

Study of the Biodegradable Poly(ϵ -caprolactone)/Clay Nanocomposite Foams

Hao Liu, Changyu Han, Lisong Dong

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Changchun 130022, China

Received 30 March 2009; accepted 4 September 2009

DOI 10.1002/app.31395

Published online 2 November 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this article, biodegradable poly(ϵ -caprolactone)/layered silicate nanocomposites were prepared and characterized. The dispersion state of modified clay in PCL matrix and its effect on thermal, rheological and mechanical properties of PCL were studied. The PCL/clay nanocomposites were then foamed using chemical foaming method. Cellular parameters such as mean cell size, cell wall thickness and cell densities of

nanocomposite foams with different clay loading were collected. Effect of layered silicate on the structure and mechanical properties of PCL foams were evaluated. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3120–3129, 2010

Key words: poly(ϵ -caprolactone); layered silicate; nanocomposite; foam

INTRODUCTION

Nowadays, tremendous amounts and varieties of plastics, notably polyolefins, polystyrene and poly(vinyl chloride) produced mostly from fossil fuels, are consumed and discarded into the environment, ending up as wastes that can not degrade spontaneously. On the dealing with these wastes, whether it is using incineration or landfill, will more or less bring about environmental problems. For these reasons, there is an urgent need for the development of biodegradable polymers that could degrade via a natural composting process. Accordingly, biodegradable aliphatic polyesters such as poly(ϵ -caprolactone) (PCL), polylactide (PLA), poly(butylene succinate) (PBS), etc. are of increasing commercial interest. However, relatively low thermal stability and mechanical properties impede their applications. Polymer/layered silicate nanocomposites are paid much attention to because the introduction of nanometer scale silicate pellets contributes to improvement of the mechanical properties of the polymer.¹ Also, Thermal stability, gas barrier properties, melt viscosity, and biodegradation rate are among the properties that can be achieved by these multiphase systems.²

Therefore, nanocomposites of biodegradable polymers such as PCL,^{3–6} PLA,^{7–10} PBS,^{11–13} etc. are widely studied.

On the other hand, polymer foams represent a group of lightweight materials that have been widely used. However, the foam applications are limited by their inferior mechanical strength, poor surface quality, and low thermal and dimensional stability. One way to solve these problems could be the foaming of polymer/layered silicate nanocomposites. A small amount of well-dispersed nanoparticles in the polymer may serve as nucleation sites to facilitate the bubble nucleation process. Plate-like nanoparticles may also reduce gas diffusivity in the polymer matrix. In addition, the presence of nanoparticles may enhance mechanical and physical properties, the heat distortion temperature, and fire resistance of polymer foams.¹⁴ Accordingly, plenty of works about polymer/clay nanocomposite foams have been reported. However, most of these works are about foaming using supercritical fluids,^{15–23} only a few of them are foaming using chemical foaming agents.^{24–28}

In our previous study,²⁹ we prepared biodegradable PCL foams using chemical foaming method and the structure-property relationship of PCL foams were studied. However, the applications of PCL foams are limited by the relatively poor mechanical properties and high production cost of the PCL matrix. As mentioned previously, to solve these problems one of the options is the preparation of PCL/layered silicate nanocomposite foams. Introduction of nanoscaled silicate pellets may improve

Correspondence to: L. Dong (dongls@ciac.jl.cn).

Contract grant sponsor: National Science Foundation of China; contract grant numbers: 50473028, 50703042.

the performance of PCL matrix and thus enhance the properties of PCL foams. Moreover, nanoscaled silicate pellets could also benefit the foaming process, bringing about changes in the cellular structure, which may also improve the performance of the foams. In this study, PCL/clay nanocomposites were prepared and characterized. Clay exfoliation results, crystallization behavior, rheological and mechanical properties of PCL/layered silicate nanocomposites were studied. Further, PCL/clay nanocomposites were foamed using chemical foaming method. Effect of layered silicate on the cellular structure and mechanical properties of nanocomposite foams was studied.

EXPERIMENTAL

Materials

A commercial PCL with weight average molecular mass of 8×10^5 was purchased from Solvay, United Kingdom. BPO, an initiator for PCL crosslinking, was purchased from Shanghai Chemical Reagent, China. Azodiformamide (AC), a chemical foaming agent, was obtained from Shanghai Guanya Chemical, China. Zinc oxide (ZnO) used to lower the decomposition temperature of AC was bought from Beijing Chemical, China. Commercial nanoclay with a trade name of DK2, a montmorillonite modified by methyl tallow bis-2-hydroxyethyl ammonium, was supplied by Fenghong Chemical Industry, China. These chemicals were used as received, except for BPO that was recrystallized before use.

Preparation of crosslinked PCL/clay nanocomposites

PCL can only be foamed using AC as the foaming agent when it is crosslinked. Hence crosslinked PCL/clay nanocomposites were prepared and characterized. PCL was blended with clay in a laboratory internal mixture at 90°C and 40 rpm for 5 min, the content of clay is 0, 5, 10, 20, and 30 wt % respectively. BPO (2 wt %) was also added to act as the crosslinking initiator. Then the samples were hot pressed at 130°C for 10 min, in which stage BPO was fully decomposed and PCL was crosslinked. The gel fraction of the PCL/clay composites was determined by extracting the composites with boiling chloroform as the solvent for 24 h. Approximately 0.2 g sample was cut into small pieces and placed in preweighted nickel fine mesh. After extraction the samples was washed with acetone and vacuum dried to constant weight.

Characterization of PCL/clay nanocomposites

The morphology of PCL/clay nanocomposites was characterized by wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). WAXD was performed using a Rigaku D/max 2500VPC X-ray diffractometer with reflection geometry and CuK_α radiation (wavelength $\lambda = 0.154$ nm), operated at 40 kV and 20 mA, with a scan speed of 1°/min and 2θ range of 1–10°. TEM was also adopted to characterize the nanocomposite structure. The nanocomposites were cryogenically sectioned into ultra-thin slices at about –40°C using a Leica Ultracut and then mounted on 200 mesh copper grids. The samples were observed on a JEOL2010 TEM operated at 200 kV accelerating voltage with LaB_6 filament.

