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Barrier and Mechanical Properties of Poly(caprolactone)/Organoclay Nanocomposites

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Summary: In this study, biodegradable poly(caprolactone) (PCL) hybrids with two types of organoclays: Cloisite 30B (30B) and Cloisite 93A (93A) have been prepared by melt mixing and their barrier performance to air permeation and mechanical properties were investigated. The hybrids of PCL/30B were found to be nanocomposites resulted from the strong interaction between organic modifier of 30B and PCL and those of PCL/93A were microcomposites. The barrier performance of PCL/30B nanocomposite film to air permeation was much more improved than pure PCL and PCL/93A microcomposites at low organoclay concentration. With the increase of organoclay content the permeability coefficient was also increased that could attributed to the extra tortuous pathway for gas permeation caused by organoclay exfoliation. The barrier behaviour of PCL/30B nanocomposites could be approximately described by a theoretical model developed for composites. The mechanical properties measurements showed that the reinforcement of organoclay 30B in nanocomposites is more significant than 93A in microcomposites. Both tensile modulus and tensile strength were increased in PCL/30B nanocomposites even at at low amount of organoclay without much loss of strain at break as compared to pure PCL. The significant improvements in both barrier and mechanical properties in PCL nanocomposites could be attributed to the fine dispersion state of organoclay 30B platelets in PCL matrix and the strong interaction between organic modifier of 30B and matrix molecules.

Keywords: barrier; mechanical properties; nanocomposites; organoclay; poly(caprolactone)

Introduction

The enhanced properties of polymer nanocomposites consisting silicate clays have been attracting extensive research interests in polymer/silicate nanocomposites in recent years.[1-4] The platelets of silicate occur naturally in stacks and each layer has thickness of ~1 nm with the aspect ratios varying from 10 to 1000. Their elastic (Young's) moduli are ~10^2 times higher than those of a typical thermoplastic or thermoset, and ~10^5 times those of a

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typical elastomer.[5] In order to become effective reinforcement, these stacks must be exfoliated (delaminated) to disperse them in the polymeric matrix as highly anisotropic nanofillers, i.e. forming nanocomposite. Because of at least one dimension in nanoscale, the dispersion of such platelets results in significant enhancement in many properties as compared to the neat polymer matrix such as elastic moduli, gas barrier properties and flame retardancy et al.

In principle, there are mainly three methods for preparing polymer-based nanocomposites: intercalation of a suitable monomer into the interspaces of layered clay followed by polymerisation (in-situ polymerisation); direct polymer intercalation from solution and melt.[2] Of these methods, the melt intercalation is very popular for industrial processing because of the convenience that could be processed with conventional equipments and economic reason.

Because blends of thermoplastic polymer and silicate clay are typically incompatible, introduction of an organic modifier onto the surface of silicate clay to mediate the polarity between the hydrophilic silicate surface and the hydrophobic polymer, thus called organoclay, has been widely adopted for easily delaminating clay layers into the polymer matrix during melt compounding. Thus, as expected, the organoclay dispersability within a polymer matrix depends on the type and quantity of surfactant employed as well as processing conditions.

Poly(caprolactone) (PCL) is a biodegradable thermoplastic and has been of interest for medical applications since it was developed, such as the use in medical devices and drug delivery systems, and recently it has also been applied to the food packaging industry.[6] As its Tg is around −50 °C, the mechanical properties of PCL at room temperature is lower than other commodity polymers such as polyethylene and polypropylene. In order to enlarge the application range we focused on the PCL based nanocomposites by melt blending with organoclays. In the previous study, the dependence on the processing conditions and the role and effects of organic modifier for the preparation of PCL nanocomposites have been well studied.[7] In this study, we paid attention to the ability of exfoliated clays to improve the gas barrier characteristics and mechanical properties of PCL by employing two different types of organoclays. The influence of exfoliation of organocaly platelets on the improvement of such properties respected to the pure PCL were compared and discussed. The dispersion states of different organoclays were correlated with their contribution to the properties improvement.

