corp. (Tokyo, Japan). The physical properties of GPE and PGPE used in this study are summarized in Table I. The epoxy harder, 25% aqueous solution of ϵ -PL (degree of polymerization 25–35), was supplied from Chisso Corporation (Tokyo, Japan). Sodium (Na^+) MMT, Kunipia F, cation exchange capacity [CEC]: 115 mequiv/100 g) was supplied by Kunimine Industries (Tokyo, Japan).

Curing reaction of PGPE or GPE with PL

To a solution of PGPE (3.00 g, epoxy group 17.7 mmol) in ion-exchanged water (27.0 g) was added a 25 wt % aqueous solution (9.08 g) of PL (amino group 17.7 mmol) and stirred for 1 h at room temperature. The homogeneous solution was poured on a poly(tetrafluoroethylene) plate and cured at 80°C for 24 h and then 110°C for 24 h to give PGPE cured with PL in epoxy/amine ratio 1/1 (PGPE-PL1) as a

pale brown sheet. The PGPE cured with PL in epoxy/amine ratio 2/1 (PGPE-PL2) and the GPE cured with PL in epoxy/amine ratio 1/1 and 2/1 (GPE-PL1 and GPE-PL2) also were prepared in a similar manner as PGPE-PL1.

Preparation of composite of PGPE-PL or GPE-PL with MMT

A mixture of MMT (0.363 g) and ion-exchanged water (11.7 g) was stirred for 24 h at room temperature. The obtained MMT suspension was added to a solution of PGPE (2.91 g, epoxy group 17.2 mmol) in ion-exchanged water (26.2 g), the mixture was stirred for 24 h at room temperature, and then a 25 wt % aqueous solution (8.80 g) of PL (amino group 17.2 mmol) was added and stirred for 1 h at room temperature. The obtained mixture was poured on a poly(tetrafluoroethylene) plate and cured at 80°C for 24 h and then 110°C for 24 h to create a PGPE-PL1/MMT composite with a MMT content of 6.6 wt % (PGPE-PL1/M7). The PGPE-PL1/MMT composites with MMT contents of 10.8, 14.7, and 20.3 wt % (PGPE-PL1/M11, PGPE-PL1/M15, and PGPE-PL1/M20, respectively) also were prepared in a similar manner with PGPE-PL1/M7.

Measurements

Fourier transform infrared (FTIR) spectra were recorded on a FTIR 8100 (Shimadzu, Kyoto, Japan) by the KBr-pellet or attenuated total reflectance (ATR) method. The differential scanning calorimetry (DSC) was performed on a Diamond DSC (Perkin-Elmer Japan, Yokohama, Japan) in a nitrogen atmosphere at a heating rate of 10°C/min. Dynamic mechanical analysis (DMA) of the rectangular films (length 35 mm, width 6 mm, thickness 0.3 mm) was performed on a Rheograph Solid (Toyo Seiki, Tokyo, Japan) with a chuck distance of 20 mm, a frequency of 10 Hz, and a heating rate of 2°C/min. X-ray diffraction (XRD) analysis was performed at ambient temperature on a RINT-2100 X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) at a

TABLE I
Physical Properties of Glycerol-Based Epoxy Resins Used in This Study

Compound (abbreviation)	Epoxy functionality	Epoxy equivalent weight (g/equiv)	Viscosity (cps, 25°C)
Glycerol polyglycidyl ether (GPE)	2.0	140	150
Polyglycerol polyglycidyl ether (PGPE)	4.1	169	1300

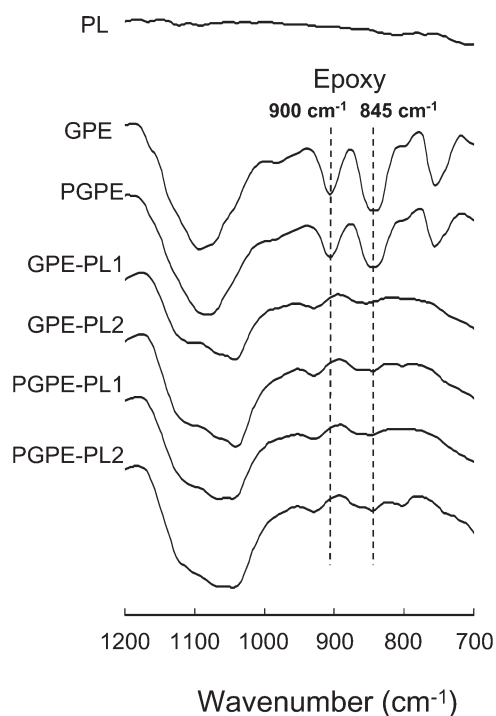


Figure 2 FTIR spectra of reagents and cured epoxy resins.