The thermal behavior of PCL/clay nanocomposites was tested using a DSC-7 Perkin–Elmer instrument with samples of about 8 mg sealed in aluminum pans under nitrogen atmosphere in the temperature range between –100 and 100°C at a heating rate of 10 K/min. The melting and crystallization temperatures together with melting enthalpy of the samples were derived from the second heating scan to eliminate effects of heat histories. The crystallinity (X_c) was calculated by eq. (1).

$$X_c = \frac{\Delta H_m}{W_p \times \Delta H_m^0} \quad (1)$$

where W_p is the weight fraction of PCL, ΔH_m is the enthalpy of melting for nanocomposites, and ΔH_m^0 is the enthalpy of melting for 100% crystalline PCL, which is taken as 136 J/g as reported in the literature.³⁰

Rheological properties of PCL/clay nanocomposites were measured using a parallel plate rheometer Physica MCR 300 (Anton-Paar GmbH) at 200°C under nitrogen atmosphere. Two hundred degree celsius was selected as the operation temperature because it is the foaming temperature. Samples with thickness of about 1 mm and diameter of about 25 mm were measured at angular frequency between 0.1 and 100 1/s at low strains (0.1–1%).

The mechanical properties of PCL/clay nanocomposites were tested using an Instron 1211 testing machine with a 10 kN load cell. Samples with dumbbell shape were measured at a crosshead speed of 10mm/min at 25°C in the tensile mode. Five specimens of each sample were tested and the average value was calculated.

Preparation of PCL/clay nanocomposite foams

PCL/clay nanocomposites were foamed using chemical foaming method. The foaming process was

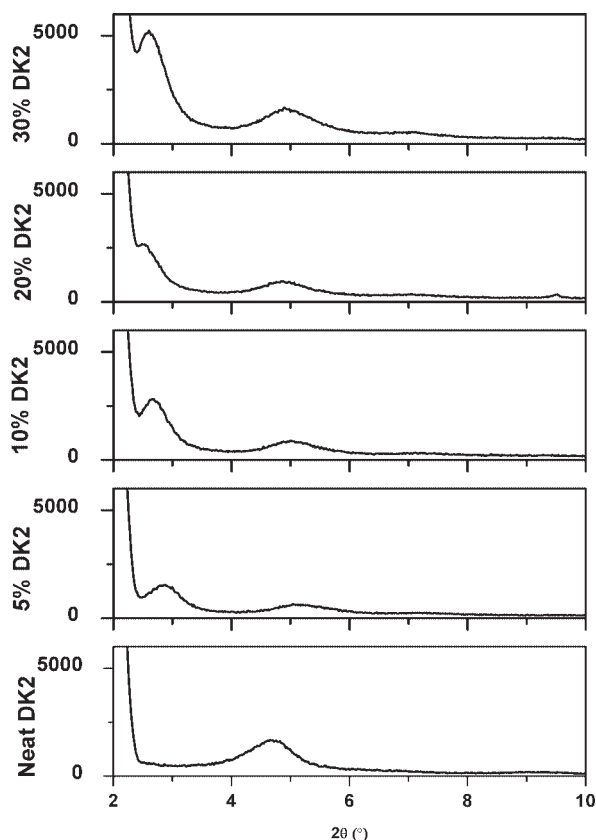


Figure 1 WAXD patterns of clay in PCL matrix.

described in detail in our previous work.²⁹ Foams with different clay loading and same AC content were prepared. All the samples were left in air at room temperature for 48 h before any structural characterization and mechanical testing.

Characterization of PCL/clay nanocomposite foams

According to ASTM D 1622–98, the apparent density of the foam was obtained by the ratio of the weight

over the volume of each sample. The dimensions were measured with vernier caliper, and the weight was measured with analytical balance. The foam density was calculated by dividing sample's weight by its volume. More than five specimens were measured to minimize the errors.

The cryogenically fractured surfaces of the PCL/clay nanocomposite foams were coated with gold and then observed with an AK-840 (JEOL) SEM. The SEM images of nanocomposite foams were analyzed by Scion Image[®] Software to obtain cell parameters. The cell size was calculated as average diameter of more than 200 cells. For the actual cell diameter is always larger than its measured counterpart because most cells will not be truncated through their maximal cross-section therefore underestimating the value. According to ASTM D3576, the actual average diameter of a perfectly spherical cell can be calculated by eq. (2),

$$d = \frac{4}{\pi} \delta \quad (2)$$

where d is the actual average diameter and δ is the calculated average diameter. Because of uneven thickness of the cell walls, the middle part was measured as cell wall thickness. Mean cell size was calculated as average value of more than 100 cells. Cell density was calculated by eq. (3) suggested by Nam,²²

$$N_c \cong 10^4 [1 - (\rho_f/\rho_m)]/d^3 \quad (3)$$

where N_c is the cell density in cells/cm³, ρ_f and ρ_m are densities of the foam and the polymer matrix, respectively, and d is the average cell diameter in mm.