Experimental

Materials and preparation of PCL/organoclay hybrids

PCL, under the commercial name of CAPA 680, was commercially purchased from Solvay Interox Ltd, UK. The two types of organoclay used in the preparation of nanocomposites for the reason of comparison, were purchased from Southern Clay Products Inc, USA, under the commercial names of Cloisite 30B and 93A (whereafter referred as 30B and 93A, respectively). According to the product information from producer, these two organoclays consisting of a same 2:1 montmorillonite (MMT) are organics-treated differently. 30B contains a quaternary ammonium ion containing methyl tallow bis-2-hydroxyethyl (MT2EtOT) and 93A contains methyl dihydrogenatedtallow ammonium (M2HT) as the organic modifier.

A Haake Rheomix®600 internal mixer with two roller rotors was used for the preparation of the PCL/organoclay hybrids with different compositions. This mixer is attached to a measuring drive unit Haake Rhecord® 9000. The processing temperature was set at 100 °C. The rotor rotating speed and mixing time were fixed at 100 rpm and 12 minutes. The components were first dry blended at pre-determined compositions and subsequently melt-mixed in the mixer. After mixing, the samples were dumped out and compressed into *ca.* 2 mm thick plates by a calender for further characterisation.

Air permeability measurement

The gas permeability of air for the resulted PCL/organoclay hybrids was measured at 25°C by the differential pressure method based on ASTM D1434 using a gas permeability test equipment which was assembled in our lab.[8] A schematic diagram of the tester is shown in Figure 1, in which a gas permeates through the sample film driven by the pressure difference in two champers. The air pressure in chamber I was kept constant and that in chamber II is 0 at the beginning of the test. During the experiment process, the pressure rise rate (dp/dt) in chamber II were measured automatically at predetermined time interval. Based on the experiment arrangement, the permeability coefficient P could be calculated according to the following equation:

$$J = P\frac{\Delta p}{l} \tag{1}$$

where J is the flux of air, Δp is the pressure rise in chamber II and *l* is the thickness of the sample film. The detailed procedure has been described previously [8].

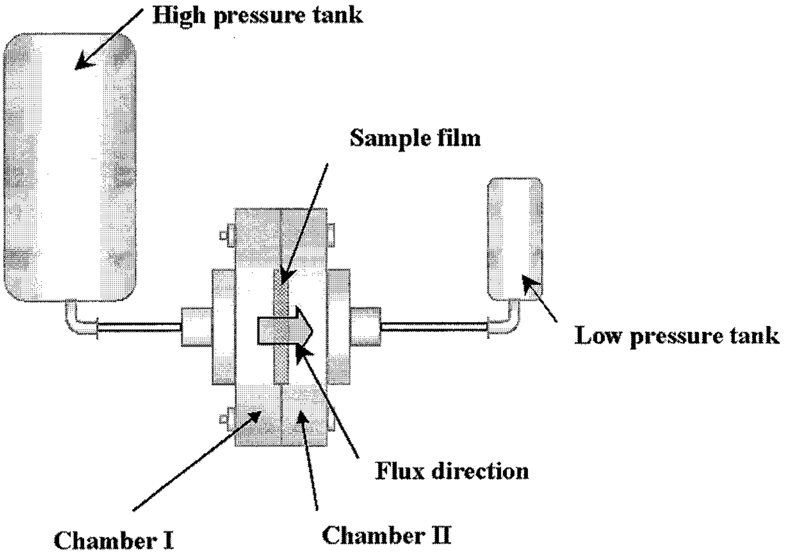

Figure 1. The schematic diagram of air permeability test equipment.

