

Preparation and properties of poly(vinyl alcohol)–clay nanocomposite materials

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Abstract

A series of polymer–clay nanocomposite (PCN) materials that consist of poly(vinyl alcohol) (PVA) and layered montmorillonite (MMT) clay are prepared by effectively dispersing the inorganic nanolayers of MMT clay in organic PVA matrix via an in situ free radical polymerization with AIBN as initiator. Organic vinyl acetate monomers are first intercalated into the interlayer regions of organophilic clay hosts and followed by a one-step free radical polymerization. The prepared poly(vinyl acetate)–clay (PVAc–clay) solution are then saponified via direct-hydrolysis with NaOH solution to form PVA–clay nanocomposite materials. The as-synthesized PCN materials are typically characterized by Fourier-Transformation infrared (FTIR) spectroscopy, wide-angle X-ray diffraction and transmission electron microscopy.

The molecular weights of poly(vinyl alcohol) (PVA) extracted from polymer–clay nanocomposite (PCN) materials and bulk PVA are determined by gel permeation chromatography (GPC) analysis with THF as eluant. The viscosity property of PCN materials with different feeding amount of MMT clay is studied by an Ubbelohde capillary viscometer. The morphological image of as-synthesized materials is studied by scanning electron microscopy (SEM) and optical polarizing microscope (OPM). Effects of the material composition on the thermal stability, mechanical strength, optical clarity of PVA along with a series of PCN materials, in the form of fine powder and free-standing film, are also studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analyzer (DMA) and UV–visible transmission spectra, respectively.

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1. Introduction

Nanocomposite materials consisting of inorganic nanolayers of montmorillonite clay and organic polymers have evoked intense research interests lately because their unique characteristics create many potentially commercial applications. PCN are reported to promote the thermal [1], mechanical [2], molecular barrier [3], flame retardant [4] and corrosion protection properties [5–7] of polymers at low clay loading based on the recently published literatures. The earlier historical development involving the PCN materials can be traced back to 1990 based on the research work of polyamide–clay nanocomposite by Toyota's research group [8]. Subsequently, lots of PCN material systems are developed by the dispersing of alkylammo-

nium-exchanged forms of montmorillonites in various polymeric matrix such as nylon [8], poly(methyl methacrylate) [9], epoxy resin [10], polyimide [11], polystyrene [12], etc.

Recently, PCN materials that consist of PVA and layered materials are found to display novel properties, which can be observed from two dissimilar chemical components combining at the molecular level. There are several publications associated with the preparation and properties of PVA–clay nanocomposite materials prepared by solution dispersion technique [13–15]. However, preparation and property studies of PVA–clay nanocomposite materials by in situ polymerization have not been reported.

In this paper, we prepare a series of PCN materials by effectively dispersing the inorganic nanolayers of MMT clay in organic PVA matrix via an in situ free radical polymerization with AIBN as initiator and followed by

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direct-hydrolysis with NaOH solution. The as-synthesized PCN materials are characterized by Fourier-transformation infrared (FTIR) spectroscopy, wide-angle X-ray diffraction (XRD) and transmission electron microscopy (TEM). The molecular weights of PVA extracted from PCN materials and bulk PVA are determined by GPC analyses with THF as eluant. Viscosity of PCN materials with different feeding amount of MMT clay is studied by Ubbelohde viscometer. The morphological images of as-synthesized materials are also studied by SEM and OPM. Effects of the material composition on the thermal stability, mechanical strength, optical clarity of PVA along with a series of PCN materials, in the form of fine powder and free-standing film, are also studied by TGA, DSC, DMA and UV–visible transmission spectra, respectively.

2. Experimental section

2.1. Chemicals and instrumentations

Diallylamine (98%, Lancaster), methanol (Tedia, ACS grade), vinyl acetate (99%, Fluka), 2,2-azobis-isobutyronitrile (AIBN) (99%, Showa), hydroquinone (99%, Merck), sodium hydroxide (98%, Acors), N-methyl-2-pyrrolidinone (NMP) (99.97%, Tedia), poly(methyl methacrylate) (Acros, $M_w = 350,000$), lithium chloride (Acros, 99%), tetrahydrofuran (THF) (99%, Merck), *N,N*-dimethylacetamide (DMAc) (98%, Aldrich) were used as received without further purification. Hydrochloric acid (37%, Riedel-de Haën) was applied to prepare the 1.0 M HCl aqueous solution. The used montmorillonite clay consisted of an unit cell formula $[\text{Na}_{0.48}\text{K}_{0.01}\text{Ca}_{0.01}\text{Ti}_{0.01}](\text{Fe}_{0.20}\text{Al}_{1.44}\text{Mg}_{0.31})(\text{Si}_{3.39}\text{Al}_{0.07})\text{O}_{10}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and a CEC value of 98 mequiv./100 g was provided by Pai-Kong Ceramic Company, Taiwan.

