

Effective Preparation and Characterization of Montmorillonite/Poly(ϵ -caprolactone)-Based Polyurethane Nanocomposites

Eun Hwan Jeong,¹ Jie Yang,¹ Han Sup Lee,¹ Seung Won Seo,² Du Hyun Baik,³ Jeonghan Kim,⁴ Ji Ho Youk⁵

¹Department of Advanced Fiber Engineering, Division of Nano-Systems, Inha University, Incheon 402-751, Republic of Korea

²R&D Center for Fibers and Textiles, Hyosung Co., Anyang 431-080, Republic of Korea

³Department of Textile Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea

⁴Chemicals Research Institute, Kolon Central Research Park, Yongin-city 446-797, Republic of Korea

⁵Department of Advanced Fiber Engineering, and Intelligent Textile System Research Center, Inha University, Incheon 402-751, Republic of Korea

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ABSTRACT: In this study, montmorillonite (MMT)/poly(ϵ -caprolactone)-based polyurethane cationomer (MMT/PCL-PUC) nanocomposites were prepared and their mechanical properties, thermal stability, and biodegradability were investigated. PCL-PUC has 3 mol % of quaternary ammonium groups in the main chain. The MMT was successfully exfoliated and well dispersed in the PCL-PUC matrix for up to 7 wt % of MMT. The 3 mol % of quaternary ammonium groups facilitated exfoliation of MMT. The 1 wt % MMT/PCL-PUC nanocomposites showed enhanced tensile properties relative to the pure PCL-PU. As the MMT content increased in the MMT/PCL-PUC nanocomposites, the degree of microphase separation of PCL-PUC decreased

because of the strong interactions between the PCL-PUC chains and the exfoliated MMT layers. This resulted in an increase in the Young's modulus and a decrease in the elongation at break and maximum stress of the MMT/PCL-PUC nanocomposites. Biodegradability of the MMT/PCL-PUC nanocomposites was dramatically increased with increasing content of MMT, likely because of the less phase-separated morphology of MMT/PCL-PUC. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 803–809, 2008

Key words: poly(ϵ -caprolactone) (PCL); polyurethane cationomer (PUC); montmorillonite (MMT); nanocomposites; exfoliation; hydrolytic degradation

INTRODUCTION

Recently, montmorillonite (MMT)/polyurethane (PU) nanocomposites have been extensively studied in efforts to improve the properties of the PU and thereby extend its application fields.^{1–8} The key step in polymer nanocomposite technology is exfoliation of the individual MMT layers.⁹ For preparation of MMT/polymer nanocomposites, organically modified MMT (O-MMT) has been widely used. O-MMT is usually synthesized by introducing cationic organic modifiers such as alkylammonium or alkylphosphonium between MMT layers by a cationic-exchange reaction. These cationic organic modifiers improve the exfoliation of the MMT layers, thereby resulting in enhanced thermal and mechanical prop-

erties of the MMT/polymer nanocomposites. In our previous study,¹⁰ poly(tetramethylene oxide)-based polyurethane cationomer (PTMO-PUC) containing 3 mol % of quaternary ammonium groups was synthesized and MMT/PTMO-PUC nanocomposites were prepared. It was found that the introduction of small amounts of cationic groups in the main chain of the matrix polymer is a very useful approach for the preparation of MMT/polymer nanocomposites.

Biodegradable polyurethanes are an important class of biomaterials due to their excellent physical properties and relatively good biocompatibility.¹¹ Their mechanical properties and biodegradability can be tailored by varying the chemistry and molecular weight of their components for different applications. Biodegradable polyurethanes are generally synthesized by incorporating soft segments susceptible to hydrolysis, such as poly(ϵ -caprolactone) (PCL), poly(alkylene adipate), poly(lactide), and poly(glycolide).^{12–19} Among these biodegradable polyurethanes, PCL-based PUs (PCL-PUs) has been the most widely studied. They are of particular note because the PCL soft segment possesses a particularly high moduli

Correspondence to: J. H. Youk (youk@inha.ac.kr).

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and an ultimate tensile stress, and a relatively slow degradation rate *in vitro*.^{17–19} Therefore, there is strong motivation to develop MMT/PCL-PU nanocomposites to extend the application fields of PCL-PU. In the present study, PCL-PU cationomer (PCL-PUC) containing 3 mol % of quaternary ammonium groups was synthesized and used as a matrix polymer of MMT nanocomposites. The effects of using small amounts of cationic groups on the exfoliation of MMT and resulting mechanical properties, thermal stabilities, and biodegradability of the MMT/PCL-PUC were investigated. The effect of exfoliated MMT layers on the biodegradability of MMT/biodegradable polymer nanocomposites has not been extensively studied thus far. In the case of MMT/poly(L-lactide) (PLLA) nanocomposite scaffolds, it was reported that they showed faster biodegradation than pristine PLLA.^{20,21} The MMT layers increased the nucleation density of the PLLA and subsequently decreased its glass transition temperature and degree of crystallinity, which resulted in an enhanced PLLA biodegradation rate. It is anticipated that the biodegradability of the MMT/PCL-PUC nanocomposites will be affected by both the content and the extent of exfoliation of MMT.

