

EFFECT OF NANO-FILLER DISPERSION ON THE THERMAL, MECHANICAL AND WATER SORPTION PROPERTIES OF GREEN ENVIRONMENTAL POLYMER*

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Abstract Partially exfoliated nanocomposite (**2**) has been synthesized by intercalation of poly(propylene carbonate) (PPC) into commercial clay, Cloisite 20B (PPC/C-20B). Nanocomposite **2** was characterized physico-chemically and exhibited high thermal, mechanical and anti-water sorption properties as compared to PPC and intercalated nanocomposite (**1**) of PPC/C-20B having same amount of clay. TGA results revealed that the thermal decomposition temperature ($T_{d, 50\%}$) of **2** increased significantly, being 40 K and 17 K higher than that of pure PPC and **1**, respectively, while DSC measurements indicated that the nano-filler dispersion of **2** increased the glass transition temperature from 21°C to 31°C. Accordingly, **2** showed high elastic modulus, hardness and anti-water absorption capacity. These thermal, mechanical and anti-water absorption improvements are of great importance for the application of PPC as packaging and biomaterials.

Keywords: Poly(propylene carbonate); Cloisite 20B; Nanocomposite; Solution intercalation; Thermal property; Mechanical property; Water absorption property.

INTRODUCTION

Carbon dioxide is the main cause of greenhouse effect and environmental pollution which recently has attracted great scientific interest^[1–3]. One of the main use of carbon dioxide is its conversion into a green environmental biodegradable polymer called poly(propylene carbonate) (PPC). PPC can be prepared by copolymerization reaction of carbon dioxide and propylene oxide^[4]. Synthetic procedure and chemical structure of PPC is depicted in Fig. 1. PPC is a polymer which can degrade by using bio agents into H₂O and carbon dioxide, and thus synthesis of PPC can fix and recycle carbon dioxide in the environment. This polymer has interesting chemical and physical properties such as compatibility, impact resistance, translucence, innocuousness *etc*, which can be used as adhesives, solid electrolytes, barrier materials, plasticizers and new materials for packaging applications^[5, 6]. Having eco-friendly nature and fascinating applications in various fields, PPC has great demand

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to enhance its thermal, mechanical and anti-water sorption properties.

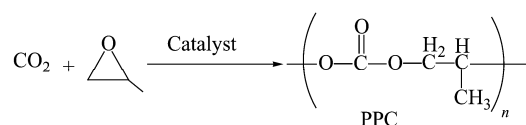


Fig. 1 Synthetic scheme and chemical structure of poly propylene carbonate (PPC)

All over the world, the advancement of biodegradable materials with meticulous properties has been a matter of great research contest to the scientific community. These ingredients have a tendency to replace synthetic polymer in all the applications which are the source of enormous quantity of waste. However, biodegradable polymers alone have imperfect physical and mechanical properties which currently do not allow them to substitute fully the mainstream plastics^[7]. One of the best methods to improve various properties of biodegradable polymers is bio-nanocomposition which can be obtained by blending of biopolymer with inorganic nano-filler. Nanoclays such as montmorillonite or hectorite are typically used as nano-fillers to enhance the thermal stability, mechanical toughness, biodegradation rate *etc.* of biodegradable polymers and widen their applications^[8–11]. Clays have small size and large active surface area which bind strongly by interfacial interaction with polymers and this strong interaction is responsible for enhancement of various physical and chemical properties of the polymer. Clays are well known inorganic nano-fillers and widely used for nanocomposite synthesis in various polymers to improve the desired properties of polymers and expand their applications in assorted fields^[12–16].

Therefore, in the present investigation we have made an attempt to develop nanocomposites by incorporating of commercial clay, Cloisite 20B (C-20B) into PPC matrix so as to improve the PPC performance. In view of the isotropic nature of ionic interactions, the resulting nanocomposites demonstrated excellent thermal and mechanical properties. PPC/clay nanohybrids were confirmed on the basis of FT-IR spectrum while the morphologies were corroborated *via* X-ray diffraction (XRD). Further the effect of C-20B on thermal, mechanical and water absorption properties of PPC have been studied on the basis of TGA, DTG, DSC, nanoindentation and microbalance and interestingly partially exfoliated PPC/C-20B nanocomposite (**2**) showed high thermal, mechanical and anti-water sorption properties.