FTIR spectra were recorded from pressed KBr pellets using a BIO-RAD FTS-7 FTIR spectrometer. Wide-angle powder XRD study of the samples was carried out by Rigaku D/MAX-3C OD-2988N X-ray diffractometer with copper target and Ni filter at a scanning rate of $4^\circ/\text{min}$. The samples for TEM study was first prepared by putting PVA-clay powder into poly(methyl methacrylate) (PMMA) capsules and by curing the PMMA at 100°C for 24 h in a vacuum oven. Then the cured PMMA containing PCN materials were microtomed with Reichert-jung Ultracut-E into 60–90 nm thick slices. Subsequently, one layer of carbon about 10 nm thick was deposited on these slices on mesh 100 copper nets for TEM observations on a JEOL-200FX with an acceleration voltage of 120 kV. The molecular weight of polymer extracted from all samples as well as bulk PVA was determined by GPC. Waters GPC model 2 II equipped with a model 590 programmable solvent delivery module, a differential refractometer detector and a Styragel HT column were employed to perform the GPC studies. The intrinsic viscosity measure-

ments of as-synthesized materials was carried out using an Ubbelohde capillary viscometer, Schott Avs310, in solvent of DMAc with concentration of 0.5 g/dl at 30°C . The morphological images of as-synthesized materials were evaluated by a SEM with a model JEDL JSM-6330F and an Olympus DP10 polarizing microscope. SEIKO Thermal Analysis System equipped with model TGA/SDTA 851 TGA was employed to perform the thermal analyses from 50 to 900°C temperature range at a heating rate of $20^\circ\text{C}/\text{min}$ under N_2 flow. DSC was performed on a DSC-910S in the 40 – 290°C range under N_2 flow at the programmed heating rate of $10^\circ\text{C}/\text{min}$. Dynamic mechanical analyses for the free-standing film of samples were performed from -50 to 190°C with a Perkin–Elmer DMA 7e analyzer at a heating rate of 5°C at a fixed frequency of 1 Hz. The UV–visible transmission spectra of the polymer in the form of membrane were recorded on a Hitachi U-2000 UV–visible spectrometer at room temperature.

2.2. Preparation of organophilic clay [5–7]

The organophilic clay is prepared by a cationic-exchange reaction between the sodium cations of MMT clay and alkylammonium ions of intercalating agent, diallylamine. Typically, 5 g of MMT clay with a CEC value of 98 mequiv./100 g is stirred in 800 ml distilled water (beaker A) at room temperature for 24 h. A separate solution containing 0.571 g of diallylamine in another 100 ml of distilled water (beaker B) is under magnetically stirring and follows by adding 1.0 M HCl aqueous solution to adjust the pH value to about 3–4. After stirring for 1 h, the diallyl ammonium chloride solution (beaker B) is added at a rate of approximately 10 ml/min with vigorous stirring to the MMT suspension (beaker A). The mixture is stirred for 24 h at room temperature. The organophilic clay is recovered by ultracentrifuging (9000 rpm, 30 min) and filtering the solution in a Buchner funnel. Purification of products is performing by washing and filtering samples repeatedly for at least three times to remove any excess of ammonium ions. Upon drying under dynamic vacuum for 48 h, the organophilic clay is obtained.

2.3. Preparation of PVA and PVA-clay nanocomposite materials

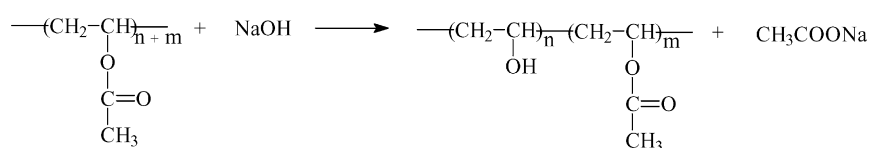
As a typical procedure for the preparation of PVA or PCN materials via an in situ free radical polymerization, an appropriate amount of organophilic clay, calculated by 0 wt% (0 g, for PVA), 0.15 wt% (0.015 g), 0.3 wt% (0.03 g), 1 wt% (0.1 g), 1.5 wt% (0.15 g), 3 wt% (0.3 g), 5 wt% (0.5 g) with respect to vinyl acetate, is introduced into 100 ml of methanol under magnetically stirring for 24 h at room temperature. Vinyl acetate monomer, calculated by 100 wt% (10 g, for PVA), 99.85 wt% (9.985 g), 99.7 wt% (9.97 g), 99 wt% (9.9 g), 98.5 wt% (9.85 g), 97 wt% (9.7 g), 95 wt% (9.5 g) respectively, is dissolved in 8 ml of

methanol and subsequently added to the solution of dispersed organophilic clay. The mixture was then stirred and heated up to 60–65 °C. Upon addition of 2 ml methanol solution containing initiator AIBN (0.02 g, 1/1000 mole ratio with respect to vinyl acetate monomer), the mixing solution is stirred for 4 h at 60–65 °C. Hydroquinone (0.1 g) is then added to quench the reaction. After further reacting for 5 min, the prepared poly(vinyl acetate) (PVAc) or PVAc–clay solution is cooled to 40 °C and subsequently mixed with 20 ml of methanol under magnetically stirring for further direct-hydrolysis reaction. A separate solution

weights of both extracted and bulk PVA are determined by GPC analyses with THF as eluant.