scanning rate of $2.0^{\circ}/\text{min}$, with the use of $\text{Cu K}\alpha$ radiation (wavelength, $\lambda = 0.154 \text{ nm}$) at 40 kV and 14 mA. Tensile tests of the rectangular films with the same size as the DMA measurement were performed at 25°C with an Autograph AG-I (Shimadzu, Kyoto, Japan) based on the standard method for testing the tensile properties of plastics (JIS K7113-1995). Span length was 20 mm and the testing speed was 10 mm/min. Five specimens were tested for each set of samples, and the mean values and the standard deviation were calculated. Biodegradability was determined according to JIS K6950-2000 (ISO 14851-1999) by measuring a biochemical oxygen demand (BOD) in the aerobic aqueous medium containing activated sludge. Phosphate buffer (pH 7.4, 200 mL) containing 0.25 mM CaCl_2 , 0.09 mM MgSO_4 , 0.09 mM NH_4Cl , and 0.9 μM FeCl_3 was mixed in a glass bottle. To the mixture, 4.35 mL of activated sludge containing 30 mg insoluble part, which was obtained from sewerage facilities of Chiba Institute of Technology, and 20 mg of the sample pulverized after immersion in liquid nitrogen were added. The dispersion was steadily stirred with a magnetic stir bar. BOD was measured at 25°C by the use of a BOD tester 200F (Taitec Corporation, Koshigaya, Saitama, Japan). Carbon dioxide was absorbed into 50% sodium hydroxide aqueous concentrate in a cup equipped within the glass bottle. The volume of the consumed oxygen was directly measured with a scaled cylinder. Transmission electron microscopy (TEM) was performed on a H-500 electron micro-

scope (Hitachi High-Technologies Corporation, Tokyo, Japan) with a 100 kV accelerating voltage. The films were sectioned into roughly 120-nm thin sections at -70°C with an ultramicrotome with a diamond knife and then mounted on 200-mesh copper grids.

RESULTS AND DISCUSSION

Characterization of the cured products of glycerol-based epoxy resins and PL

The average functionality of epoxy groups per molecule of glycerol-based epoxy resins GPE and PGPE are 2.0 and 4.1, respectively (Table I). As a bio-based curing reagent, PL, which has 25–35 pendant primary amino groups per molecule, was used. Because all the reagents are soluble in water, the epoxy resin and PL were mixed in water in epoxy/amine molar ratio of 1 : 1 and 2 : 1 and cured finally at 110°C . Figure 2 shows the FTIR spectra over the wavelength range of $1200\text{--}700 \text{ cm}^{-1}$ for the reagents and the obtained cured resins. In the spectra of GPE and PGPE, the absorption peaks characteristic to epoxy ring are observed at 900 and 845 cm^{-1} . These peaks almost disappeared for the cured products (GPE-PL1, PGPE-PL1) with an epoxy/amine ratio of 1 : 1. However, although the theoretical stoichiometry of the epoxy/amine ratio is 2 : 1, the peaks related to epoxy ring remain slightly in the spectra of the cured products (GPE-PL2, PGPE-PL2) with epoxy/amine ratio of 2 : 1. It is considered that the secondary amino-group formed by the reaction of one epoxy and one amino group is sterically hindered and is hard to react with the second epoxy group. Also, the absorption peak caused by the $\text{C}=\text{O}$ stretching of the peptide bond was observed at 1630 cm^{-1} for the cured resins, in a similar manner to PL, suggesting that the peptide bond is retained even after the curing reaction at 110°C .