EXPERIMENTAL

Materials

Poly propylene carbonate (PPC) and Cloisite 20B were purchased from Sigma-Aldrich Chemicals, USA, and other chemicals and solvents were of reagent grade and used without further purification.

Preparation of Nanohybrids

PPC/C-20B nanocomposite **2** was synthesized by dissolving PPC (2 g) in 30 mL acetone and added dropwise into a dispersed solution of C-20B (0.1 g in acetone 10 mL) and stirred for 7 h at 70°C. The solvent from the suspension was evaporated and the product was dried at 25°C for 24 h in vacuum oven. Nanocomposite **1** is an intercalated PPC/C-20B nanocomposite having same amount of clay as nanocomposite **2**. The preparation and performance of nanocomposite **1** are given in our previous work^[4]. The data of nanocomposite **1** are used here for comparison with the permission of the publisher, The Membrane Society of Korea.

Characterization

X-ray diffraction patterns (XRD) were taken with a computer controlled RINT 2000, Rigaku diffractometer using the Ni-filtered Cu-K α radiation ($\lambda = 0.15405$ nm) which was operated at 40 kV and 20 mA. The general morphologies of nanocomposites were evaluated by transmission electron microscopy (LIBRA 120). FT-IR (Fourier transform infrared spectrometer) spectra were recorded in KBr dispersion on a JASCO model FT-IR. Thermogravimetric analysis (TG) is conducted using a Perkin-Elmer apparatus with a heating rate of 10 K/min

in the temperature range from 30°C to 600°C in nitrogen. The glass transition temperature (T_g) of nanocomposites was analyzed by a Perkin-Elmer DSC-7 differential scanning calorimeter in a N_2 environment. The samples were heated at a rate of 10 K/min from -10°C to 70°C , then quenched to -10°C and finally heated again to 70°C at a rate of 10 K/min. The T_g was gotten from the second heating run. Nanoindentation experiments were performed using a fully calibrated Nano Indenter XP (Nanoinstruments Innovation Center, MTS Systems, USA) equipped with a standard Berkovich indenter. During each test run, a personal computer collected and stored data for calculating hardness, modulus and the load and displacement as the indenter was driven into the sample (loading segment) and then withdrawn from it (unloading segment). The data were then used to construct the load-displacement plot. A total of 8 indentations were made on each of the specimens. Water absorption was measured using a thin film diffusion analyzer (Cahn Instruments, Model D-200, CA). For water uptake studies, the PPC nanocomposite membrane was first dried in vacuum oven at 100°C for 12 h. The weight of the completely dried samples (W_d) was initially measured using microbalance. Then the membrane was kept in a humidified chamber with de-ionized water until no further water uptake took place (4 h). A water uptake study was carried out at room temperature. When there was no water uptake, the film was removed out of the chamber and the free water was removed from the membrane by using blotting paper. Again the weight of the membrane was measured (W_s) with micro balance. Then the water uptake (S) was calculated using the following equation.

$$S (\%) = \frac{W_s - W_d}{W_d} \times 100$$

RESULTS AND DISCUSSION

Physico-chemical Characterization of Nanocomposite

The morphological structure of organic/inorganic composites is very important characteristic because it ultimately affects many physical properties of the polymer composites, such as thermal stability, mechanical property, water and gas permeability, *etc.* In order to obtained high thermal, mechanical and water anti-sorption properties of PPC, Cloisite 20B was selected as an inorganic nano-filler for PPC/clay nanocomposites. Cloisite 20B is organophilic in nature and has high basal spacing and thus PPC can intercalate into the interlayer space of the clay. The influence of C-20B on the morphology of the PPC/C-20B nanocomposite was explored *via* X-ray diffraction (WAXD), and the basal spacing of C-20B and PPC/C-20B nanocomposites was calculated from the d_{001} peak using the Bragg's equation. The results were depicted in Fig. 2.