3. Results and discussions

PVA has been used for many industrial applications such as paper processing, textile sizing and finishing, adhesives and binders, dispersant and molded products. The typical preparative scheme of PVA can be represented as follows:



containing 0.2 g of NaOH in 20 ml of methanol under mechanically stirring is heated to 40 °C. To this NaOH solution, the as-prepared PVAc or PVAc–clay solution is added dropwise. After stirring for 10 min at 40 °C, the hydrolyzing solution is cooled down to room temperature to yield PVA or PVA–clay nanocomposite materials. As-synthesized PVA or PVA–clay precipitates are then collected through filtering, washing with methanol and drying under dynamic vacuum at 40 °C for 48 h.

2.4. Polymer recovery

A reverse cationic-exchange reaction is employed to separate bound PVA from inorganic component in the nanocomposite [16]. As a typical extraction procedure, 2 g of fine powder of as-synthesized PCN materials is dissolved in ~100 ml of methanol (beaker A). Separately, 10 ml stock solution of 1 wt% LiCl_(s) in distilled water is prepared (beaker B). Both beakers are under vigorous magnetically stirring for 3–4 h at room temperature. After combining the contents of the two beakers, the mixture is stirred for additional 24 h followed by Soxhlet extraction at 85–90 °C for 48 h. Extract solution is evaporated on a rotavapor under a reduced pressure to yield PVA fine powders. Molecular

On the other hand, montmorillonite (MMT) is a clay mineral containing stacked silicate sheets measuring ~10 Å in thickness and ~2200 Å in length, respectively [17]. It possesses a high aspect ratio and a platy morphology. The chemical structures of MMT containing two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either magnesium or aluminum hydroxide. The Na⁺ and Ca⁺² residing in the interlayer regions can be replaced by organic cations such as alkylammonium ions by a cationic-exchange reaction to modify the hydrophilic layered silicate to be organophilic. MMT has a high swelling capacity, which is significant for efficient intercalation of the polymer, and is composed of stacked silicate sheets that provide improved thermal stability, mechanical strength, fire retardant and molecular barrier properties.

To synthesize the PCN materials, first of all, organophilic clay is prepared by a cationic-exchange reaction between the sodium cations of MMT clay and alkylammonium ions of intercalating agent, diallylamine. Organic vinyl acetate monomers are subsequently intercalated into the interlayer regions of organophilic clay hosts and followed by a one-step free radical polymerization with AIBN as initiator. The as-prepared poly(vinyl acetate) (PVAc) or PVAc–clay solution are then saponified via direct-hydrolysis with NaOH solution to form PVA or PVA–clay nanocomposite

Table 1
Relations of the composition of PVA–MMT clay nanocomposite materials with thermal analyses measured by TGA and DSC

Compound code	Feed composition (wt%)		Thermal analyses				
	Vinyl acetate	Clay	<i>T_d</i> (°C)	Char yield (wt%)	<i>T_g</i> (°C)	<i>T_m</i> (°C)	
PVA	100	0	229.51	5.36	61.35	–	202.62
CLVA0.15	99.85	0.15	234.62	6.12	76.99	185.91	218.31
CLVA0.3	99.7	0.3	244.84	7.54	76.44	195.57	227.59
CLVA1	99	1	254.95	9.81	79.92	163.09	217.98
CLVA1.5	98.5	1.5	254.95	11.51	76.99	162.28	220.02
CLVA3	97	3	263.21	13.52	80.56	195.63	227.69
CLVA5	95	5	270.13	15.02	80.98	197.23	233.52

materials. The composition of the PCN materials is varied from 0 to 5 wt% of clay with respect to the PVA content as summarized in Table 1.

3.1. Characterization

The representative FTIR spectra of the organophilic clay, bulk PVA and PCN materials are shown in Fig. 1. The characteristic vibration bands of PVA are shown at 3420 (–OH), 2943 (–CH₃), 2891 (–CH₂), 1450 (O=C–OR), 1110 (C–O–C) and 862 cm^{–1} (–CH), and those of diallylamine–MMT clay are shown at 3489 (–NH), 1650 (C=C), 802 (–CH₂), 1043 (Si–O), 518 (Al–O) and 468 cm^{–1} (Mg–O) [5–7]. As the loading of organophilic MMT clay is increased, the intensities of organophilic MMT clay bands become stronger in the FTIR spectra of PCN materials. Fig. 2 shows the wide-angle powder XRD patterns of organophilic clay and a series of PCN materials. In Fig. 2(A), the powder XRD patterns don't show any diffraction peak in $2\theta = 2-10^\circ$ as opposed to the diffraction peak at $2\theta = 6.35^\circ$ (d spacing = 13.91 Å) for organophilic clay, indicating the possibility of having exfoliated silicate layers of organophilic clay dispersed in PVA matrix. When the wide-angle powder XRD patterns are scanned from $2\theta = 2$ to $2\theta = 60^\circ$, there is an intense peak appearing near $2\theta = 19.4^\circ$, corresponding to a d spacing of 4.57 Å for PVA. The intensity of this peak is decreased when the amount of organophilic clay dispersing in PCN materials increase, as shown in curve (a)–(g) of Fig. 2(B). There are two factors may affect the crystalline behavior that existing in PVA. First, the crystalline behavior is decreased due to the pristine polymer become amorphous when molecular weight of PVA is decreased by in situ polymerization of PCN materials. Second, the crystalline behavior is suppressed by the introduction of organophilic clay into polymer matrix in the form of an intercalated or exfoliated layer structure. These are further studied by running a wide-angle powder XRD of extracted PVA from CLVA5 as shown in curve (j) of Fig. 2(b). The extracted PVA shows