Compressive behavior of the nanocomposite foams was chosen as the mainly mechanical property. Uniaxial compression was carried out at room

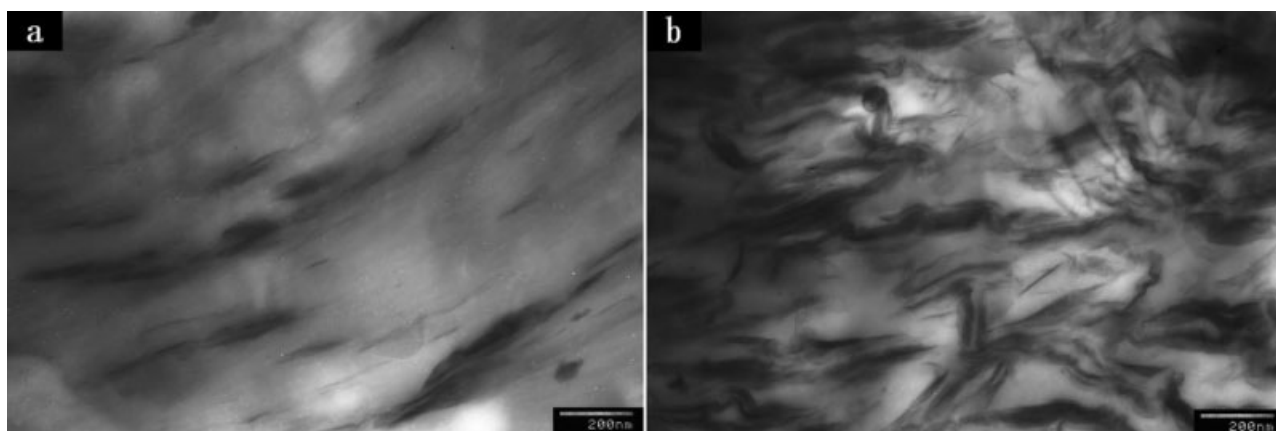


Figure 2 TEM observation of clay in PCL matrix. (a) 5 wt %, (b) 30 wt %.

TABLE I
Gel Fraction of PCL/Clay Nanocomposites

Clay content (wt %)	Gel fraction (%)
0	82.4
5	80.8
10	79.5
20	73.9
30	64.5

temperature using an Instron 1221 Testing machine with a 10 kN load cell. A constant crosshead speed of 1.0 mm/min was used and stress–strain curves were obtained. Foam specimens with original thickness of about 6 mm were cut into square pieces in the dimension of 15 × 15 mm. At least five specimens with the same density were tested and uniaxial compressive modulus was calculated as the slope of the initial linear part of stress–strain curve.

RESULTS AND DISCUSSION

Morphology of PCL/clay nanocomposites

The property improvements by introduction of layered clay are mainly due to the large surface area of the exfoliated particles and their contact with the polymer matrix.³¹ Accordingly, the dispersion state of clay in the nanocomposites is of great interest. To observe the distribution state of clay in PCL matrix, WAXD tests of PCL/clay nanocomposites were performed and WAXD patterns were showed in Figure 1. Neat clay has an initial (001) peak at about $2\theta = 4.7^\circ$ (corresponding to $d_{001} = 1.9$ nm). In the case of PCL/clay nanocomposites with clay content of 5 wt %, the peak is shifted to $2\theta = 2.8^\circ$ ($=3.2$ nm), corresponding to the (001) plane of the silicate layers in the PCL matrix. With increasing clay loads, this peak becomes stronger and shifts to lower diffraction angle. This phenomenon may be due to the increased melt strength brought about by increasing clay loading. As a result the shear force while blending was increased and better intercalating was achieved. However, the peak shifts to higher angle at 30 wt % clay loading, which could due to the flocculation at high clay content.

TEM allows a qualitative understanding of the internal structure through direct visualization. To get better observation of internal structures of the nanocomposites in the nanometer scale, PCL/clay nanocomposites were observed by TEM, shown in Figure 2. Partially exfoliated and intercalated structure can be observed in the case of nanocomposites with clay content of 5 wt %. Randomly stacked and flocculated silicate layers can be observed in the PCL matrix when clay increased to 30 wt %. The result shows that clay can be evenly dispersed in the PCL matrix even when the loading was as high as

30 wt %. However, more flocculation can be found with increasing loading of clay.

Thermal and mechanical properties of PCL/clay nanocomposites

The gel fraction of nanocomposites was shown in Table I. The result shows that presence of clay may hinder the effective crosslinking of PCL. The gel fraction of nanocomposites was decreased as increasing loading of clay.

DSC curves of PCL and PCL/clay nanocomposites with 5 wt %, 10 wt %, 20 wt % and 30 wt % clay are shown in Figure 3. Comparing the shapes of melting peaks of PCL and PCL/clay nanocomposites, addition of clay to PCL does not change the crystal forms and the crystal structure of PCL. Table II gives a summary of the crystallization and melting data of PCL and PCL/clay nanocomposites. The melting temperature (T_m) of the nanocomposites is very close to that of neat PCL. And additions of a small amount of clay into the PCL matrix results in slightly increase in the crystallization temperature (T_c) of the polymer matrix. According to Gopakumar,³² exfoliated clay did as a crystal nucleating agent. Clay at low content can be partially exfoliated according to WAXD and TEM results. The exfoliated clay has some nucleating effect, causing a crystallization rate slightly higher than that of neat PCL. Similar results have been reported by Di.³³ Furthermore, clay's effect on hindering crosslinking might also benefit the crystallization behavior of PCL/clay nanocomposites. However, further loading of the clay reduces the mobility of PCL molecules and hinders the crystallization. Accordingly, maximum value of X_c is achieved at 5 wt % clay loading.

The rheological properties of polymer materials are important for their processing and may explain

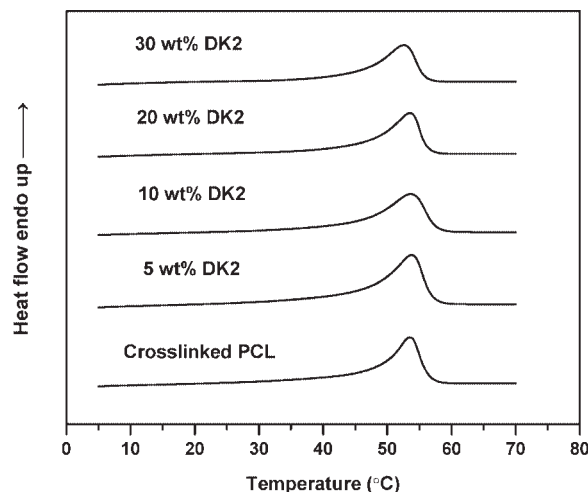


Figure 3 DSC curves of nanocomposites with different clay loading.