EXPERIMENTAL

Materials

PCL ($M_n \approx 1250$), 4,4'-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BD), *N*-methyldiethanolamine (MDEA), dibutyltin dilaurate, iodomethane, *N,N*-dimethyl formamide (DMF), and tetrahydrofuran (THF) were purchased from Aldrich and used as received. Cloisite-30B, to be used as an organically modified MMT (O-MMT), was purchased from Southern Clay. The PCL and Cloisite-30B were dried overnight at 90°C to remove the moisture prior to their use.

Synthesis of PCL-PUC

For the synthesis of PCL-PU, a two-step procedure was used. In the first step, isocyanate-terminated prepolymers were synthesized by reacting PCL with an excess of MDI at 50°C for 1.5 h under a nitrogen atmosphere. In the second step, dibutyltin dilaurate was added to the prepolymers as a catalyst. A chain extension reaction of the prepolymers was carried out by dropping BD and MDEA dissolved in DMF onto the prepolymers. The reaction temperature was slowly raised to 80°C for 2 h with stirring. The subsequent molar ratio of MDI/BD/MDEA/PCL was 4.0/2.76/0.24/1.0. For the synthesis of the PCL-PUC, additional quaternization of the PCL-PU main chains was carried out by introducing 1.0 equiv. of iodome-

thane for 1.0 equiv. of MDEA. The cationic content in PCL-PUC was 3 mol % (the theoretical molar ratio of $[N^+]/[N^0] = 3\%$). The final chemical structure of the PCL-PUC is shown in Scheme 1.

Preparation of MMT/PCL-PU and MMT/PCL-PUC nanocomposites

Both MMT/PCL-PU and MMT/PCL-PUC nanocomposites were prepared via solution blending. For the preparation of the MMT/PCL-PU nanocomposites, PCL-PU was dissolved in DMF at a concentration of 0.1 g/mL. A predetermined amount of Cloisite-30B was dispersed in 50 mL of DMF and ultra-sonicated for 1.5 h. This dispersion was added to the PCL-PU solution and stirred at 50°C for 2 h. The resulting MMT/PCL-PU solution was poured into a glass dish and dried slowly at 45°C. The thickness of the resulting PU nanocomposite films ranged from 0.6 to 0.8 mm. The contents of O-MMT were 1, 3, 5, and 7 wt %.