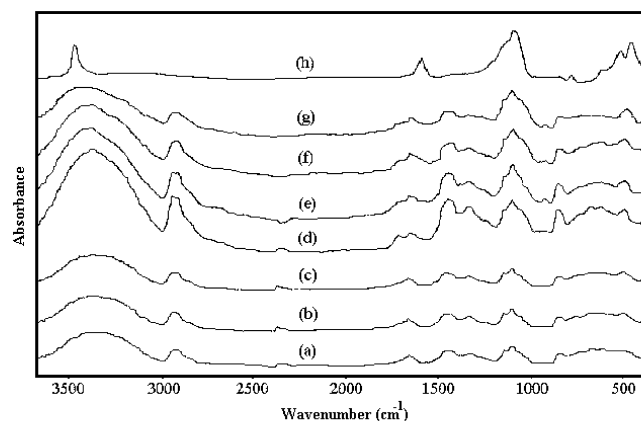


Fig. 1. Representative FTIR spectra of (a) PVA (b) CLVA0.15 (c) CLVA0.3 (d) CLVA1 (e) CLVA1.5 (f) CLVA3 (g) CLVA5 (h) organophilic clay.

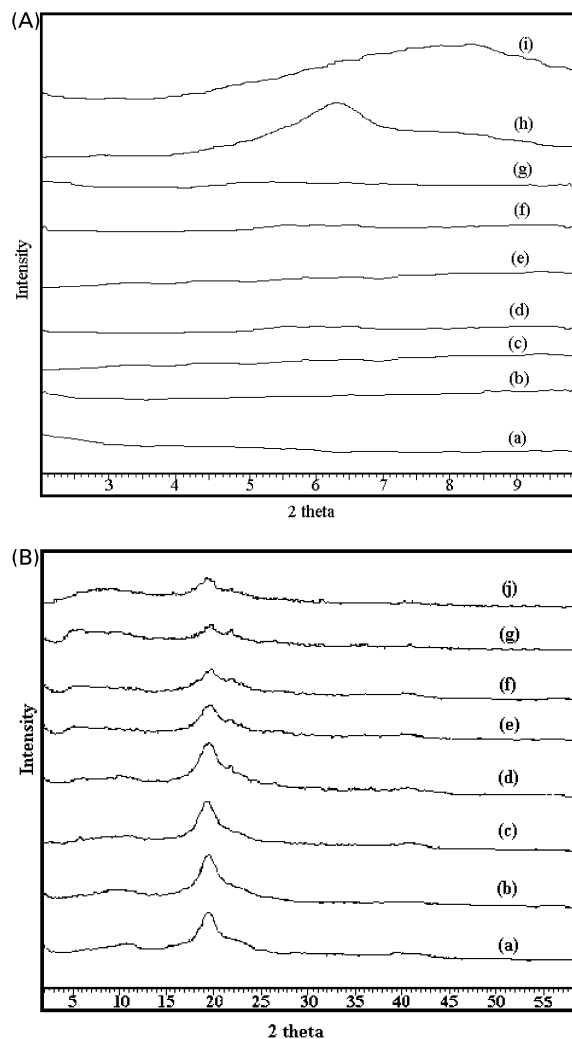


Fig. 2. Wide-angle powder XRD patterns of (a) PVA (b) CLVA0.15 (c) CLVA0.3 (d) CLVA1 (e) CLVA1.5 (f) CLVA3 (g) CLVA5 (h) organophilic clay (i) clay (j) extracted PVA from CLVA5.

similar intensity (at the peak $2\theta = 19.5^\circ$, d -space = 4.55 Å) compare to the CLVA5 (at the peak $2\theta = 19.7^\circ$, d -space = 4.50 Å), and also small intensity compare to bulk PVA. This implies that the difference in crystalline behavior of CLVA5 and bulk PVA is mainly attributing to the intrinsic PVA properties for different molecular weights.