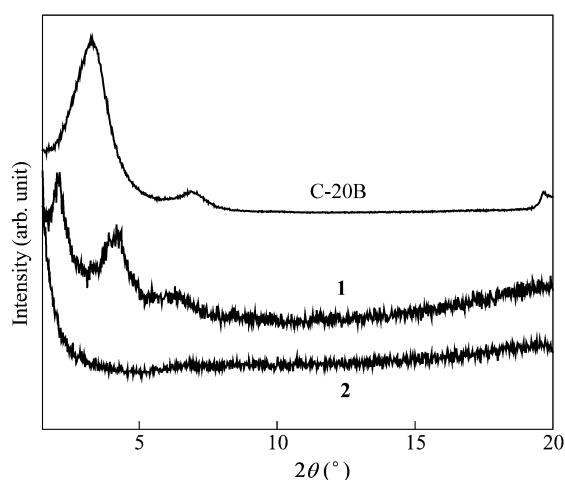


Fig. 2 Powder XRD patterns of C-20B, nanocomposite 1 (data taken from Ref. [4]) and nanocomposite 2

The X-ray diffraction pattern (XRD) of C-20B clearly shows a well crystalline peak at $2\theta = 3.22^\circ$ (2.74 nm) which disappears in the pattern of nanocomposite **2** after treatment with PPC in acetone at high temperature. The nanocomposite **2** exhibits a weak peak at 2θ of 6.8° (1.30 nm) indicating that the sheets of the clay are disturbed and the structure of this nanocomposite looks partially exfoliated. In case of nanocomposite **1**, the peak spacing of 2.74 nm for C-20B changed to 4.42 nm after treatment with PPC in acetone at room temperature^[4]. This momentous augment in the basal space indicates that the PPC has been intercalated into the sheets of the clay and increases the basal spacing of the sheets. These WAXD results suggest that, the incorporation of C-20B gives high effect on morphological structure of PPC. WAXD results further suggest that solvent and temperature affect the morphological structure of nanocomposites cause enhancement in their thermal and mechanical properties.

Figure 3 illustrates the morphology of nanocomposites **1** and **2**. Nanocomposite **1** showed stacked layers while **2** exhibited stacked layers as well as stacks lack layer with good distribution within the polymer matrix. The partially exfoliated layers are responsible for the disappearance of diffraction peaks in XRD. Figure 4 shows the FT-IR spectra for PPC, nanocomposite **1**, nanocomposite **2** and C-20B. FT-IR spectrum of PPC exhibits absorption bands at 2800–2900, 1750, 1360, 1220 and 775 cm^{-1} which correspond to C–H, C=O and C–O stretching vibrations. C-20B shows absorption bands at 1050, 914, 3400–3600 cm^{-1} which are responsible for the stretching mode of Si–O, Al–Al–OH and silanol groups^[4]. C-20B also displays absorption bands at 2926, 2852 and 1470 cm^{-1} which can be ascribed to C–H stretching and bending, respectively, of the alkylammonium existing inside the layer of the clay. FT-IR spectrum of nanocomposites **1** and **2** show all characteristic peaks of C-20B and PPC which suggest the successful development of nanocomposites.

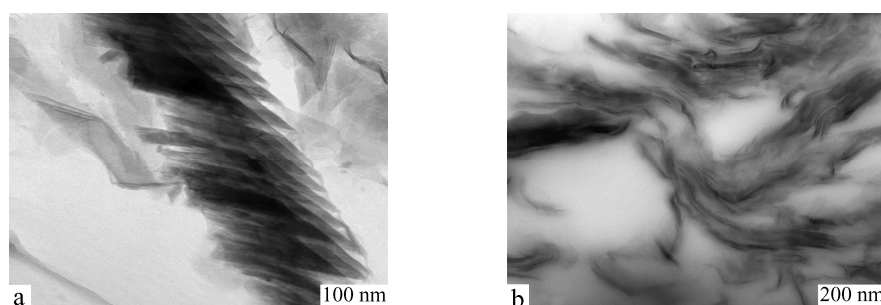


Fig. 3 TEM images of nanocomposite **1** (a) and nanocomposite **2** (b)