Hydrolytic degradation tests

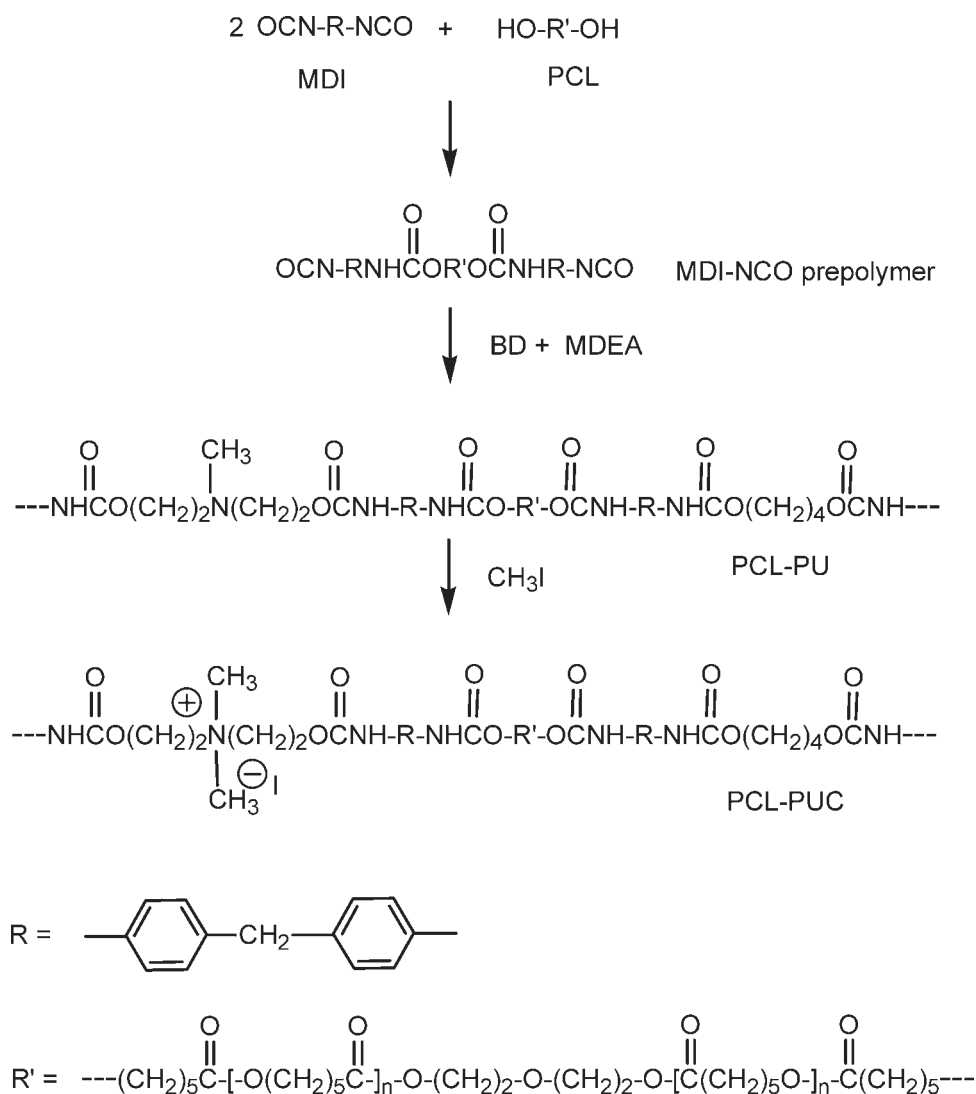
Hydrolytic degradation of the MMT/PCL-PU and the MMT/PCL-PUC nanocomposites was carried out in a 3% NaOH solution at 37°C. Nanocomposite films with dimensions of $20 \times 20 \times 1 \text{ mm}^3$ were placed in a 3% NaOH solution. After a predetermined time, the hydrolytically degraded nanocomposite film was removed, washed with distilled water, and completely dried in a vacuum oven at 25°C. The degree of degradation was determined from the weight loss:

$$\text{Weight loss (\%)} = \frac{W_o - W_t}{W_o} \times 100 \quad (1)$$

where W_o is the dry weight before degradation and W_t is the dry weight at time t .

Characterization

The molecular weight of the base PU was determined by Gel Permeation Chromatography (Young Lin SP930D solvent delivery pump, RI750F refractive index detector). THF was used as an eluent at a flow rate of 1.0 mL/min at 40°C. Three columns of highly crosslinked polystyrene-divinylbenzene microspheres (PLGel; Polymer Laboratories) with pore sizes of 10^3 , 10^4 , and 10^5 \AA were used for separation. Polystyrene standards were used for calibration. A wide angle X-ray scattering (WAXS) analysis was carried out using a Rigaku DMAX-2500 diffractometer to measure the d -spacing of MMT. Each sample was scanned from $2\theta = 1\text{--}10^\circ$ at a scan rate of $0.01^\circ/\text{min}$. The wavelength of the X-ray beam was 0.154 nm (Cu $K\alpha$ radiation). Transmission electron microscope (TEM)



Scheme 1 Synthesis route for PCL-PUC.

images of the PU nanocomposites were obtained using a transmission electron microscope (Philips CM 200) with an operating voltage of 120 kV. The TEM specimens were prepared using a MTX ultramicrotome with a cryogenic system. Tensile tests were performed using an Instron (Hounsfield, H10K-S) UTM according to ASTM D 638. All of the samples were punched out using an ASTM D 638 type-IV die. The crosshead speed was 25 mm/min. A thermogravimetric analysis was performed with a TGA-50 (Shimadzu) at a heating rate of 20°C/min in a temperature range from 50 to 600°C. Small angle X-ray scattering (SAXS) measurements were performed using a Rigaku DMAX-2500 diffractometer. The experiments were carried out at room temperature using Cu K α radiation ($\lambda = 0.154$ nm, wavelength), operating at 40 kV and 200 mA. Each scan was recorded in a range of $2\theta = 0.08\text{--}2^\circ$ in step-by-step mode with increments of 0.01° . The absolute intensity data are presented as a function of the

magnitude of the scattering vector, q , where $q = 4\pi\sin\theta/\lambda$ and 2θ is the scattering angle.