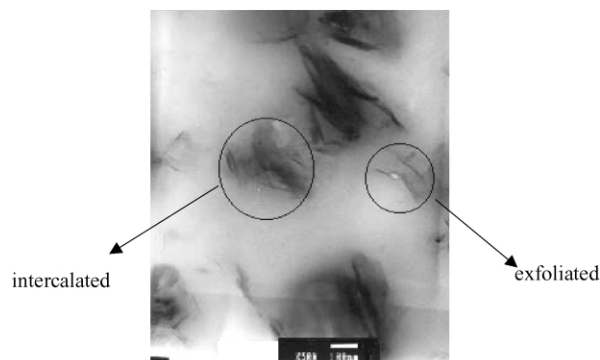


Fig. 3. TEM of CLVA5.

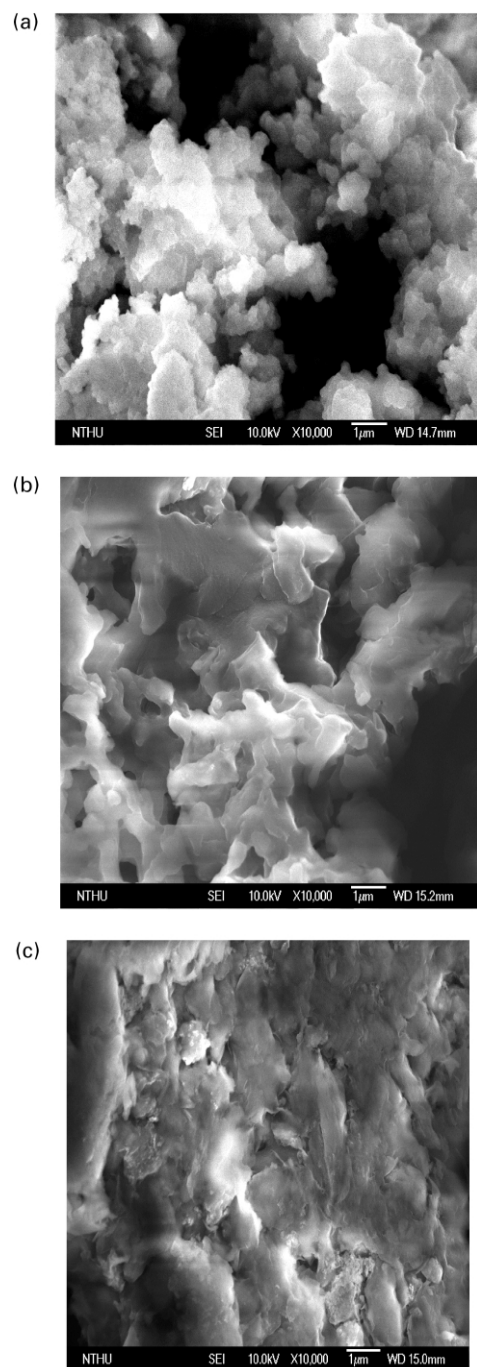


Fig. 4. Scanning electron micrographs of (a) PVA (b) CLVA1.5 (c) CLVA5.

The molecular weights of extracted PVA are found to be lower significantly than that of the bulk PVA by GPC analyses as described below. The changing of crystalline behavior can be further evidenced by the studies of the morphological image of as-synthesized materials by SEM and OPM.

In Fig. 3, the TEM of PCN materials with 5 wt% clay loading showed that the lamellar nanocomposite has a mixed nanomorphology. Individual silicate layers, along with two, three and four layer stacks, are exfoliating in the

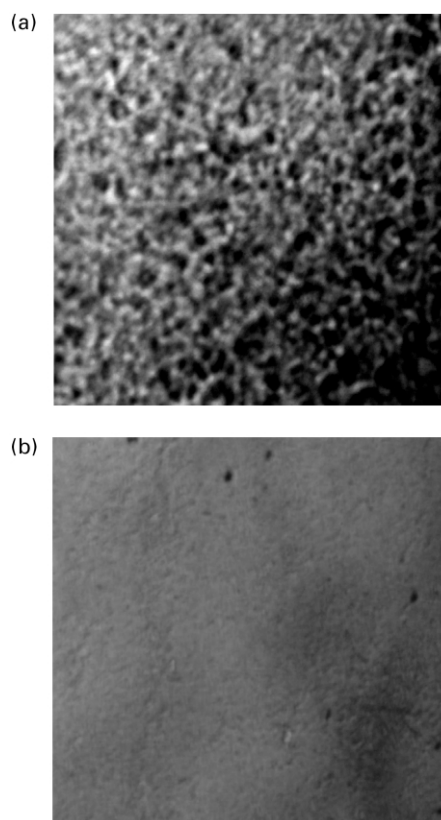


Fig. 5. Polarizing microscope images of (a) PVA (b) CLVA5.

PVA matrix. In addition, some larger intercalated tactoids could also be identified.