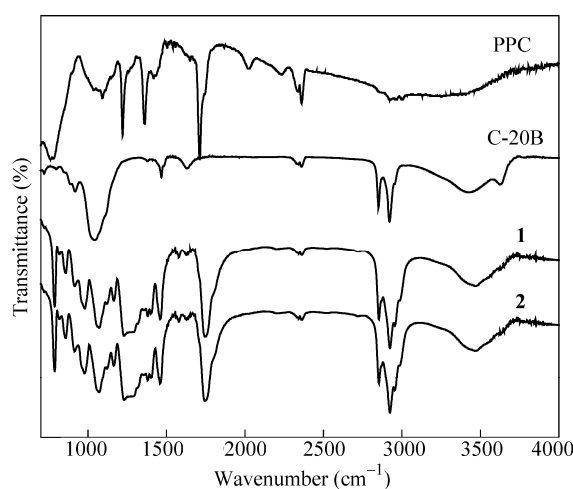


Fig. 4 FT-IR spectra of PPC, C-20B, nanocomposite **1** (data taken from Ref. [4]) and nanocomposite **2**

Thermal Degradation Properties

The influence of clay on the thermal property of PPC was studied by TGA under nitrogen atmosphere, and results are shown in Fig. 5. PPC and nanocomposites exhibited the same pattern of thermal degradation which indicated that the introduction of clay into the PPC matrix did not alter the thermal degradation mechanism of PPC^[1–3]. Generally PPC undergoes two steps of thermal decomposition *i.e.* scission reaction of the backbone, followed by an unzipping reaction^[17]. Finally, carbon dioxide and propylene oxide were produced. The first weight loss occurred roughly from 220°C to 250°C is account to around 91% weight loss, and the second step from about 300°C to 356°C is account to around 8% weight loss in PPC. In nanocomposites the degradation step occurred between around 50°C and 250°C (8%) is due to the low thermal stability of organic moiety within the C-20B of the nanocomposites. The second stage of decomposition started from around 250°C to 307°C, was attributed to major weight loss due to decomposition of polymeric network. Although the onset of weight loss of PPC nanocomposites occurs at a lower temperature than that of pure PPC, the incorporation of inorganic precursors highly influenced the thermal stability of the organic matrix. By comparing the TGA curves of PPC with the nanocomposites, **1** and **2** exhibited higher thermal stability than pure PPC. C-20B has high thermal stability which is responsible for the improvement of thermal stability after its incorporation into PPC matrix. Of the two nanocomposites, **2** shows higher thermal stability which indicates that thermal stability strongly depends on inherent effect and morphological imperfectness of C-20B.

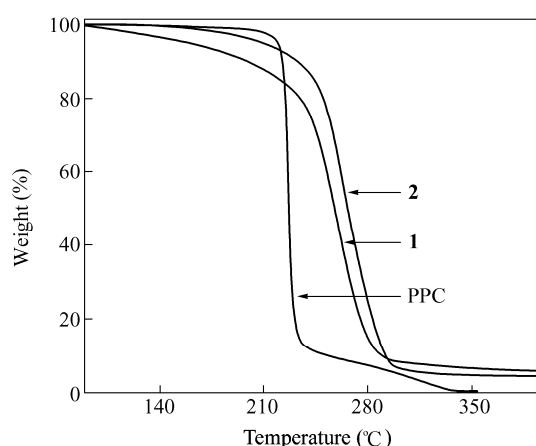


Fig. 5 TG curves of PPC, nanocomposite **1** (data taken from Ref. [4]) and nanocomposite **2**

Table 1 summarizes the 5%, 10% and 50% weight loss decomposition temperatures of PPC and nanocomposites, defined as $T_{d,5\%}$, $T_{d,10\%}$ and $T_{d,50\%}$, respectively. The nanocomposites **1** and **2** showed a notable 23 K and 40 K increase of the PPC thermal stability at $T_{d,50\%}$ which clearly demonstrates the importance of clay in the nanocomposite. These results confirm that incorporation of nano-filler has great influence on the thermal stability of the organic matrix and the higher thermal stability of **2** also confirms that the thermal properties of nanocomposites are strongly dependent on the dispersion of nano-fillers. If the nano-fillers are well dispersed in the polymer matrix, it will show higher thermal properties than those composites with poor dispersion of nano-fillers^[18, 19]. Thus lower thermal stability of **1** is due to lower dispersion (aggregation) of nano-filler and thus morphology is an important factor for the thermal stability of nanocomposites.