TABLE II
Summary of the Crystallization and Melting Data of PCL/Clay Nanocomposites

Clay content (wt %)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	X_c (%)
0	54.3	25.7	59.2	43.5
5	54.5	30.3	62.0	45.6
10	54.4	31.1	59.3	43.6
20	54.3	30.9	59.6	43.8
30	53.3	30.8	58.0	42.6

the foam morphology changes as the introduction of layered silicate in PCL matrix. Thus rheological behavior of PCL/clay nanocomposites was measured at 200°C, which is the foaming temperature. Previous studies^{4,33} showed that the improved storage modulus (G'), loss modulus (G'') together with complex viscosity (η^*) were achieved by introduction of layered silicate for neat PCL. However, significant changes in the rheological behavior of nanocomposites were found when PCL was crosslinked. Figure 4 shows the G' , G'' , and η^* of PCL/clay nanocomposites. G' of nanocomposites with low clay loading show small shear rate dependence, which is the typical crosslinking behavior. And the shear rate dependence becomes more obvious in high clay content. Furthermore, G'' remains almost unchanged with increasing clay loadings at clay content lower than 10 wt %, then it increases a lot in samples with further clay loading. Similar phenomenon can be observed in η^* results. All the results show a turning point at 10 wt % clay loading. The rheological properties of PCL/clay nanocomposites with different clay loading were compared and shown in Figure 5. The results show that effect of clay on melt behavior of PCL matrix varies with clay loading. Below 10% concentration nanocomposites' melt strength is lowered as the increase of clay, and then in clay content higher than 10% melt strength is improved. Previous rheological characterization of uncrosslinked PCL/clay nanocomposites shows that introduction of clay improves the melt behavior of neat PCL.⁴ Whereas, addition of clay hinders the effective crosslinking of PCL, which leads to lower gel fraction and lowers the melt strength. At low clay loadings clay's effect on hindering crosslinking is greater than its effect on improving melt strength. Consequently, rheological properties of PCL/clay nanocomposites' are slightly reduced with the introduction of clay. However, in relative high clay loading, the amount of clay is high enough to make PCL/clay nanocomposites achieve better rheological properties than neat PCL.

Young's modulus and elongation at break of PCL/clay nanocomposites with different clay loading are shown in Figure 6. As expected, the Young's modulus of PCL/clay nanocomposites increases with increasing clay content, indicating effective

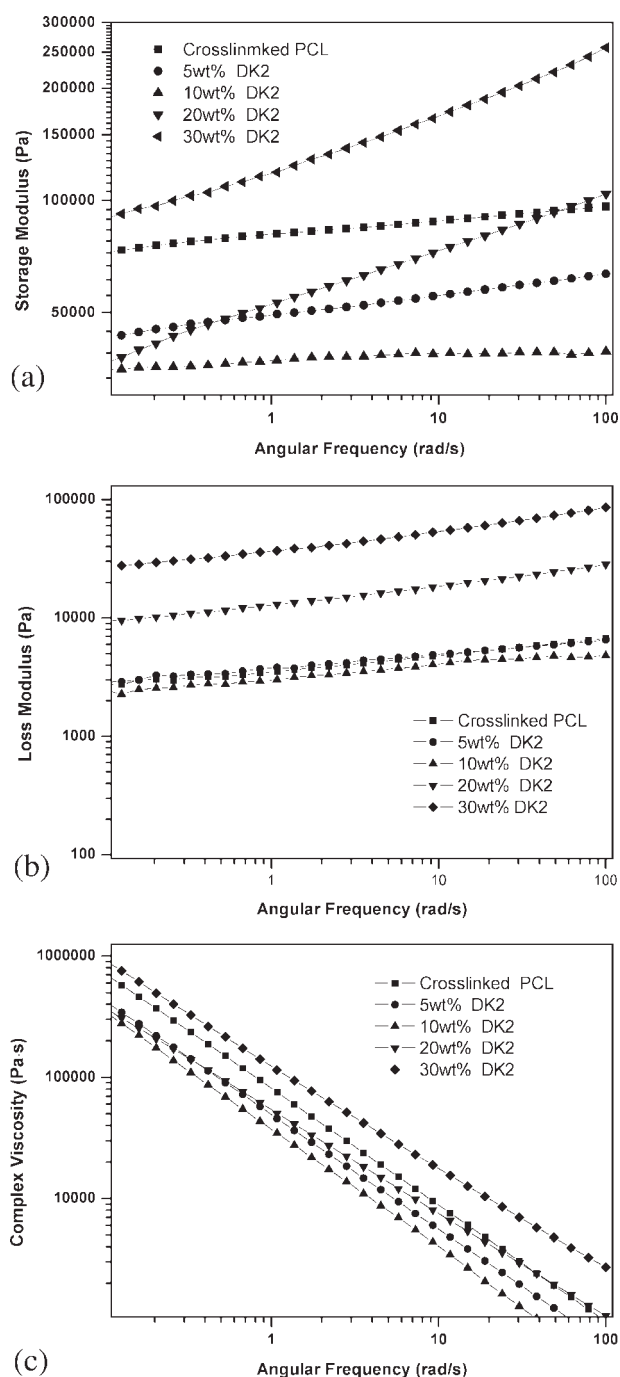


Figure 4 Rheological behaviors of PCL/clay nanocomposites.