Table II summarizes the T_g measured by DSC for the cured resins. The GPE-PL1 and PGPE-PL1 showed greater T_g than GPE-PL2 and PGPE-PL2, respectively. The result, that the resin cured with the epoxy/amine ratio of 1 : 1 has greater T_g than the 2 : 1 cured resin, suggests that the former has greater cross-linking density than the latter, which is in

TABLE II
 T_g Measured by DSC for the Cured Resins

Sample abbreviation	Epoxy/amine molar ratio	T_g [DSC] ($^{\circ}\text{C}$)
GPE-PL1	1.0/1.0	37
GPE-PL2	2.0/1.0	33
PGPE-PL1	1.0/1.0	47
PGPE-PL2	2.0/1.0	35

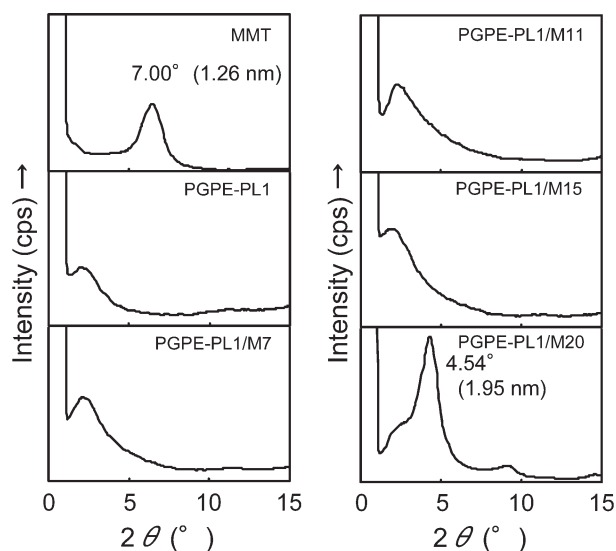


Figure 3 XRD charts of MMT and PGPE-PL1/MMT composites.

agreement with our FTIR results. When the cured resins with the same epoxy/amine ratio are compared, the PGPE-PL had greater T_g than the GPE-PL. This result is attributed to greater epoxy functionality of PGPE than GPE.

Characterization of PGPE-PL1/MMT composites

To improve the thermal and mechanical properties of the glycerol-based epoxy resin cured with PL, the composites with MMT were prepared. For this purpose, the combination of PGPE and PL in an epoxy/amine ratio of 1 : 1 (PGPE-PL1), which showed the highest T_g among the cured glycerol-based epoxy resins, was adopted. In the preparation of the polymer-layered silicate nanocomposites, long chain alkylammonium-modified MMTs often are used because the matrix polymer is generally hydrophobic. However, because both PGPE and PL are soluble in water, hydrophilic sodium MMT was used in this study. The XRD charts of the PGPE-PL1/MMT composites prepared by mixing of PGPE, PL, and MMT in water and subsequent curing at 110°C are shown in Figure 3. For PGPE-PL1/MMT composites with an MMT content of 7–15 wt %, there appeared no XRD peak other than the peak around $2\theta = 2.3^\circ$ observed in PGPE-PL1, suggesting the formation of exfoliated nanocomposites. However, the PGPE-PL1/M20 showed a couple of strong and weak peaks at 4.54° and 9.10° corresponding to the [001] and [002] planes of the MMT aluminosilicate. From the angular location of the peaks and Bragg condition, the interlayer distance (d) is calculated to be 1.95 nm. The value is higher than the interlayer distance of MMT (1.26 nm), suggesting the formation of intercalated nanocomposite.

Figure 4 shows the TEM images of PGPE-PL1/M7 and PGPE-PL1/M20. It is obvious that exfoliated nanocomposite where MMT homogeneously distributed is formed for PGPE-PL1/M7. However, aggregated clay platelets where matrix resins are intercalated are observed for PGPE-PL1/M20, indicating that the MMT content is too large to be a homogeneous exfoliated nanocomposite. These results are in agreement with the XRD data.

Properties of PGPE-PL1/MMT composites

Table III summarizes the T_g measured by DMA and 5% weight loss temperature (T_d) measured by TGA for the PGPE-PL1/MMT composites. Both the T_g and T_d increased with increasing MMT content until 14.7% and decreased at 20.3%. The improvement of heat resistance is attributed to the restriction of molecular motion by the formation of exfoliated nanocomposite. The low T_g and T_d of PGPE-PL1/M20 is related to the aggregation of clay platelets and/or the hindrance of the reaction of epoxy and amine caused by the presence of excess clay.