Table 1. TGA results of PPC and PPC/C-20B nanocomposites **1** (data taken from Ref. [4]) and **2**

Sample name	PPC	1	2
$T_{5\%}$ (°C)	230	175	187
$T_{10\%}$ (°C)	234	239	229
$T_{50\%}$ (°C)	239	262	279

The role of clay as thermal stabilizer was also studied by DTG analysis, and the results are presented in Fig. 6. The DTG peak of PPC is quite narrow which becomes much coarser and wider after incorporation of C-20B. This indicates that addition of C-20B improves the fast thermal decomposition of PPC. Thus C-20B acts as superior insulator which increases thermal stability of PPC. The clay layers behave like a mass transport barrier for thermally low stable compounds by causing difficulty in heat conduction and thus the nanocomposites give wider and coarser DTG peaks.

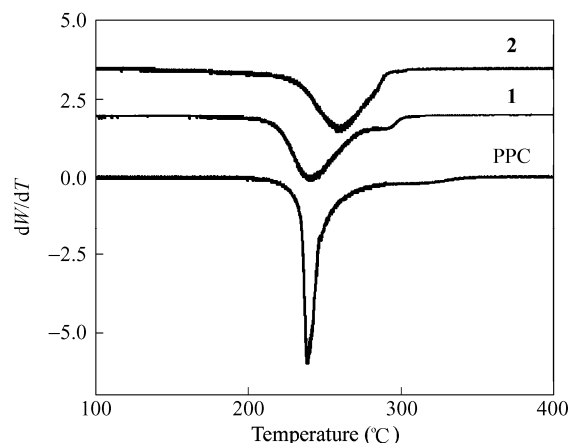


Fig. 6 DTG curves of PPC, nanocomposite **1** (data taken from Ref. [4]) and nanocomposite **2**

The glass transition temperatures of PPC and PPC/C-20B nanocomposites were elucidated by DSC analyses, which are shown in Fig. 7 and Table 2. The pure PPC exhibits a glass transition temperature (T_g) at 21°C. With the addition of C-20B, the glass transition temperatures of PPC/C-20B nanocomposites obviously increased, and the nanocomposite **2** shows a T_g at 31°C, which is 10 K higher than that of PPC. The high glass transition temperature of nanocomposites is due to the strong interaction among clay layers and polymer matrix which results in restriction of segmental motion of PPC molecular chains. The improvement of thermal stability and glass transition temperature concluded that nanocomposition is a proficient approach to enhance the thermal stability of PPC.