RESULTS AND DISCUSSION

Chen et al.²² first prepared MMT/PCL-PU nanocomposites. They synthesized PCL prepolymers containing MMT and used them as chain extenders during the polymerization of PCL-PU. The MMT layers in the MMT/PCL-PU nanocomposites were fully exfoliated. However, unfortunately, the molecular weight of the PCL-PU decreased as the amount of the PCL prepolymers containing MMT increased, possibly due to the formation of a microgel of the PCL prepolymers during polymerization of the PCL-PU. However, in the present study, high molecular weight PCL-PU was first synthesized and then MMT nanocomposites were prepared by a solution intercalation method. The molecular weight and polydis-

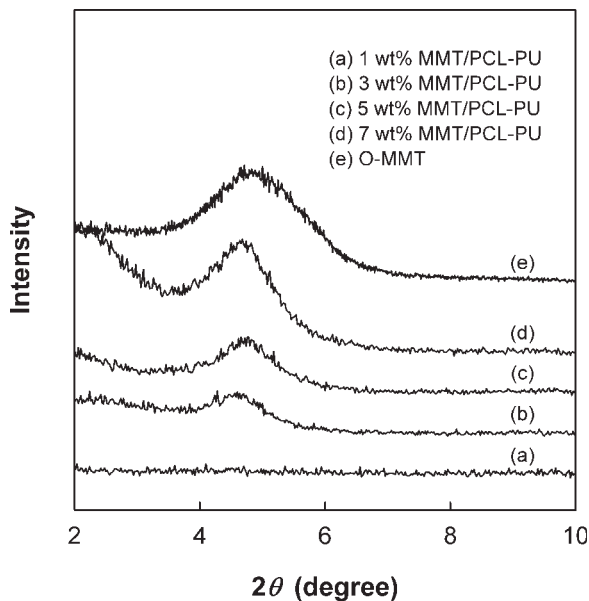


Figure 1 WAXD patterns of Cloisite-30B and the MMT/PCL-PU nanocomposites.

persity index of the PCL-PU were 35,000 g/mol and 1.90, respectively.

Figure 1 shows the WAXD patterns of O-MMT and the MMT/PCL-PU nanocomposites. The pristine O-MMT showed a (001) diffraction peak at 4.8° (d -spacing between the silicates in MMT ~ 1.85 nm). Generally, the d -spacing of organoclay in polymer nanocomposites depends on the method of preparing the nanocomposites and the interaction between the polymer matrix and the organoclay. This diffraction peak disappeared only for the 1 wt % MMT/

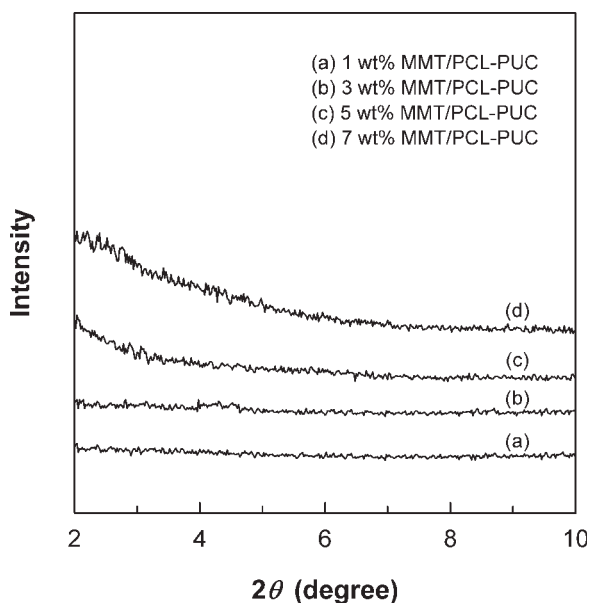


Figure 2 WAXD patterns of the MMT/PCL-PUC nanocomposites.

PCL-PU nanocomposite, indicating that the MMT was successfully exfoliated at a MMT content of 1 wt %. Figure 2 shows the WAXD patterns of the MMT/PCL-PUC nanocomposites. For all of the MMT/PCL-PUC nanocomposites, the diffraction peak completely disappeared, implying that most of the MMT was successfully exfoliated and well dispersed in the PCL-PUC matrix. The exfoliation and dispersion of the MMT layers in the PCL-PUC matrix was dramatically enhanced by the quaternary ammonium groups in the PCL-PUC main chain. Figure 3 shows the TEM image of the 7 wt % MMT/PCL-PUC nanocomposites. The MMT layers were well exfoliated and distributed within the MMT/PCL-PUC nanocomposites up to 7 wt % of MMT. In practice, quaternary ammonium groups in the PCL-PUC could be tethered to the MMT layers.