Figure 5 shows DMA curves of PGPE-PL1/MMT composites. Although the improvement of storage modulus (E') at -20 to 20°C corresponding to the glassy state of the composites were not so large, the E' at around 60 – 120°C corresponding to the rubbery state increased with increasing MMT content. The E' below 60°C of PGPE-PL1/M20 was lower than that of PGPE-PL1/M15.

Figure 6 shows the tensile properties at 25°C for the PGPE-PL1/MMT composites. In agreement with

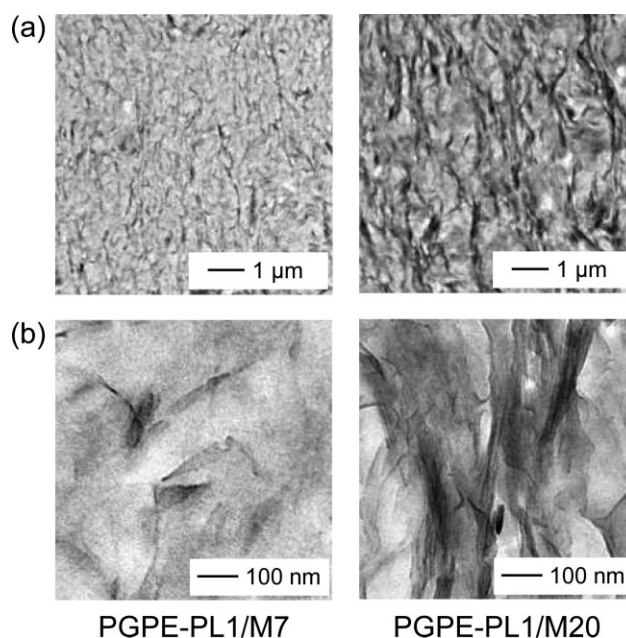


Figure 4 TEM images of PGPE-PL1/M7 and PGPE-PL1/M20: (a) low magnification and (b) high magnification.

TABLE III
Thermal Properties of PGPE-PL1/MMT Nanocomposites

Sample abbreviation	MMT content (wt %)	T_g [DSC] (°C)	T_g [DMA] (°C)	5% weight loss temperature (°C)
PGPE-PL1	0	47	58	298
PGPE-PL1/M7	6.6	58	62	312
PGPE-PL1/M11	10.8	59	66	317
PGPE-PL1/M15	14.7	56	73	322
PGPE-PL1/M20	20.3	34	44	316

the result of DMA, the tensile modulus increased with increasing MMT content in the range of 0–14.7% and decreased at 20.3%. The prominent improvement by the addition of MMT is attributed to the reinforcement effect due to homogeneously distributed clay platelets and the restriction of molecular motion of the polymers bound between silicate layers. The latter factor results in the change from a soft polymer to a rigid polymer due to a transition from rubbery state to glassy state of the samples at the measurement temperature 25°C. Regarding tensile strength, clear tendency on MMT content was not elucidated because the error bar was large. However, all the nanocomposites had considerably greater tensile strength than the PGPE-PL1 without MMT. The addition of MMT more than 7 wt % resulted in a decrease of tensile strength. The increase of MMT content for exfoliated nanocomposite causes an increase of the interface between clay and matrix polymer, resulting in a decrease of tensile strength due to the interfacial delamination. The tensile modulus and strength of PGPE-PL1/M7 (2.3 GPa, 43 MPa) are almost comparable to those of the bisphenol A diglycidyl ether cured with diethylene triamine (2.1 GPa, 69 MPa).²²

Figure 7 shows biodegradability by measuring BOD in the aerobic aqueous medium containing activated sludge for the PGPE-PL1 and PGPE-PL1/

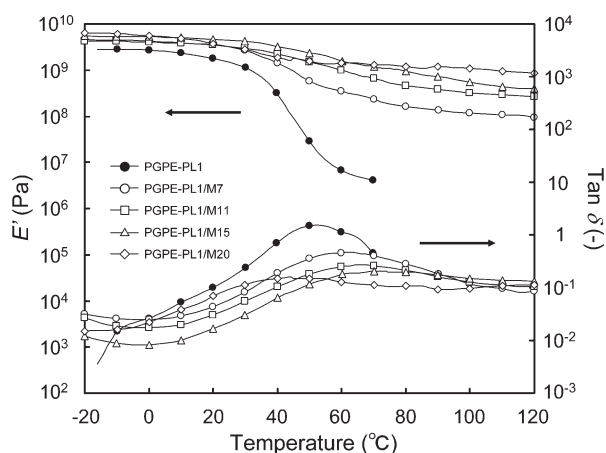


Figure 5 Temperature dependency of E' and $\tan \delta$ for PGPE-PL1/MMT composites.