3.2. Morphological image studies

The morphological image of as-synthesized materials is studied by SEM and OPM. The SEM images in Fig. 4 show that the morphology of PCN becomes much smooth than pure PVA. The granules shape of PVA indicates some crystalline behavior occurring in pure polymer. The incorporation of MMT clay seems to destroy the orientation of crystalline polymer and to convert the polymer morphology approaching to amorphous state. This observation is also conformed by OPM, as shown in Fig. 5. For the polarizing microscope studies, bulk PVA and 5 wt% of PCN fine powders are dissolved in NMP to give typically 0.1 wt% solutions. After filtering, the as-prepared solutions are cast onto microsilde glasses (1.0 cm × 1.0 cm) followed by drying in air for 24 h at 40 °C to give coatings for conoscopy observation of OPM. The CLVA5 shows much smooth morphology that is different to crystallites of PVA observation. This result is consistent with the wide-angle powder XRD patterns as described previously.

3.3. M_w of extracted and bulk PVA

Molecular weights of the various polymer samples extracted from the nanolayers of MMT clays are obtained

Table 2
Molecular weights and intrinsic viscosities of bulk and extracted PVA

Compound code	Molecular weights ^a			Viscosity ^b [η] (dL/g)
	M_w	M_n	Polydispersity	
PVA	60,731	7101	8.55	0.4123
CLVA0.15	53,392	9944	5.37	0.3888
CLVA0.3	21,817	6654	3.28	0.3612
CLVA1	17,756	3116	3.24	0.3375
CLVA1.5	15,824	4908	3.22	0.2783
CLVA3	13,624	5123	2.65	0.1636
CLVA5	10,944	4309	2.54	0.1529

^a As determined from GPC measurements.

^b As determined by an Ubbelohde capillary viscometer.

by GPC analyses. The molecular weights of the THF-soluble polymer extracted from all samples as well as bulk PVA display mono-modal peak distributions corresponding to a molecular weight value, as shown in Table 2. The molecular weights of extracted PVA are found to be lower significantly than that of the bulk PVA, implying the structurally restricted polymerization conditions existing in the intragallery region of the MMT clay [18]. Furthermore, the intrinsic viscosities of the PVA–clay nanocomposite materials are also studied by an Ubbelohde capillary viscometer. As shown in Fig. 6, the intrinsic viscosities of as-prepared nanocomposite solutions is found to decrease gradually as the clay loading increases, indicating that the molecular weights of PVA decrease with increasing clay loading, reflecting that the appearance of clay platelets may hinder the polymerization degree of vinyl acetate monomers. The results are consistent with the previous GPC studies.

3.4. Thermal properties of fine powders

Fig. 7 shows a typical TGA thermogram of weight loss as a function of temperature for PCN materials along with PVA, as measured under nitrogen atmosphere. In general,

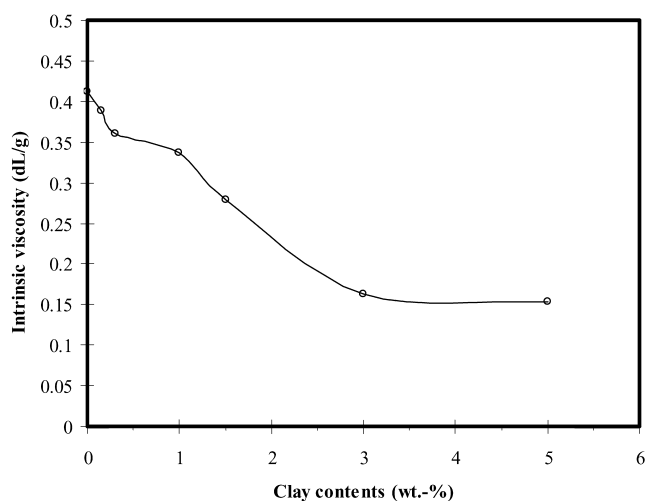


Fig. 6. Relationships between viscosity and clay loading as obtained from Ubbelohde viscometer measurements.

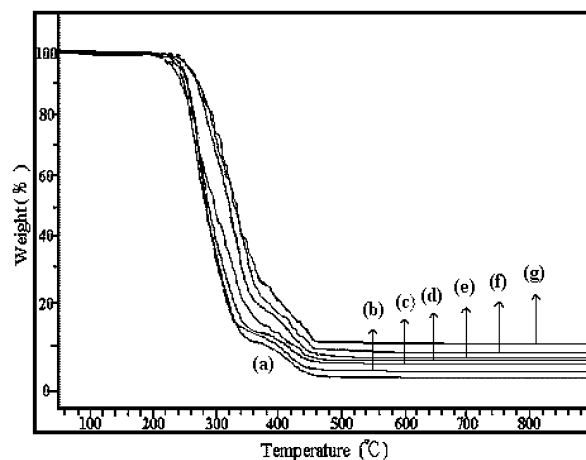


Fig. 7. TGA curves of (a) PVA (b) CLVA0.15 (c) CLVA0.3 (d) CLVA1 (e) CLVA1.5 (f) CLVA3 (g) CLVA5.

major weight losses are observed in the range of ~ 200 – 500 $^{\circ}\text{C}$ for PVA and PCN fine powders, which may be correspondent to the structural decomposition of the polymers. Evidently, the thermal decomposition of those PCN materials shift slightly toward the higher temperature range than that of PVA, which confirms the enhancement of thermal stability of intercalated polymer [9]. After ~ 600 $^{\circ}\text{C}$, the curve all became flat and mainly the inorganic residue (i.e. Al_2O_3 , MgO , SiO_2) remained. From the amounts of the residue at 900 $^{\circ}\text{C}$, the inorganic contents in the original PCN materials could be obtained, which are slightly higher than the values obtained from the bulk PVA.