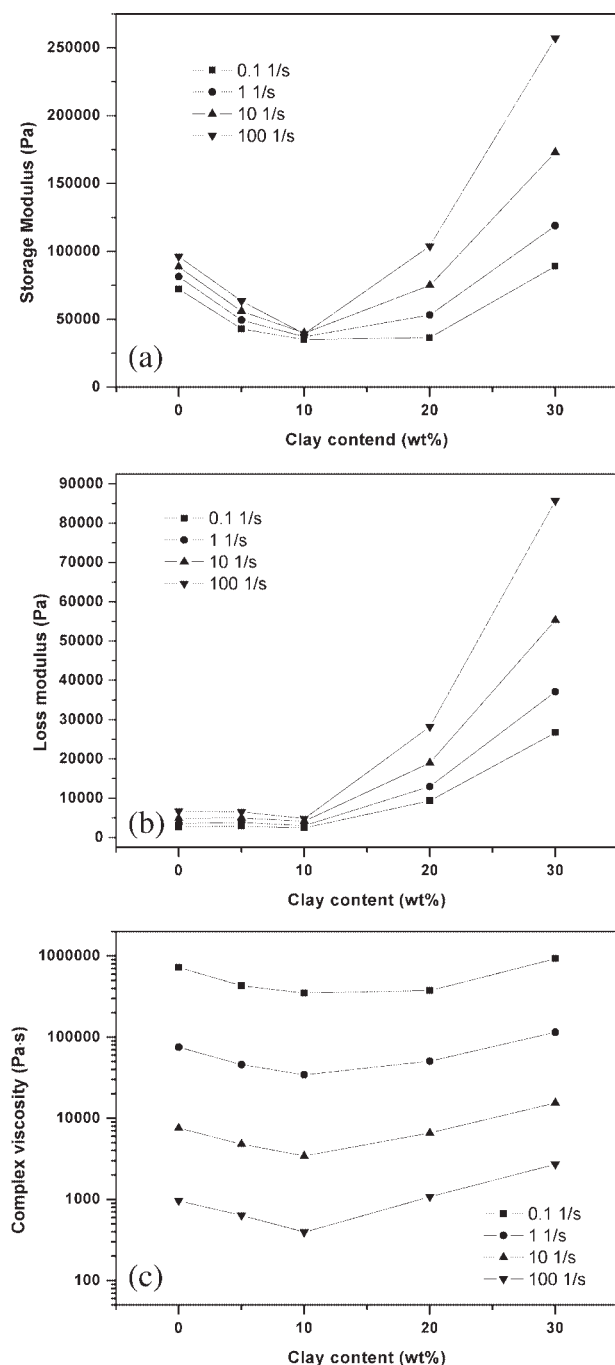


Figure 5 Effect of clay loading on the rheological behaviors of PCL/clay nanocomposites.

reinforcement. However, effect of clay on elongation at break varies with clay contents. Elongation at break increases with increasing clay loading in relatively low clay content. And rapid decline in ductility can be observed at clay loading higher than 10 wt %. Similar phenomenon has been reported in uncrosslinked PCL/clay nanocomposites.³⁴ This phenomenon may be due to the different dispersion state of clay particles in PCL matrix. At low loading more layered silicates are exfoliated in PCL matrix.

Greater levels of organoclay intercalating lead to more evenly dispersed smaller filler particles which translate into better reinforcement. Whereas at high loadings layered silicates are prone to agglomerate, leading to decrease of the ductility. Moreover, the reduced gel fraction at low clay content could also bring about the increasing of the elongation at break.

Morphology of PCL/clay nanocomposite foams

PCL/clay nanocomposite foams were prepared using AC as the foaming agent. In previous work we found the foaming grade mainly relies on the content of foaming agent,²⁹ hence fixed AC content is used to study effect of clay on the foams' morphology. SEM micrographs of neat PCL and PCL/clay nanocomposite foams with different clay loading are shown in Figure 7. It can be found that all the foams have a closed-cell structure. Cellular structure varies with different clay loading. Table III shows the statistical data of foam's structure parameters. The statistical cell size distribution of nanocomposite foams were also calculated and showed in Figure 8.

Density of clay is higher than that of PCL, and therefore density of nanocomposite foams is higher than neat PCL foams. Cellular parameters of PCL/clay nanocomposite foam are closely linked with the rheological property. Effect of clay on foam's structure depends on its content and 10 wt % layered silicate content is the turning point. PCL/clay nanocomposites foams with 5% clay content have the minimum cell size and maximum cell density. The cell wall thickness slightly decreases at lower clay loading and then increases markedly at high clay content. This phenomenon can be explained by the rheological properties of PCL/clay nanocomposites. Below 10 wt % introduction of small amount of clay slightly reduces the melt strength of

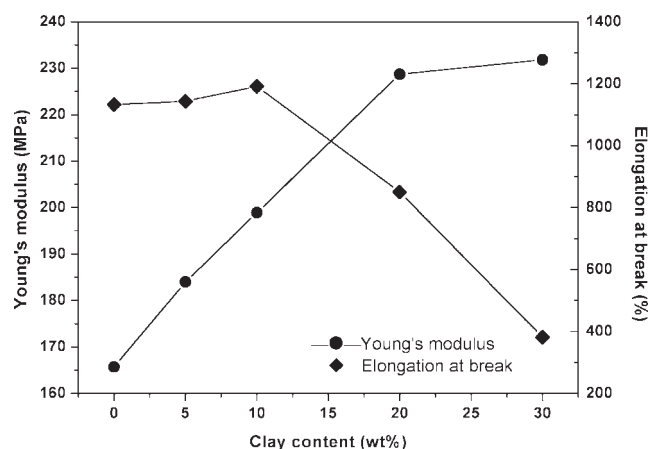


Figure 6 Mechanical properties of PCL/clay nanocomposites with different clay loading.