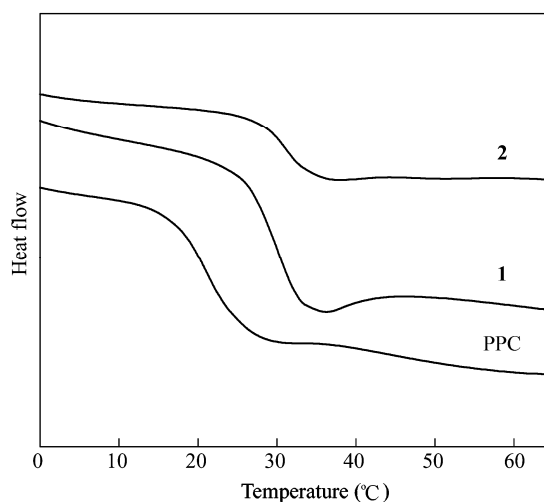


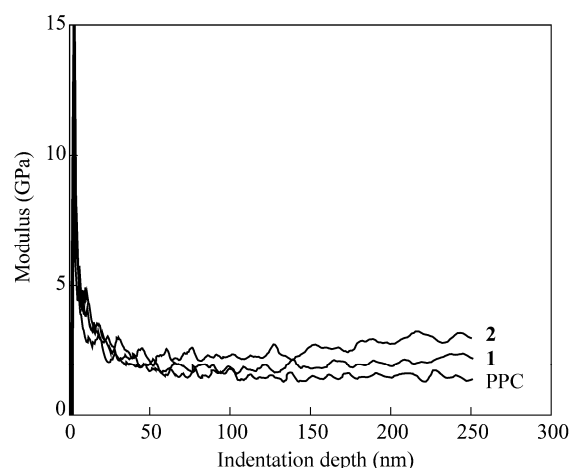
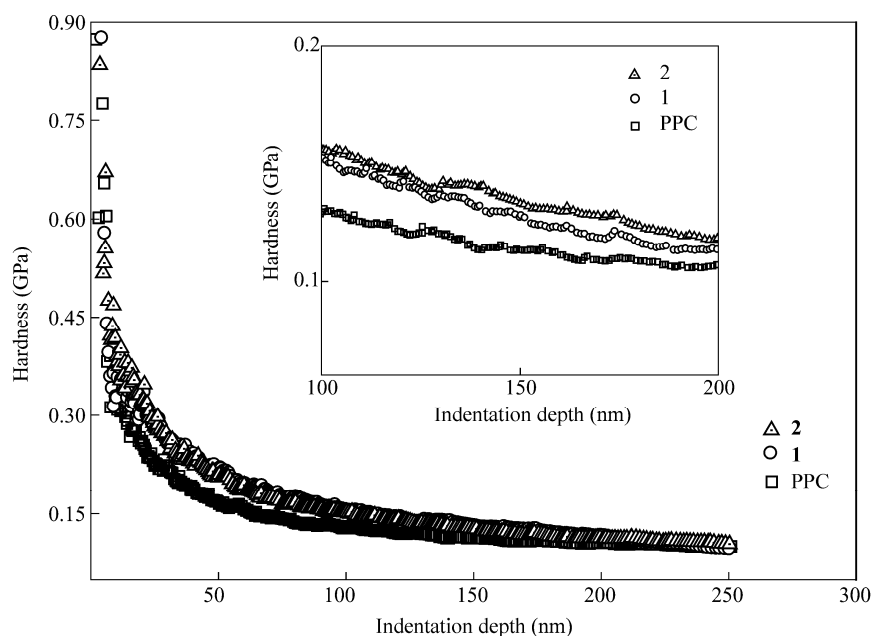
Fig. 7 DSC curves of PPC, nanocomposite **1** (data taken from Ref. [4]) and nanocomposite **2**

Table 2. DSC results of PPC and PPC/C-20B nanocomposites **1** (data taken from Ref. [4]) and **2**

Sample name	PPC	1	2
T_g ($^{\circ}\text{C}$)	21	30	31

Mechanical Properties

Mechanical properties of nanocomposites **1** and **2** were elucidated by nano-indentator in order to study the effect of nano-filler on modulus and hardness of PPC for biomedical applications^[20]. From biomedical applications point of views, the polymeric materials should exhibit high resistance against the stresses applied by various parts of the body. Thus polymeric materials should show high hardness and modulus^[21].

**Fig. 8** Elastic modulus of PPC, nanocomposite **1** and nanocomposite **2****Fig. 9** Hardness of PPC, nanocomposite **1** and nanocomposite **2**

Nanoindentation is a powerful method which can offer nano-mechanical properties (modulus and hardness) at surface layers in comparison to classical tensile tests. To evaluate the effect of clay loading on elastic modulus

and hardness of PCC, the modulus and hardness values of PCC/C-20B nanocomposites were measured, and the results are presented in Table 3 and shown graphically in Figs. 8 and 9. From Fig. 8, it is observed that nanocomposites **1** and **2** have higher elastic modulus than pure PPC which confirms that the clay loading increases the elastic modulus. The nanoclay fillers have high elastic modulus and exhibiting strong interfacial interaction with polymer. These high interfacial interaction and reinforcing behaviors of nanoclay result in the enhancement of elastic modulus and hardness of PPC. Of the two nanocomposites, **2** exhibited higher elastic modulus which may be related to the clay morphology within the matrix. It has been shown that the intercalated clay morphology induces lower mechanical properties than the exfoliated one^[20]. This effect can be explained by a more heterogeneous structure of the nanocomposite **1**, probably due to the difficulty in obtaining a homogeneous material in case of intercalated nanocomposite^[21].