DSC traces of PVA and PCN materials are shown in Fig. 8. PVA exhibits an endotherm at 61.35 $^{\circ}\text{C}$ corresponding to the glass transition temperature (T_g) of PVA [15]. All the PCN materials are found to have a high T_g compared to the bulk PVA, as shown in Table 1. This is tentatively attributed to the confinement of the intercalated polymer chains within the clay galleries that prevents the segmental motions of the polymer chains. Another endotherm of bulk PVA at higher temperature (ca. 202.62 $^{\circ}\text{C}$), corresponding

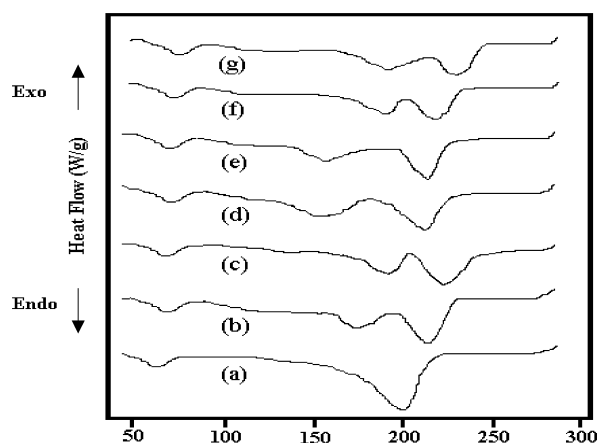


Fig. 8. DSC curves of (a) PVA (b) CLVA0.15 (c) CLVA0.3 (d) CLVA1 (e) CLVA1.5 (f) CLVA3 (g) CLVA5.

to the crystalline melting point (T_m) of PVA, is also found in the DSC thermograms. Furthermore, it is interesting to find that the appearance of two distinct T_m peaks in all the PCN materials, as shown in Fig. 8(b)–(g) and Table 1. For example, the CLVA0.15 has a higher T_m value of 218.31 °C and a lower T_m value of 185.91 °C compared to the T_m 202.62 °C, of pure PVA. This implies that two crystalline phases such as a syndiotactic sequences and an atactic sequence may exist after incorporation of clay into the PVA [15].

3.5. Mechanical strength of membranes

For mechanical property studies, bulk PVA and PCN fine powders are dissolved in H₂O to give typically 1 wt% solutions for the membrane formation. The as-prepared solutions are cast onto glass plate (5.0 cm × 5.0 cm) followed by drying in air for 24 h at 40 °C to give coatings of ca. ~20 μm, measured by digimatic micrometer (Mitutoyo), in thickness. As shown in Fig. 9, the moduli of the PCN membranes with 0.15 wt% ($E' = 3.57 \times 10^9$ Pa) and 1.5 wt% ($E' = 4.27 \times 10^9$ Pa) clay loading (Fig. 9(b) and (c)) at -50 °C are found to be higher than the PVA ($E' = 3.23 \times 10^9$ Pa) (Fig. 9(a)), indicating the storage modulus of PVA is promoted as clay loading increases.

3.6. Optical clarity of membrane

The membranes of bulk PVA and PCN materials used for optical property measurements are prepared to have film thickness of ~20 μm. Fig. 10(a)–(g) shows that the UV–visible transmission spectra of pure PVA and PCN membranes. The transmission spectra of pure PVA and PCN membranes in the visible light regions (200–800 nm) are slightly affected by the presence of the low clay loading in the PCN membranes. However, the spectra of as-prepared membrane at higher clay loading (e.g. CLVA5) exhibits

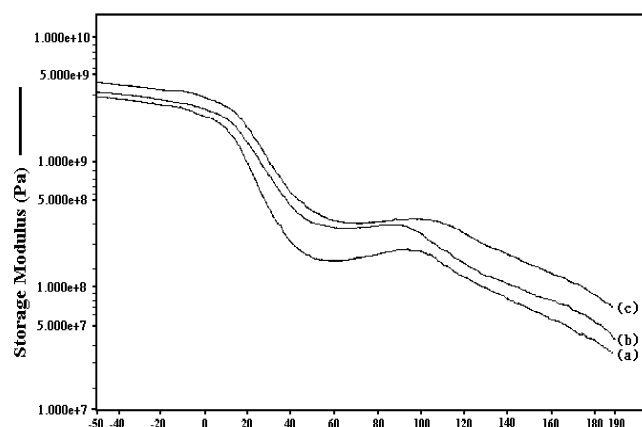


Fig. 9. Relationship between the storage modulus (E') and temperature as obtained from DMA measurements on the membranes of (a) PVA (b) CLVA0.15 (c) CLVA1.5.