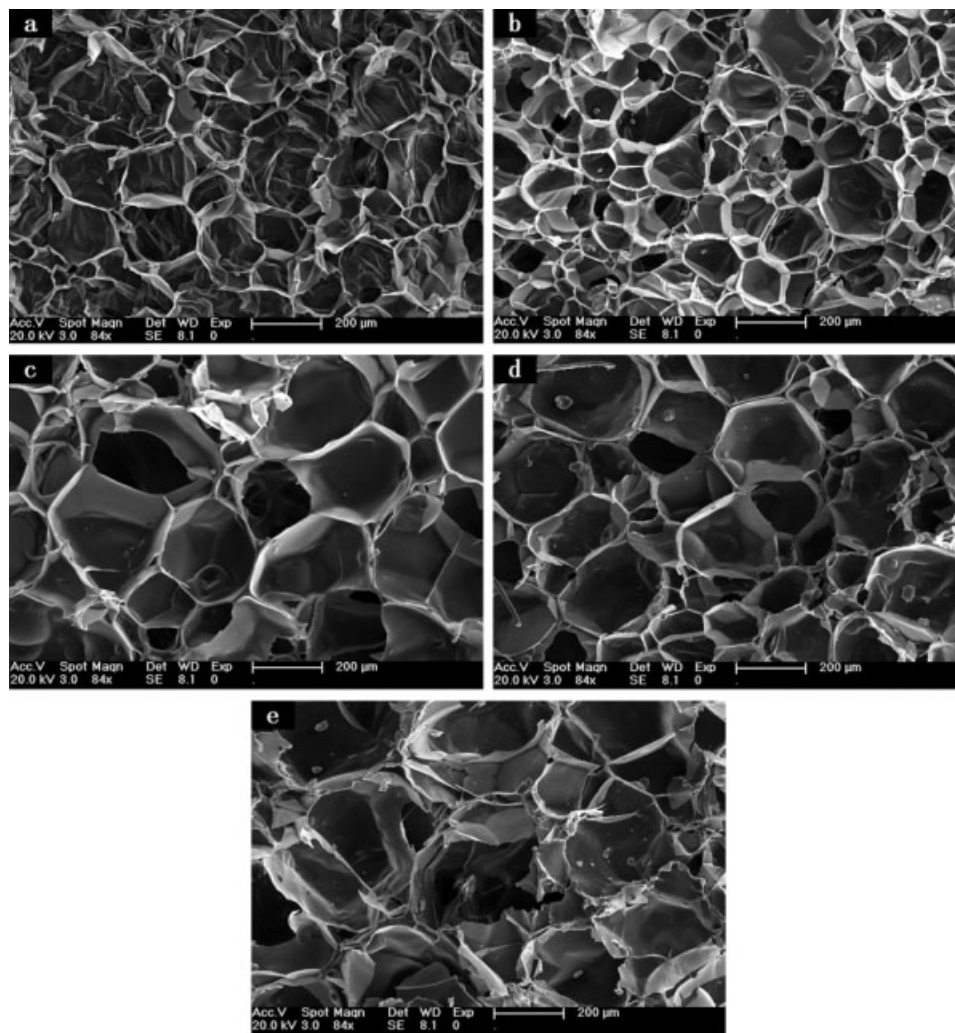


Figure 7 SEM images of PCL/clay nanocomposite foams with different clay loading. (a) Neat PCL, (b) 5, (c) 10, (d) 20, (e) 30 wt %.

nanocomposites. The exfoliated clay at low loading can provide nucleating sites in the heterogeneous nucleating process, making smaller cell size, higher cell density and thinner cell wall of nanocomposite foams. The rheological properties of PCL/clay nanocomposites changed a lot when clay content is higher than 10 wt %. And distinct changes of storage modulus, loss modulus and complex viscosity have been found in samples with 30 wt % clay content, which makes markedly increase in both

cell size and cell wall thickness. Statistical cell size distribution of nanocomposite foams confirms the layered silicate's role as the foaming nucleating agents. Neat PCL foams have a relatively wide distribution of cell size. With introduction of small amount of layered silicate, the cell size distribution gets narrower and more cells are less than 100 μm . However, with further clay loading the nucleation effect was reduced and the cell size distribution was broadened.

TABLE III
Structure Parameters of PCL/Clay Nanocomposite Foams

Clay content (wt %)	Mean cell size (μm)	Cell wall thickness (μm)	Cell density (cells/ cm^3)	Relative density
0	151.0	1.48	2.72×10^6	0.064
5	85.4	1.05	1.48×10^7	0.080
10	95.0	1.07	1.07×10^7	0.082
20	116.2	1.74	5.89×10^6	0.076
30	155.2	2.29	2.47×10^6	0.078