The effect of the well-exfoliated MMT layers on the tensile properties of PCL-PUC was investigated. Figure 4 shows the stress-strain curves of the PCL-PU, PCL-PUC, and MMT/PCL-PUC nanocomposites, and their tensile properties are summarized in Table I. All of the samples were annealed at 110°C for 24 h prior to the measurements. Tensile properties of the PCL-PU were enhanced by introducing 3 mol % of quaternary ammonium groups in the main chain. In segmented PU, most ionic centers belong to the hard segments, and therefore, ionic groups lead to increased modulus and strength of PU.²³ The Young's modulus of the MMT/PCL-PUC nanocomposites increased with increasing MMT content because of the increased interfacial interaction

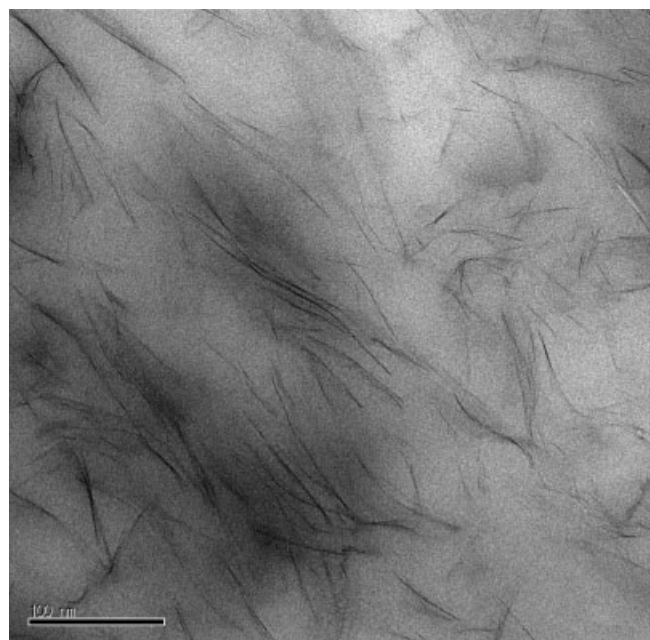


Figure 3 TEM micrograph of the 7 wt % MMT/PCL-PUC nanocomposites.

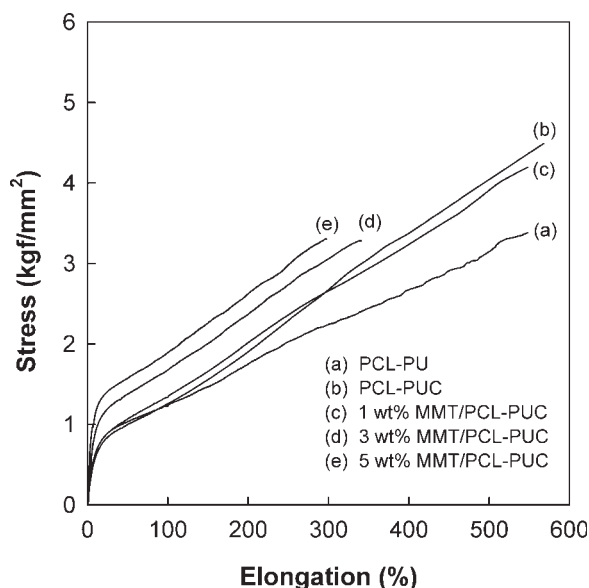


Figure 4 Tensile properties of the PCL-PU, PCL-PUC, and MMT/PCL-PUC nanocomposites.

between the MMT layers and polymer matrix. However, the elongation at break and maximum stress of the MMT/PCL-PUC nanocomposites were maintained at a level close to that of the PCL-PUC only at an MMT content of 1 wt %, and decreased as the content of MMT was further increased.

The resulting morphologies of the MMT/PCL-PUC nanocomposites are believed to be a major factor underlying their mechanical properties. Figure 5 shows the SAXS patterns of the PCL-PU, the PCL-PUC, and the MMT/PCL-PUC nanocomposites. As the content of MMT increased in the MMT/PCL-PUC nanocomposites, the degree of microphase separation of the PCL-PUC decreased. Tien and Wei²⁴ prepared benzidine-modified (BZD) MMT/PU nanocomposites and determined the degree of phase separation by measuring the concentration of the carbonyl groups participating in hydrogen bonding by using FTIR spectroscopy. The hydrogen bonding index of carbonyl groups in BZD-MMT/PU nanocomposites was decreased with increasing amounts of BZD-MMT irrespective of the hard segment ratio,

TABLE I
Tensile Properties of the PCL-PU, PCL-PUC, and MMT/PCL-PUC Nanocomposites

Samples	Max stress (kgf/mm ²)	Elongation at break (%)	Young's modulus (kgf/mm ²)
PCL-PU	3.38	548	0.65
PCL-PUC	4.55	568	0.62
1 wt % MMT/PCL-PUC	4.18	548	0.68
3 wt % MMT/PCL-PUC	3.27	340	1.96
5 wt % MMT/PCL-PUC	3.30	296	5.26
7 wt % MMT/PCL-PUC	2.55	242	11.61