Table 3. Modulus and hardness results of PPC and PPC/C-20B nanocomposites **1** and **2**

Properties	PPC	1	2
Modulus (GPa)	1.414	1.950	2.340
Hardness (GPa)	0.105	0.114	0.121

Nanocomposite **1** enhanced the elastic modulus of PCC from 1.41 GPa to 1.95 GPa, while that of **2** increased from 1.41 to 2.34 GPa. The hardness of PCC was increased for nanocomposites **1** and **2** from 0.105 GPa to 0.114 GPa and 0.121 GPa, respectively. Thus clay loading into the polymer matrix may enhance the modulus and hardness and this improvement in the mechanical properties supports the DSC results. As seen from DSC results, **2** shows low crystallinity than **1** which is due to the well dispersion of clay layers inside the polymer structure. This dispersion of clay increases the entanglement of clay with PCC and results in higher interfacial interactions which results in high thermal and mechanical properties.

Water Absorption

In packaging applications, high moisture content considerably restricts the use as potential packaging materials. Thus, the water sorption behaviors of the PPC and PPC/C-20B nanocomposites were gravimetrically investigated at 25°C and 100% relative humidity, and the results are depicted in Fig. 10^[22, 23]. All nanocomposite films with C-20B showed relatively lower water uptake. It indicates that the water resistance capacity of PPC is greatly enhanced by the composite systems. This indicates that the additions of C-20B into the PPC matrix decreases the transmission rate and reduce the amount of penetrant which results in reduction of absorption capacity of PPC. Also the additions of C-20B into the PPC matrix reduce the ability of penetrant molecules to diffuse through PPC.

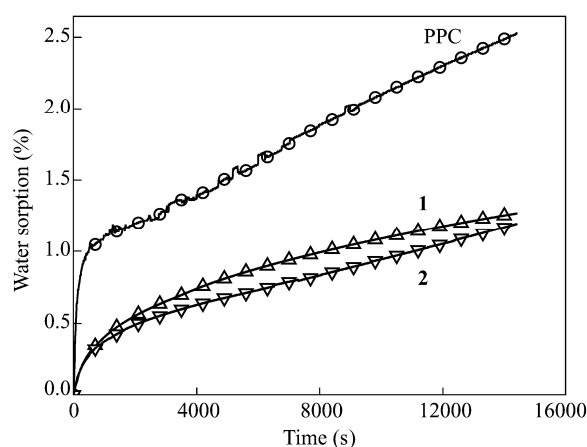


Fig. 10 Water absorption curves of PPC, nanocomposite **1** (data taken from Ref. [4]) and nanocomposite **2**

The degree of water absorption decreased with increase in loading levels of inorganic fillers. The lower degree of water absorption of PCC/C-20B as compared to PCC may be due to the stronger interfacial adhesion and hydrophobicity of nanocomposites due to the organoclay. Nanocomposites found many potential applications in engineering sectors because of their high thermal property, mechanical property, strength and fracture toughness. Despite of these improvements, nano-fillers have also shown outstanding barrier capability and significantly decrease the moisture and gas permeability. The decrease in moisture absorption can reduce the internal damage and enhance long-term performance of polymers. Generally organophilic clay creates bonds with PPC which possibly cause resistance to the water molecule and thus the interface between nanoclay and polymer cannot be affected by a large amount migration of water molecules.

CONCLUSIONS

PPC/OMMT nanocomposites were prepared by solution intercalation method. The nanocomposites may have intercalated and exfoliated structures as revealed by XRD. The thermal stability, glass transition temperature and mechanical properties of PPC are improved by adding C-20B into PPC matrix. The PPC/C-20B nanocomposite **2** with partially exfoliated morphology showed better thermal, mechanical and anti-water sorption properties. These improvements could be attributed to the enough amount and good dispersion of C-20B in PPC matrix. The nanocomposition provides an efficient way to improve both the thermal, mechanical and anti-water sorption properties of PPC and consequently widely expands its application fields.

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