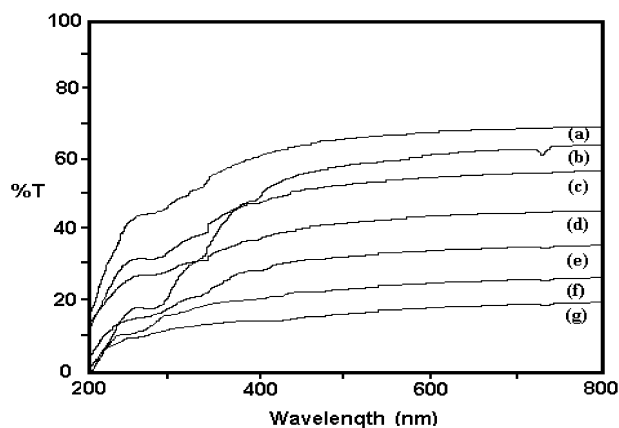


Fig. 10. UV–visible transmission spectra of (a) PVA (b) CLVA0.15 (c) CLVA0.3 (d) CLVA1 (e) CLVA1.5 (f) CLVA3 (g) CLVA5.

lower optical clarity, reflecting that there is strong scattering of MMT clay resulting in lower transparency of the UV–visible light.

4. Concluding remarks

A series of nanocomposite materials that consist of PVA and layered montmorillonite (MMT) clay are prepared by effectively dispersing the inorganic nanolayers of MMT clay in organic PVA matrix via an in situ free radical polymerization of vinyl acetate monomer and followed by direct-hydrolysis with NaOH solution. As-synthesized PCN materials are characterized by FTIR spectroscopy, XRD and TEM. Morphological images of as-synthesized PCN materials are studied through SEM and OPM. The crystalline morphology of pure PVA converts approaching to amorphous state as the MMT clay loading increases. This is consistent with the observation of XRD patterns, in which an intense peak appearing at $2\theta = 19.4^\circ$ for PVA is decreased when the loading of MMT clay increase in PCN materials.

Molecular weights of extracted PVA exhibit a decreased molecular weight compared to the bulk PVA, indicating the structurally restricted polymerization conditions in the intragallery region of the MMT clay. Thermal stability, mechanical strength and optical clarity of PVA as well as a series of PCN materials, in the form of fine powder and membrane, are also investigated by TGA, DSC, DMA and UV–visible transmission spectra, respectively. The incorporation of nanolayers of MMT clay in PVA matrix results in an increase in thermal decomposition temperature, char yield, glass transition temperature and mechanical strength based on TGA, DSC and DMA studies. The UV–visible transmission spectra exhibit lower transparency when MMT content increases.

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References

- [1] Lan T, Kaviratna PD, Pinnavaia TJ. *Chem Mater* 1994;6:573.
- [2] Tyan H-L, Liu Y-C, Wei K-H. *Chem Mater* 1999;11:1942.
- [3] Wang Z, Pinnavaia TJ. *Chem Mater* 1998;10:3769.
- [4] Gilman JW, Jackson CL, Morgan AB, Hayyis Jr R, Manias E, Giannelis EP, Wuthenow M, Hilton D, Philips SH. *Chem Mater* 2000;12:1866.
- [5] Yeh J-M, Liou S-J, Lai C-Y, Wu P-C, Tsai T-Y. *Chem Mater* 2001;13:1131.
- [6] Yeh J-M, Chen C-L, Chen Y-C, Ma C-Y, Lee K-R, Wei Y, Li S. *Polymer* 2002;43:2729.
- [7] Yeh J-M, Liou S-J, Lin C-Y, Cheng C-Y, Chang Y-W, Lee K-R. *Chem Mater* 2002;14:154.
- [8] Usuki A, Kawasumi M, Kojima Y, Okada A, Karauchi T, Kamigaito O. *J Mater Res* 1993;8:1774.
- [9] Lee DC, Jang LW. *J Appl Polym Sci* 1996;61:1117.
- [10] Lee DC, Jang LW. *J Appl Polym Sci* 1998;68:1997.
- [11] Tyan H-L, Liu Y-C, Wei K-H. *Chem Mater* 1999;11:1942.
- [12] Akelah A, Rehab A, Selim A, Agag T. *J Mol Catal* 1994;94:311.
- [13] Carrado KA, Thiyagarajan P, Elder DL. *Clays Clay Miner* 1996;44:506.
- [14] Wang N, Wu XS. *Parm Dev Technol* 1997;2:135.
- [15] Strawhecker KE, Manias E. *Chem Mater* 2000;12:2943.
- [16] Meier LP, Sheldon RA, Caseri WR, Suter UW. *Macromolecules* 1994;27:1637.
- [17] Yano K, Usuki A, Okada A. *J Polym Sci, Polym Chem Ed* 1997;35:2289.
- [18] Wroblewski DA, Benicewicz BC, Thompson KG, Byran CJ. *Polym Prepr (Am Chem Soc, Div Polym Chem)* 1994;35(1):265.