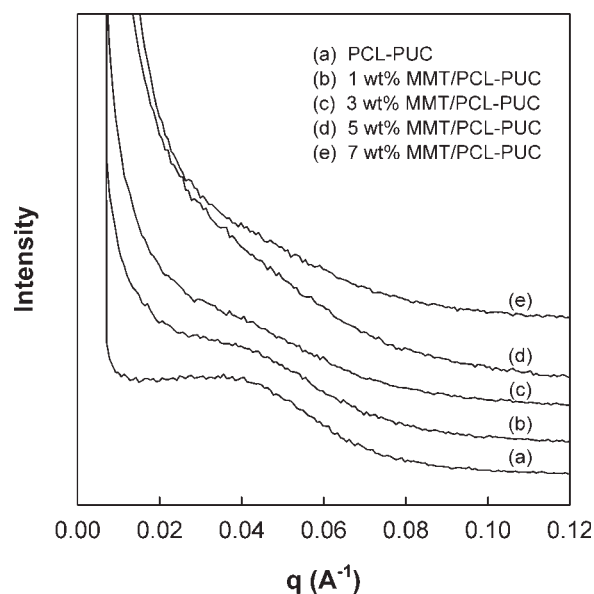


Figure 5 SAXS patterns of the PCL-PU and MMT/PCL-PUC nanocomposites.

indicating that the degree of microphase separation of the PU decreased. This is in good accordance with the results obtained in the present study. Therefore, it is believed that the decrease in the elongation at break and maximum stress of the MMT/PCL-PUC nanocomposites is likely due to the less phase-separated morphology of the PCL-PUC, which is a result of the strong interactions between the PCL-PUC and the exfoliated MMT layers.

It is known that MMT can enhance the thermal stability of a polymer by acting as a thermal insulator and a mass transport barrier to volatile products generated during decomposition. Figure 6 shows the

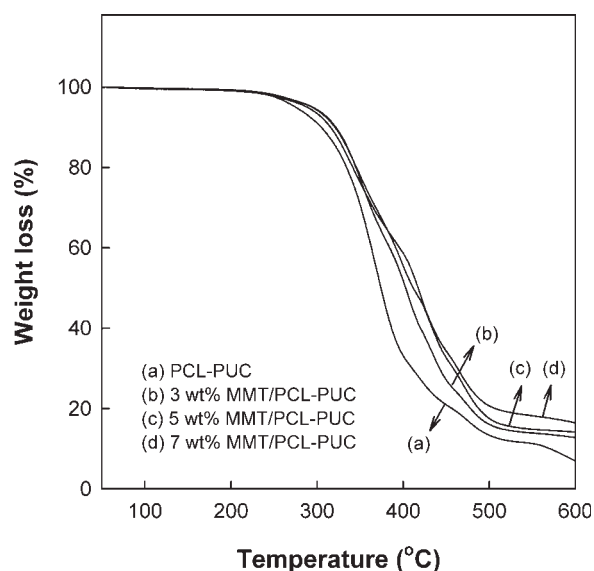


Figure 6 TGA curves the PCL-PUC and MMT/PCL-PUC nanocomposites.

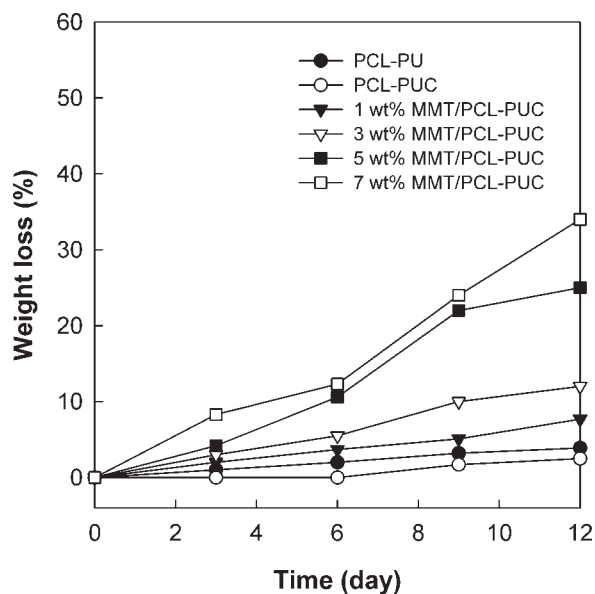


Figure 7 Hydrolytic degradation of the PCL-PU, PCL-PUC, and MMT/PCL-PUC nanocomposites.

TGA curves of the PCL-PUC and MMT/PCL-PUC nanocomposites. The initial decomposition temperature, which is defined as the temperature at which

the weight loss reaches 5 wt %, was 274°C for PCL-PUC: This value increased to 295, 294, 294, and 289°C for the 1, 3, 5, and 7 wt % MMT/PCL-PUC nanocomposites, respectively. An improvement of the thermal stability of PCL-PUC was observed. The well-exfoliated MMT layers served as a thermal barrier for delaying the thermal degradation.