Mechanical properties measurement

The mechanical properties were measured at room temperature using an Instron tensile tester: model 4204, with a crosshead speed of 130 mm/min according to ASTM D1708-02. Dumbbell-shape specimens were stamped out using a stamping knife (length of narrow portion: 20 mm; width of narrow portion: 4 mm; width of ends: 8 mm; gauge length: 20mm). The strain was measured from the separation of the clamps. The elastic modulus (Young's modulus) was calculated from the initial slope of the nominal stress-strain curve. The yield stress was calculated from the peak stress value of the nominal stress-strain curve. The reported results are based on the average of data from 6 to 10 specimens for each sample.

Results and discussion

Structural Characterization of hybrids

The resulted hybrid structure for PCL/30B and PCL/93A hybrids was examined by WAXD and in Figures 2 and 3 the WAXD patterns of 30B and PCL/30B hybrids, 93A and

PCL/93A hybrids were shown, respectively. The primary silicate reflection at 2θ =5.02° for 30B in Figure 2 corresponds to a layer spacing of 1.76 nm that is higher than 1.1 nm of pristine montmorillonite MMT because of the insert of organic modifier. For the 2 and 5 wt% 30B hybrids, there are no any noticeable peaks of 30B at low angle range were observed, which confirms the exfoliated structure of silicate layers of 30B in PCL matrix after melt mixing. For 10 wt% 30B hybrids, a broad peak at 2θ = 3.0° which is much lower than that of pristine 30B was observed indicating intercalation of 30B occurred together with exfoliation. In Figure 3 we could see that the structure of 93A was almost unchanged after mixing process with PCL melt. A new broad peak appeared around 2θ = 5.9° means somewhat collapse of the layered structure of 93A. Accordingly, the PCL/30B hybrids form nanocomposites with exfoliated and intercalated 30B and PCL/93A hybrids are micro-scale composites. The nano structure in PCL/30B nanocomposites is assumed to be resulted from the additional interaction between the hydroxyl groups in the organic modifier of 30B and the carbonyl groups in PCL. Such interaction does not exist in PCL/93A between no polar group of the modifier in 93A and PCL molecules.[7]

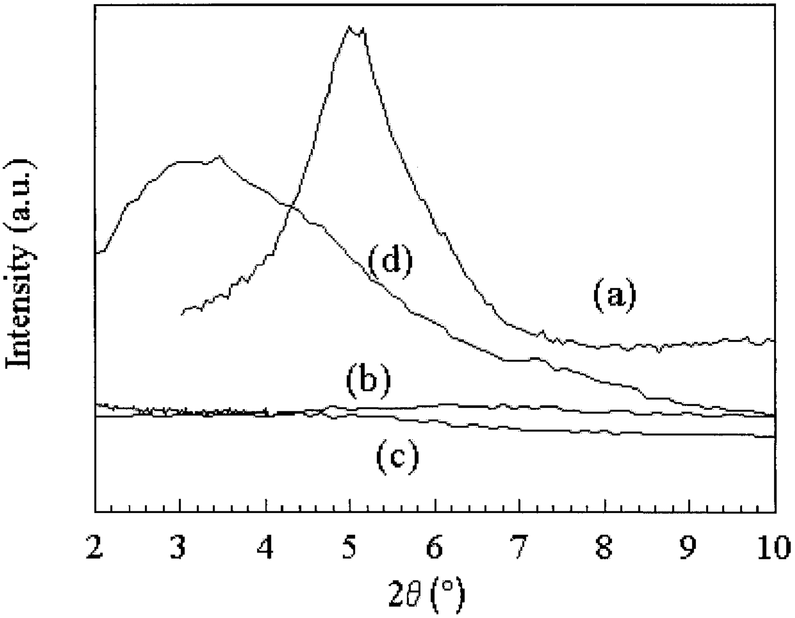

Figure 2. X-ray diffraction patterns of 30B and PCL/30B nanocomposites with different weight fractions of 30B: (a) 30B, (b) PCL/30B (2 wt%), (c) PCL/30B (5 wt%), (d) PCL/30B (10 wt%).