MMT nanocomposites. Biodegradability after 90 days of PGPE-PL1 resin was ca. 4%. The biodegradability of PGPE-PL1/MMT composites decreased with increasing MMT content until 14.7 wt %, probably as the result of the interference of substance diffusion by the formation of exfoliated nanocomposites. On the other hand, PGPE-PL1/M20 showed a little higher biodegradability than PGPE-PL1. It is considered that a high water uptake in the

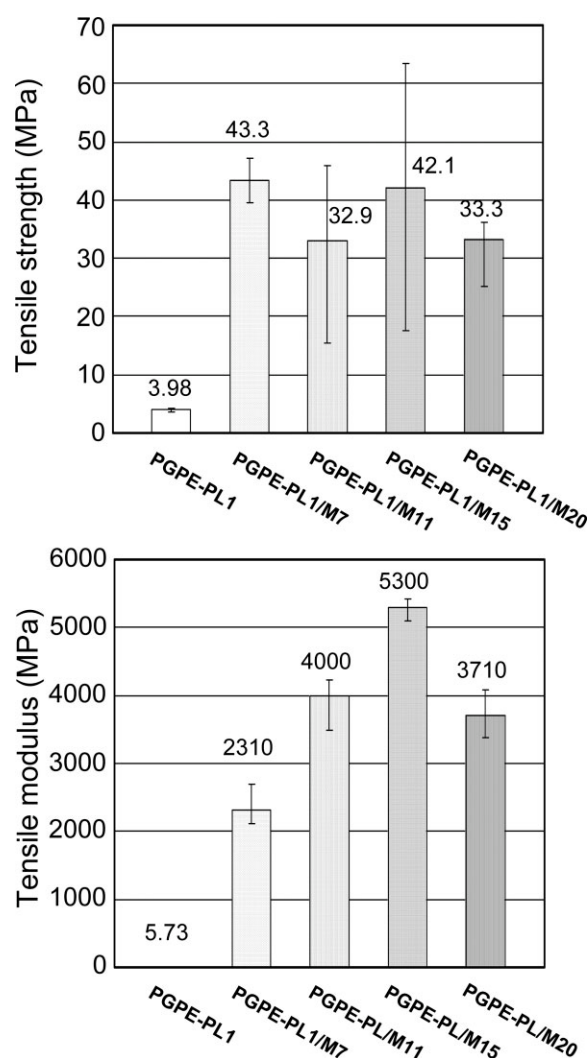


Figure 6 Tensile properties of PGPE-PL1 and PGPE-PL1/MMT composites.

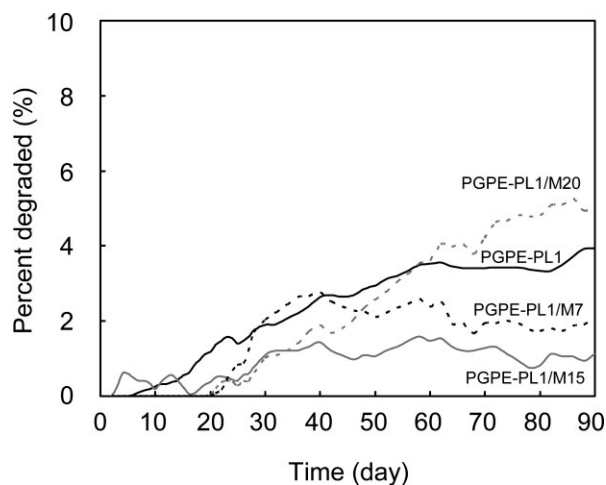


Figure 7 Biodegradability measured by BOD in an aqueous media containing activated sludge for PGPE-PL1 and PGPE-PL1/MMT composites.

aggregated part of intercalated clay platelets of PGPE-PL1/M20 as was shown in the TEM image is related to the enhancement of biodegradation.