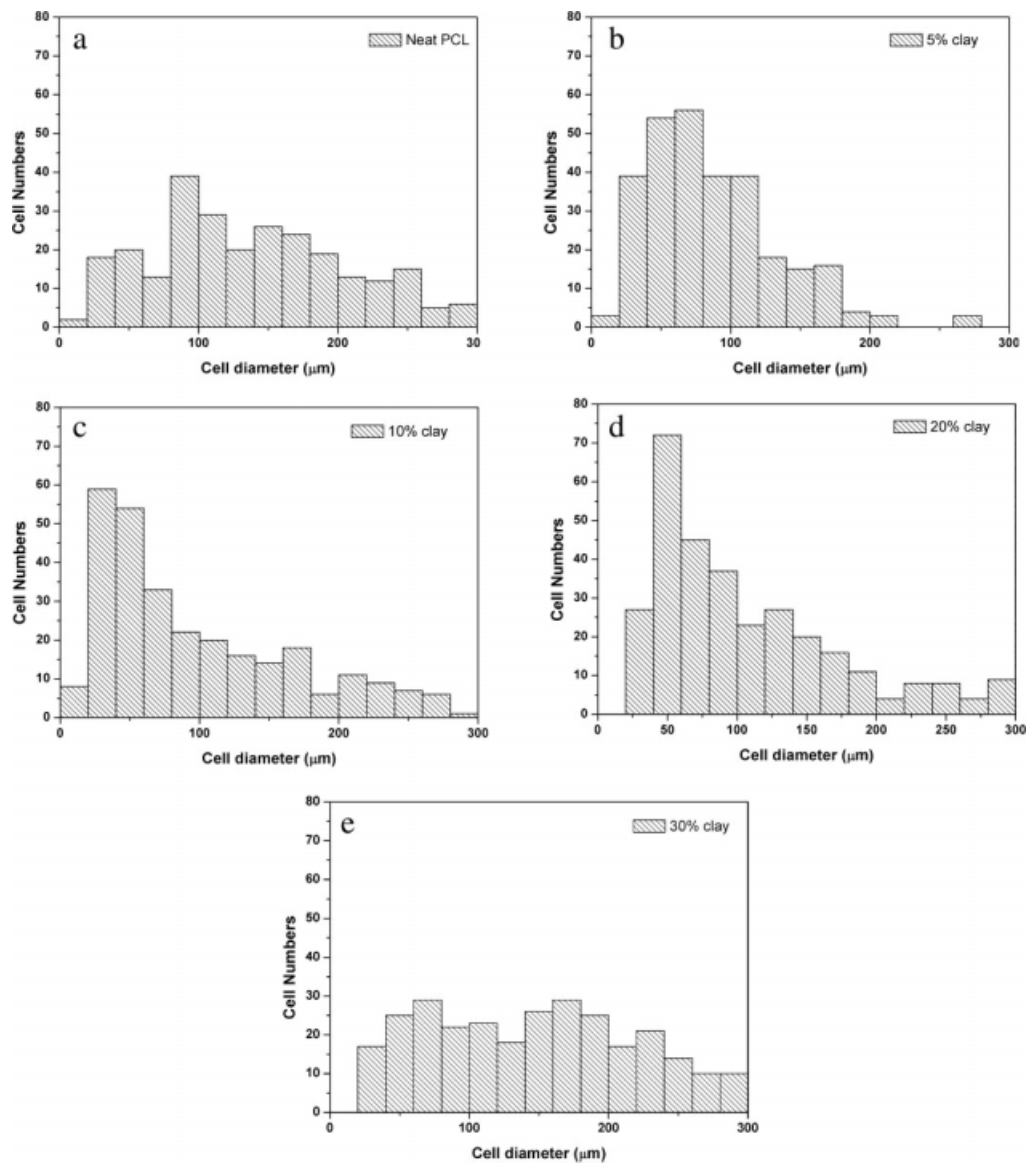


Figure 8 Statistical cell size distributions of nanocomposite foams. (a) Neat PCL, (b) 5, (c) 10, (d) 20, (e) 30 wt %.

Mechanical properties of PCL/clay nanocomposite foams

It is of great interest to study the effect of clay on the mechanical properties of nanocomposite foams. PCL/clay nanocomposite foams with fixed AC content were tested, compressive modulus and foaming rate as function of clay content are shown in Figure 9. It can be found that compressive modulus increases with increasing layered silicate content and tends to a constant value when clay content is 10 wt % or higher. Similar results about improvement of nanocomposite foams' mechanical properties have been reported for ethylene vinyl acetate copolymer/clay nanocomposite foams.²⁷ The improvement can be related to the dispersion and interaction of clay in PCL matrix. However, the increasing of compressive modulus is not only due to the addition of clay.

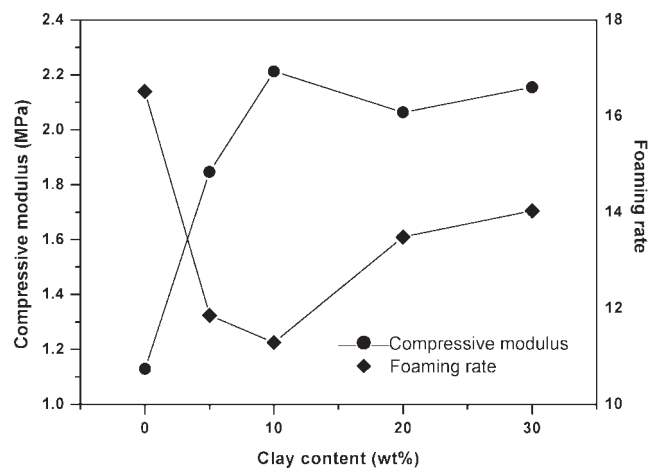


Figure 9 Compressive modulus and foaming rate of PCL/clay nanocomposites with different clay loading.

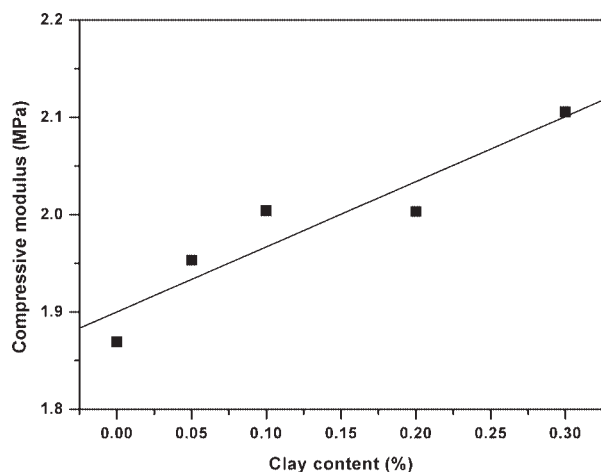


Figure 10 Compressive modulus of nanocomposite foams with similar densities and different clay loading.

The lowered foaming rate can also lead the increasing of modulus. Foaming rate is the reciprocal of relative density and decreasing of foaming rate means increasing of relative density, which can increase the compressive modulus. Therefore, neat PCL and PCL/clay nanocomposite foams with similar relative densities are chosen and compared in Figure 10 to study the effect of clay on the compressive modulus of nanocomposite foams. It can be found that compressive modulus increases linearly with increasing clay content. Introduction of clay strengthens the polymer matrix and thus increases foams' mechanical property. Furthermore, changes of cellular structure could also contribute to improvement of foams' property. Cell wall thickness increases with layered silicate content in relatively high clay content, which could bring about higher property.²⁹

CONCLUSIONS

PCL/clay nanocomposites were prepared through melt intercalation and characterized. DK2, a commercial modified layered silicate, could be evenly dispersed in the PCL matrix. Thermal analysis results showed that clay has slight crystallization nucleating effect. Maximum value of the crystallinity was achieved at 5% clay loading, when exfoliation of the layered silicate could be observed. Rheological characterization showed the effect of clay on the rheological behavior varied with different clay loading. At relatively low clay loading, the melt strength was lowered for addition of clay hindered the effective crosslinking of PCL matrix. Whereas clay's effect on improvement of melt strength played the leading roll at high loading. Furthermore, addition of clay increased the tensile modulus of nanocomposites. Introduction of the clay bene-

fited the ductility of nanocomposites, led to maximum value of elongation at break at 5 wt % clay loading.