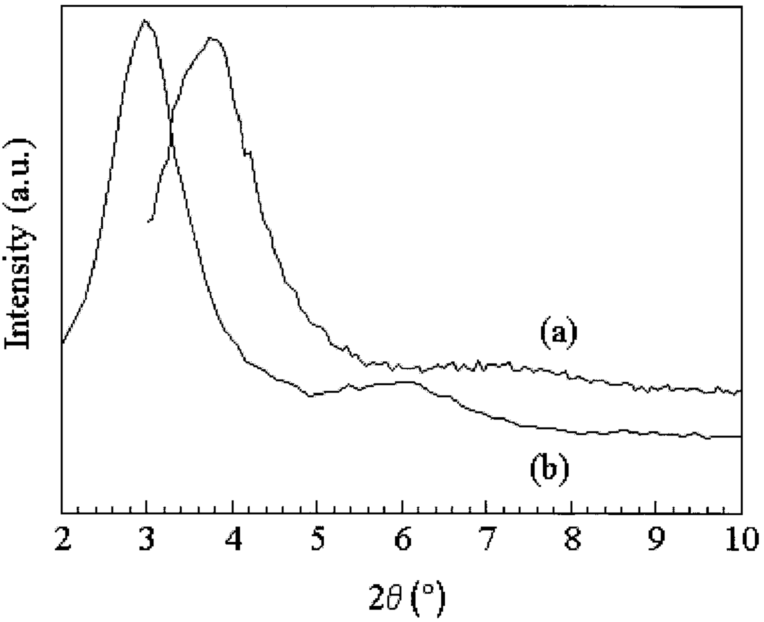

Figure 3. X-ray diffraction patterns of 93A and PCL/93A composite: (a) 93A, (b) PCL/93A (5 wt%).

Barrier performance

Inclusion of impermeable organoclay layers in PCL matrix is believed to increase the barrier properties of matrix resin by creating a maze or tortuous path that retard the progress of gas molecules through the matrix resin. The barrier properties of PCL/93A hybrids and PCL/30B nanocomposites films were investigated along with the film of neat PCL in this study. In Table 1 their air permeability coefficients measured at 25 °C are presented. The improvement of barrier characteristic was clearly shown by introduction of organoclays into PCL matrix. In both hybrids, the air permeation coefficient decreased with increasing organoclay content. However the reduction in PCL/30B nanocomposites was more significant than PCL/93A microcomposites. In PCL/30B nanocomposites the well dispersion of exfoliated 30B layers built more permeation barriers than poorly intercalated 93A tactoids. It also confirms that the origin of the barrier performance of the inclusions in composites lies in the tortuous pathway the gas molecules have to go through. Theoretical models have been developed to predict relative permeability in filler filled composites. According to a simple tortuous two dimension model,[9] the barrier performance of polymer composites containing dispersed platelet particles can be expressed by the following equation:

$$\frac{k_c}{k_m} = \frac{(1-\phi)}{1+\alpha\phi/2} \tag{2}$$

where k_c and k_m represent the gas permeability of composites and matrix polymer and ϕ and α represent the volume fraction and aspect ratio of platelets, respectively. It has been shown that this tortuous model predicted the permeability behaviour of a number of polymer systems, notably resins, reasonably well at very low loading of clay.[10] In this study, this model is examined to see if it is applicable for both PCL/organoclay nanocomposites and microcomposites. In Figure 4 the relative air permeability, k_c/k_m, for PCL/93A composites and PCL/30B nanocomposites were shown as a function of the volume fraction of respective organoclay. It can be seen that PCL/30 nanocomposites showed a rapid decrease in the air permeability at low loading levels, and levelled off with further 30B content increasing. While the poor enhancement of air barrier properties in PCL/93A composites was seen due to the non-intercalated structure of organoclay in PCL matrix. For the reason of comparison with the theoretical prediction, a constant aspect ratio of 200 was selected in the calculation according to reference[11] and was shown as theoretical prediction in Figure 4. The theoretical prediction was found to overestimate the barrier performance for PCL/30B nanocomposites. The observed discrepancy between experiment and theory could be explained by the lack of complete aligning of exfoliated or intercalated clays to the parallel direction of the PCL film (or perpendicular to the direction of air penetration), which is assumed to be a perfect arrangement in the theory.[9] The similar trend as theory prediction implies the applicability of this theory model to PCL nanocomposites, especially at low content of organoclay.