The hydrolytic degradation of aliphatic polyesters takes place through the hydrolysis of the ester backbone in a random fashion under aqueous conditions, and the degradation rate of the polyesters depends on the crystallinity, the size and form of the crystallite, the morphological structure, etc.²⁵ Since water molecules can easily diffuse into the amorphous region of the polymer, hydrolytic degradation occurs preferentially in the amorphous region rather than the crystalline region. Similarly, hydrolytic degradation of PCL-PUC takes place through the hydrolysis of the ester backbone of the PCL in the soft segment. Figure 7 shows the hydrolytic degradation of the PCL-PU, PCL-PUC, and MMT/PCL-PUC nanocomposites. PCL-PU and PCL-PUC showed a very similar hydrolytic degradability. The hydrolytic degradation of the nanocomposites was dramatically increased with increasing MMT content. Tang et al.²⁶

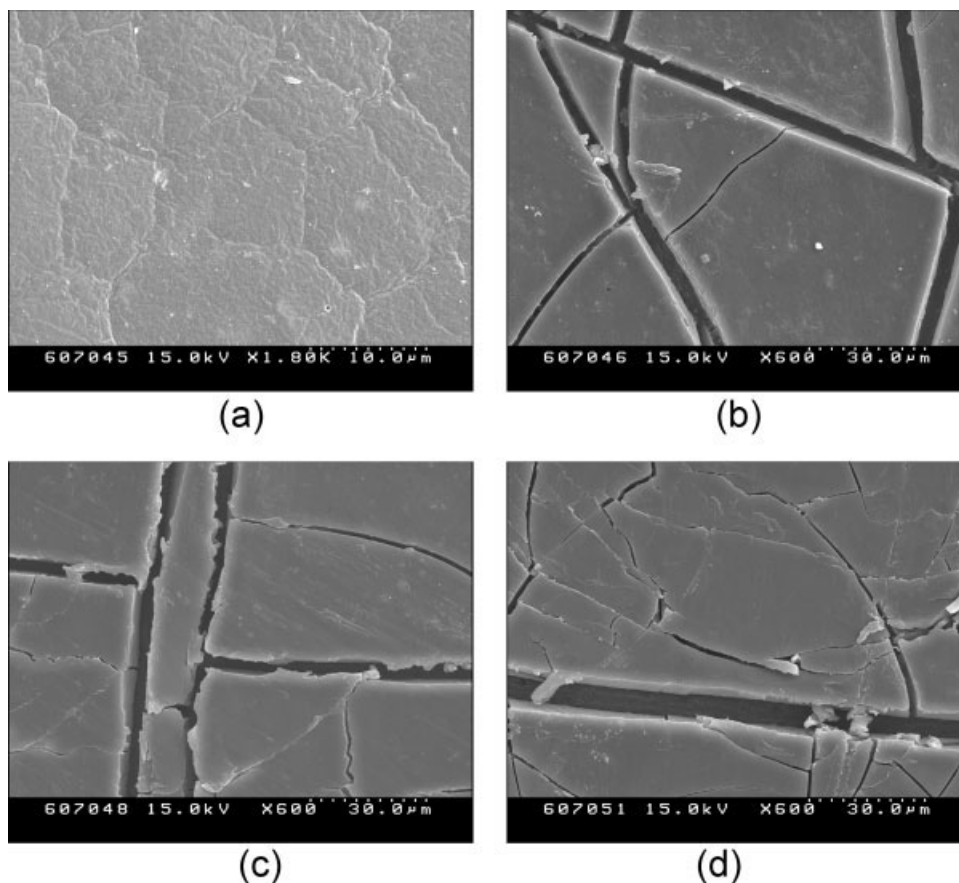


Figure 8 SEM images of the 1 wt % MMT/PCL-PUC nanocomposites hydrolytically degraded for (a) 0 day, (b) 6 days, (c) 9 days, and (d) 12 days.

synthesized polycarbonate urethanes and investigated their cholesterol esterase catalyzed hydrolysis. They found that the extent of hydrolytic degradation was highly dependent on the nature of hard segment interactions within the polymer and at the surface. As shown earlier, the MMT/PCL-PUC nanocomposites had less phase-separated morphologies and weaker hard segment interactions. Therefore, water molecules could more easily diffuse into the less phase-separated PCL-PUC matrix, resulting in faster degradation of the MMT/PCL-PUC nanocomposites. A barrier effect of the well-exfoliated MMT layers against water molecules was not observed when the MMT content was increased. Figure 8 shows the surface morphologies of the 1 wt % MMT/PCL-PUC nanocomposites at different degradation times. As degradation proceeded, the surface became rugged, and then cracks eventually appeared. These cracks became larger with further degradation. For the MMT/PCL-PUC nanocomposites containing more than 1 wt % MMT, the shape of the nanocomposite films was not maintained when the weight loss exceeded 10 wt %.