Foaming of the nanocomposites was also carried out and characterized. According to SEM results, with increasing clay content mean cell size decreased when cell wall thickness almost remained the same at low clay loadings. On contrast, at high loadings both mean cell size and cell wall thickness increased. This phenomenon was attributed to the change of melt viscosity of nanocomposites and the heterogeneous nucleation behavior of clay at low loadings. Introduction of clay strengthens the PCL matrix and thus the compressive property of PCL/clay nanocomposite foams is improved. The compressive modulus of nanocomposite foams with similar density increased with clay loading. Compared with neat PCL foams, better mechanical properties and lower cost can be achieved by developing PCL/clay nanocomposite foams, giving a promising way to develop environment friendly polymer foams.

References

- Giannelis, E. P. *Adv Mater* 1996, 8, 29.
- Ray, S. S.; Bousmina, M. *Prog Mater Sci* 2005, 50, 962.
- Lepoittevin, B.; Pantoustier, N.; Devalckenaere, M.; Alexandre, M.; Kubies, D.; Calberg, C.; Jerome, R.; Dubois, P. *Macromolecules* 2002, 35, 8385.
- Lepoittevin, B.; Devalckenaere, M.; Pantoustier, N.; Alexandre, M.; Kubies, D.; Calberg, C.; Jerome, R.; Dubois, P. *Polymer* 2002, 43, 4017.
- Kiersnowski, A.; Piglowski, J. *Eur Polym J* 2004, 40, 1199.
- Pantoustier, N.; Lepoittevin, B.; Alexandre, M.; Kubies, D.; Calberg, C.; Jerome, R.; Dubois, P. *Polym Eng Sci* 2002, 42, 1928.
- Ogata, N.; Jimenez, G.; Kawai, H.; Ogihara, T. *J Polym Sci Part B: Polym Phys* 1997, 35, 389.
- Ray, S. S.; Maiti, P.; Okamoto, M.; Yamada, K.; Ueda, K. *Macromolecules* 2002, 35, 3104.
- Ray, S. S.; Yamada, K.; Ogami, A.; Okamoto, M.; Ueda, K. *Macromol Rapid Commun* 2002, 23, 943.
- Chang, J. H.; An, Y. U.; Sur, G. S. *J Polym Sci Part B: Polym Phys* 2003, 41, 94.
- Ray, S. S.; Okamoto, K.; Maiti, P.; Okamoto, M. *J Nanosci Nanotechnol* 2002, 2, 171.
- Okamoto, K.; Ray, S. S.; Okamoto, M. *J Polym Sci Part B: Polym Phys* 2003, 41, 3160.
- Ray, S. S.; Okamoto, K.; Okamoto, M. *J Appl Polym Sci* 2006, 102, 777.
- Lee, L. J.; Zeng, C. C.; Cao, X.; Han, X. M.; Shen, J.; Xu, G. J. *Compos Sci Technol* 2005, 65, 2344.
- Zeng, C. C.; Han, X. M.; Lee, L. J.; Koelling, K. W.; Tomasko, D. L. *Adv Mater* 2003, 15, 1743.
- Manninen, A. R.; Naguib, H. E.; Nawaby, A. V.; Liao, X.; Day, M. *Cell Polym* 2005, 24, 49.
- Lee, Y. H.; Wang, K. H.; Park, C. B.; Sain, M. *J Appl Polym Sci* 2007, 103, 2129.
- Fu, J.; Naguib, H. E. *J Cell Plast* 2006, 42, 325.
- Jo, C.; Naguib, H. E. *J Cell Plast* 2007, 43, 111.
- Ema, Y.; Ikeya, M.; Okamoto, M. *Polymer* 2006, 47, 5350.
- Chang, Y. W.; Lee, D.; Bae, S. Y. *Polym Int* 2006, 55, 184.

22. Nam, P. H.; Maiti, P.; Okamoto, M.; Kotaka, T.; Nakayama, T.; Takada, M.; Ohshima, M.; Usuki, A.; Hasegawa, N.; Okamoto, H. *Polym Eng Sci* 2002, 42, 1907.
23. Fujimoto, Y.; Ray, S. S.; Okamoto, M.; Ogami, A.; Yamada, K.; Ueda, K. *Macromol Rapid Commun* 2003, 24, 457.
24. Guo, G.; Wang, K. H.; Park, C. B.; Kim, Y. S.; Li, G. *J Appl Polym Sci* 2007, 104, 1058.
25. Park, K. W.; Chowdhury, S. R.; Park, C. C.; Kim, G. H. *J Appl Polym Sci* 2007, 104, 3879.
26. Xu, Z. R.; Park, H. Y.; Kim, H. Y.; Seo, K. H. *Macromol Symp* 2008, 264, 18.
27. Park, K. W.; Kim, G. H.; Chowdhury, S. R. *Polym Eng Sci* 2008, 48, 1183.
28. Velasco, J. I.; Antunes, M.; Ayyad, O.; Lopez-Cuesta, J. M.; Gaudon, P.; Saiz-Arroyo, C.; Rodriguez-Perez, M. A.; De Saja, J. A. *Polymer* 2007, 48, 2098.
29. Liu, H.; Han, C. Y.; Dong, L. S. *Polym Eng Sci* 2008, 48, 2432.
30. De Kesel, C.; Lefevre, C.; Nagy, J. B.; David, C. *Polymer* 1999, 40, 1969.
31. Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
32. Di Maio, E.; Iannace, S.; Sorrentino, L.; Nicolais, L. *Polymer* 2004, 45, 8893.
33. Di, Y. W.; Iannace, S.; Di Maio, E.; Nicolais, L. *J Polym Sci Part B: Polym Phys* 2003, 41, 670.
34. Chen, B. Q.; Evans, J. R. G. *Macromolecules* 2006, 39, 747.