Table 1. The air permeability of PCL/organoclay hybrids.

Organoclay content (wt%)	Air permeability (cm^3 (STP) $mm/m^2/day$)	
	PCL/30B	PCL/93A
0	43.744	43.744
2	28.537	34.658
5	22.063	28.762
10	18.765	24.543

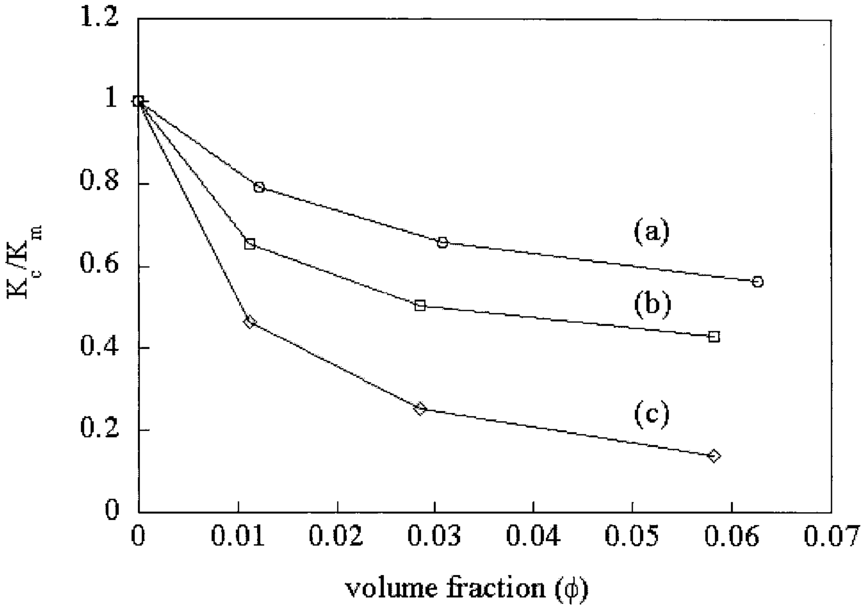

Figure 4. Air permeability ratio of composites to matrix PCL, K_c/K_m, as a function of volumetric fraction of organoclays: (a) PCL/93A, (b) PCL/30B, (c) Theory model.

Mechanical properties

Tensile properties of the pure PCL and PCL/organoclay hybrids were determined using a tensile tester by measuring load as a function of crosshead displacement. Typical stress-strain diagrams for neat PCL and PCL/organoclay hybrids containing 5 wt% of organoclay at 130 mm/min are shown in Figure 5. Table 2 shows summary of the results of the tensile test for PCL/30B nanocomposites and PCL/93A composites. As can be seen from Table 2, the yield strength and modulus for both hybrids were substantially improved relative to the neat PCL regardless of the organoclay type and they increased monotonously with increasing the organoclay content. However the nanocomposites showed more significant reinforcement than micro-composites as seen in Figure 5 and Table 2 that could be attributed to the better dispersion of organoclay 30B in PCL matrix than that of organoclay 93A. The same behaviour was also observed for polyimide/organoclay and nylon 6/organoclay nanocomposites in which better dispersion of organoclay resulted in higher tensile properties.[12,13] These values for PCL/30B nanocomposites are comparable to those of polyethylene/clay nanocomposites.[14] Because of the inclusion of rigid organoclay fillers, the fracture strain for both PCL hybrids decreased with the increasing of organoclay content. However those for nanocomposites were not changed significantly that decreased, as compared with neat PCL, from 89% at 2 wt% of 30B to 73% at 10 wt% of 30B; those for PCL microcomposites were dramatically decreased from 75% at 2 wt% of 93A to 54% at 10 wt% of 93A. The higher interaction between organoclay 30B and PCL matrix than that between 93A and PCL resulted in the higher fracture strain for PCL/30B nanocomposites than that for PCL/93A microcomposites at the same organoclay loading.