CONCLUSIONS

For all of the MMT/PCL-PUC nanocomposites, the MMT was successfully exfoliated and well dispersed in the PCL-PUC matrix up to 7 wt % of MMT. Exfoliation and dispersion of the MMT layers in the PCL-PUC matrix was dramatically enhanced by the 3 mol % quaternary ammonium groups in the PCL-PUC main chain. The Young's modulus of the MMT/PCL-PUC nanocomposites was significantly increased, but their elongation at break and maximum stress were maintained at a MMT content of 1 wt %. The phase separation of the MMT/PCL-PUC nanocomposites was retarded with increasing MMT content due to strong interactions between the PCL-PUC chains and the exfoliated MMT layers. The initial decomposition temperatures of the MMT/PCL-PUC nanocomposites were higher than that of PCL-PUC. The hydrolytic degradation of

these nanocomposites was dramatically increased with increasing MMT content.

References

1. Chen, T. K.; Tien, Y. I.; Wei, K. H. *Polymer* 2000, 41, 1345.
2. Tien, Y. I.; Wei, K. H. *Macromolecules* 2001, 34, 9045.
3. Tien, Y. I.; Wei, K. H. *J Appl Polym Sci* 2002, 86, 1741.
4. Tortora, M.; Gorrasi, G.; Vittoria, V.; Galli, G.; Ritrovati, S.; Chiellini, E. *Polymer* 2002, 43, 6147.
5. Zhang, X.; Xu, R.; Wu, Z.; Zhou, C. *Polym Int* 2003, 52, 790.
6. Xiong, J.; Liu, Y.; Yang, X.; Wang, X. *Polym Degrad Stab* 2004, 86, 549.
7. Song, L.; Hu, Y.; Tang, Y.; Zhang, R.; Chen, Z.; Fan, W. *Polym Degrad Stab* 2005, 87, 111.
8. Pattanayak, A.; Jana, S. C. *Polymer* 2005, 46, 3275.
9. Berta, M.; Lindsay, C.; Pans, G.; Camino, G. *Polym Degrad Stab* 2006, 91, 1179.
10. Jeong, E. H.; Yang, J.; Hong, J. H.; Kim, T. G.; Kim, J. H.; Youk, J. H. *Eur Polym J* 2007, 43, 2286.
11. Lamba, N. M. K.; Woodhouse, K. A.; Cooper, S. L. *Polyurethanes in Biomedical Applications*; CRC Press: New York, 1998.
12. Wang, W.; Ping, P.; Chen, X.; Jing, X. *Eur Polym J* 2006, 42, 1240.
13. Lee, S. I.; Yu, S. C.; Lee, Y. S. *Polym Degrad Stab* 2001, 72, 81.
14. Guan, J.; Sacks, M. S.; Beckman, E. J.; Wagner, W. R. *Biomaterials* 2004, 25, 85.
15. Moore, T.; Adhikari, R.; Gunatillake, P. *Biomaterials* 2005, 26, 3771.
16. Yeganeh, H.; Jamshidi, H.; Jamshidi, S. *Polym Int* 2007, 56, 41.
17. Heijkants, G. J. C.; Calck, R. V.; Tienen, T. G.; Groot, J. H.; Buma, P.; Pennings, A. J.; Veth, P. H.; Schouten, A. J. *Biomaterials* 2005, 26, 4219.
18. Woo, G. L. Y.; Mittelman, M. W.; Santerre, J. P. *Biomaterials* 2000, 21, 1235.
19. Hatakeyama, T.; Izuta, Y.; Hirose, S.; Hatakeyama, H. *Polymer* 2002, 43, 1177.
20. Lee, J. H.; Park, T. G.; Park, H. S.; Lee, D. S.; Lee, Y. K.; Yoon, S. C. *Biomaterials* 2003, 4, 2773.
21. Lee, Y. H.; Lee, J. H.; An, I. G.; Kim, C.; Lee, D. S.; Lee, Y. K.; Nam, J. D. *Biomaterials* 2005, 6, 3165.
22. Chen, T. K.; Tien, Y. I.; Wei, K. H. *J Polym Sci Polym Chem* 1999, 37, 2225.
23. Lee, J. C.; Kim, B. K. *Polymer (Korea)* 1993, 17, 687.
24. Tien, Y. I.; Wei, K. H. *Polymer* 2001, 42, 3213.
25. You, Y.; Min, B. M.; Lee, S. J.; Lee, T. S.; Park, W. H. *J Appl Polym Sci* 2005, 95, 193.
26. Tang, Y. W.; Labow, R. S.; Santerre, J. P. *J Biomed Mater Res* 2001, 57, 597.