CONCLUSIONS

Glycerol-based epoxy resins, GPE and PGPE, were cured with PL at 110°C in an epoxy/amine ratio of 1 : 1 and 2 : 1. When PGPE was used as an epoxy resin and the epoxy/amine ratio is 1 : 1, the cured neat resin showed the greatest T_g measured by DSC. Next, the nanocomposites of PGPE, PL, and MMT were prepared by the cross-linking reaction of PGPE with PL at 110°C in an epoxy/amine ratio of 1 : 1 in the presence of MMT. The XRD and TEM observations revealed that the composites with MMT content not more than 15% are exfoliated nanocomposites and the composite with MMT content 20 wt % is an intercalated nanocomposite. The T_g and storage modulus at 50–100°C measured by DMA for the PGPE-PL1/MMT composites increased with increasing MMT content until 15 wt % and decreased at 20 wt % because of the aggregation of clay platelets. The tensile strength and modulus of PGPE-PL1/M15 (42 MPa and 5.3 GPa) were much greater than those of PGPE-PL1 (4 and 6 MPa). The tensile moduli of the PGPE-PL1/MMT nanocomposites were greater than that of the bisphenol A digly-

cidyl ether cured with a polyamine (2.1 GPa). Aerobic biodegradability of the PGPE-PL1 in an aqueous medium was about 4% after 90 days, and the PGPE-PL1/MMT nanocomposites with MMT content 7–15 wt % showed lower biodegradability. Consequently, the PGPE-PL1/MMT nanocomposites were high-performance bio-based materials which do not need any organic solvents and reagents in the preparation.

References

- Kaplan, D. L. *Biopolymers from Renewable Resources*; Springer-Verlag: Berlin, 1998.
- Mohanty, A. K.; Misra, M.; Hinrichsen, G. *Macromol Mater Eng* 2000, 276, 1.
- Swern, D.; Billen, G. N.; Findley, T. W.; Scanlan, J. T. *J Am Chem Soc* 1945, 67, 1786.
- Meffert, A.; Kluth, H. U.S. Pat. 4,886,893 (1989).
- Güner, F. S.; Yağı, Y.; Erciyes, A. T. *Prog Polym Sci* 2006, 31, 633.
- Park, S. J.; Jin, F. L.; Lee, J. R. *Macromol Rapid Commun* 2004, 25, 724.
- Miyagawa, H.; Misra, M.; Drzal, L. T.; Mohanty, A. K. *Polym Eng Sci* 2005, 45, 487.
- Miyagawa, H.; Misra, M.; Drzal, L. T.; Mohanty, A. K. *Polymer* 2005, 46, 445.
- Zhu, J.; Chandrashekhara, K.; Flanigan, V.; Kapila, S. *J Appl Polym Sci* 2004, 91, 3513.
- Tamami, B.; Sohn, S.; Wilkes, G. L. *J Appl Polym Sci* 2004, 92, 883.
- Tsujimoto, T.; Uyama, H.; Kobayashi, S. *Macromol Rapid Commun* 2003, 24, 711.
- Uyama, H.; Kuwabara, M.; Tsujimoto, T.; Nakano, M.; Usuki, A.; Kobayashi, S. *Chem Mater* 2003, 15, 2492.
- Petrovic, Z. S.; Zhang, W.; Miller, R.; Javni, I. *Soc Plast Eng Ann Tech Conf* 2002, 60, 743.
- Gerbace, A. E.; Petzhold, C. L.; Costa, A. P. O. *J Am Oil Chem Soc* 2002, 79, 797.
- Raghavachar, R.; Sarnecki, G.; Baghdachi, J.; Massingill, J. *J Coat Technol* 2000, 72, 125.
- Warth, H.; Muelhaupt, R.; Hoffmann, B.; Lawson, S. *Angew Makromol Chem* 1997, 249, 79.
- Roesch, J.; Muelhaupt, R. *Polym Bull* 1993, 31, 679.
- Haas, M. J.; McAloon, A. J.; Yee, W. C.; Foglia, T. A. *Bioresour Technol* 2006, 97, 671.
- Kahar, P.; Kobayashi, K.; Kojima, M.; Okabe, M. *J Biosci Bioeng* 2002, 93, 274.
- Kahar, P.; Iwata, T.; Hiraki, J.; Park, E. Y.; Okab, E. M. *J Biosci Bioeng* 2001, 91, 190.
- Kamioka, H. N. *Food Ind* 1993, 35, 23.
- Asp, L. E.; Berglund, L. A.; Gudmundson, P. *Compos Sci Technol* 1995, 53, 27.