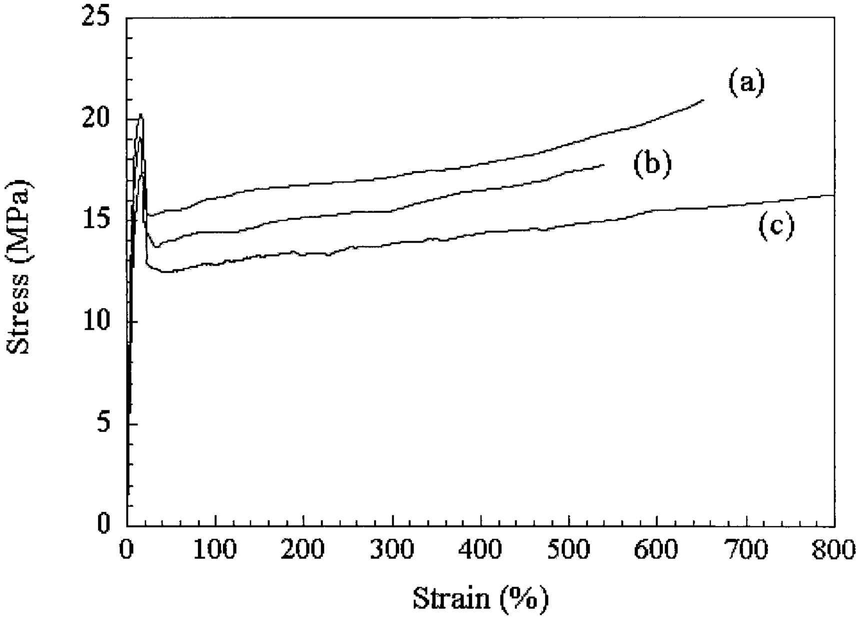

Figure 5. Stress-strain curves for PCL and two composites at a crosshead speed of 130 mm/min: (a) PCL/30B (95/5), (b) PCL/93A (95/05) and (c) PCL.

Table 2. The mechanical properties of PCL/organoclay hybrids.

Organoclay content (wt%)	Young's modulus (MPa)		Yield strength (MPa)		Elongation at break (%)	
	PCL/30B	PCL/93A	PCL/30B	PCL/93A	PCL/30B	PCL/93A
0		174.3		16.9		804
2	246.1	196.4	20.19	18.2	718	604
5	307.7	223.6	21.26	19.7	644	510
10	347.8	248.8	24.67	21.1	588	438

Conclusions

The nanocomposites based on biodegradable PCL and organoclay have been achieved by proper selection of organoclay and melt mixing processing techniques. The interaction between the matrix and organic modifier of clay favours exfoliation of organoclay layers which already becomes one of criterions for selecting pairs of organoclay and polymer matrix in order to make nanocomposites. For the reason of comparison, the microcomposites based on PCL and organoclay were also prepared in which the organoclay was only slightly intercalated. The produced nanocomposites showed more significant improvements in air barrier performance and mechanical properties with respect to the microcomposites which are resulted from the fine dispersion of organoclay layers in the PCL matrix. The strong interaction between organic surfactants of organoclay and PCL molecules causes less loss of elongation at break for PCL nanocomposites than PCL microcomposites. The observed dramatic decrease in air permeability and enhancement in mechanical properties for PCL nanocomposites are of great interest for enlarging their use in food packaging, protective coating and other applications where efficient polymeric barriers are needed.

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