

Preparation and Characterization of Transparent Poly(Methyl Methacrylate)/Na⁺-MMT Nanocomposite Films by Solution Casting

Tongfei Wu,^{1,2} Tingxiu Xie,³ Guisheng Yang^{1,3}

¹CAS Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Technology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

²Graduate University of Chinese Academy of Sciences, Beijing 100049, China

³Shanghai Genius Advanced Materials Co., Ltd, Shanghai 201109, China

Received 20 October 2008; accepted 17 February 2009

DOI 10.1002/app.30267

Published online 26 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Films of poly(methyl methacrylate) (PMMA)/sodium montmorillonite (Na⁺-MMT) nanocomposites have been successfully prepared utilizing Na⁺-MMT by N,N-dimethylformamide solution casting. The nanocomposite films show high transparency, enhanced thermal resistance, and mechanical properties in comparison with the neat polymer film. The transparency of the films was investigated by UV-vis spectra. The exfoliated dispersion of Na⁺-MMT platelets in nanocomposites were investigated by

X-ray diffraction and transmission electron microscopy. The enhanced thermal resistance and mechanical properties of PMMA were studied by thermal gravimetric analysis and dynamic mechanical analysis, respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2773–2778, 2010

Key words: poly(methyl methacrylate)/Na⁺-MMT; nanocomposite; sodium montmorillonite; transparent films; solution casting

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is an important transparent material in optical applications. Its clay nanocomposites have attracted great interest and lots of attempts to prepare these nanocomposites have been reported since the first report of polymer/clay nanocomposites from the Toyota research group.¹ Unlike conventional composites, polymer/clay nanocomposites can offer remarkable improvement in materials properties with just a few weight percent of mineral. These improvements could include an increase of moduli,^{1–4} strength, heat resistance⁵ and biodegradability of biodegradable polymers,⁶ and a decrease of gas permeability^{7–10} and flammability.^{11–14} The study of polymer/clay nanocomposites is also of fundamental interest because it provides a better understanding of polymer chain dynamics in confined states.¹

PMMA/clay nanocomposites can be prepared by *in situ* bulk polymerization, solution polymerization, suspension polymerization, pseudo-dispersion polymerization, and emulsion polymerization in presence of organic modified clay.^{15–27} The morphology of these polymer/clay nanocomposites depends on the

clay content, the chemical nature of the organic modifier, and the synthetic method.²⁸ Besides these chemical methods, solution mixing^{29–31} and shear processing, such as sonication^{17,32} and melt compounding,^{33–35} were also successfully used to prepare well-dispersed PMMA/layered silicate nanocomposites. One of the important goals in PMMA nanocomposites fabrication is to enhance thermal and mechanical properties, while at the same time limiting loss in transparency. However, advances in processing transparent PMMA/clay nanocomposites have been hindered because of the difficulties in achieving efficient dispersion and just a few works on the transparency of PMMA/clay nanocomposites have been reported.^{17,36,37} In present work, we focus specifically on the fabrication of PMMA/Na⁺-MMT composite films by DMF solution casting utilizing a technique in dispersing silicate layers in DMF, which was developed in our laboratory. The nanocomposite films show high transparency, enhanced thermal resistance, and mechanical properties in comparison with the neat polymer film.

EXPERIMENTAL PART

Materials

N,N-dimethylformamide(DMF), methyl methacrylate and 2, 2'-Azo-bis-iso-butyronitrile (AIBN) used as

Correspondence to: G. Yang (ygs@geniuscn.com).

initiator for radical polymerization were purchased from Shanghai Chemical Reagents Company and used without further treatment. Pristine Na⁺-MMT with a cation exchange capacity (CEC) of 85mequiv per 100 g was supplied by Zhejiang Fenghong Clay Chemicals Co.

Synthesis of PMMA in DMF

PMMA was synthesized from methyl methacrylate by a typical radical solution polymerization using AIBN as initiator. A mixture of 10 g methyl methacrylate, 0.12 g AIBN and 40 mL DMF were placed in a 100 mL flask equipped with a reflux condenser. Polymerization was carried out at 60°C for 12 h and the yield was 98%. PMMA were isolated and purified by reprecipitation from its acetone solution into deionized water. It was then washed with methanol and dried in vacuo. The average molecular weight is 36,000, calculated with the Mark-Houwink relation³⁸: $[\eta] = 4.68 \times 10^{-3} M_w^{0.77}$ (mL/g), and the viscosity measurements were performed in 1 g/mL toluene solution with Ubbelode capillary viscometer at 25°C.

Preparation of PMMA/Na⁺-MMT composite films

A total of 1.5 wt % Na⁺-MMT water suspension was prepared by stirring a mixture of deionized water and Na⁺-MMT at 70°C for 3 h. A total of 2 mL of this water suspension were added into 20 mL DMF to be diluted. A desired amount of this suspension was added into DMF solution with 2 wt % of PMMA at room temperature. The mixtures stirred at room temperature for several hours and were ultrasonicated for 10 min before being poured into uncovered glass Petri dishes. Gentle heating at 80°C for one day assisted in removal of DMF. A thin, tough film resulted, that could be easily lifted from the dish. Further drying of the film took place in a vacuum oven ($p = 0.01$ M Pa) at 120°C for 2 days. Corresponding to the weight percentage of Na⁺-MMT, the products were designated as neat PMMA (Na⁺-MMT: 0 wt %), PMMA1 (Na⁺-MMT: 1 wt %),

PMMA2 (Na⁺-MMT: 2 wt %), and PMMA4 (Na⁺-MMT: 4 wt %).

Characterization

The UV-vis spectra were recorded with a Cary 500 spectrophotometer (Varian, Palo Alto, CA). Spectra of the solvent-evaporated 0.21 mm thick films (measured with a hand-held micrometer) were scanned with air as the background. XRD was performed on a D/Max-III X-ray diffraction analyzer (Rigaku Corporation, Tokyo, Japan) equipped with a rotating Cu anode generator system using Cu-K_{α1} ($\lambda = 1.540\text{\AA}$) radiation. XRD data were measured at room temperature, powered at 40 kv and 25 mA. Transmission electron microscopy (TEM) was carried out on a JEM-2100F microscope (JEOL, Tokyo, Japan). The samples were ultramicrotomed on a Leica Ultracut UCT Ultramicrotome (Leica Microsystems GmbH, Wetzlar, Germany) at -50°C to give about 100 nm thick sections. Dynamic mechanical properties were measured with a Q800 DMA (TA Instruments, New Castle, DE) in multi-frequency-strain mode at a frequency of 1 Hz and a heating rate of 3°C/min as a function of temperature from -50°C to 178°C. Differential scanning calorimetry (DSC) measurements were performed on a Diamond DSC (Perkin-Elmer, Salem, Massachusetts) in a nitrogen atmosphere with heating and cooling rates of 10°C/min. TGA was conducted on a Pyris 1 TGA (Perkin-Elmer, Salem, MA) under nitrogen flow from 50°C to the temperature 550°C with a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Optical properties

Through solvent evaporation from Na⁺-MMT DMF suspension containing PMMA, PMMA/Na⁺-MMT composite films containing various contents of Na⁺-MMT were produced, as depicted in Figure 1. PMMA/Na⁺-MMT composites with a content of Na⁺-MMT below 2 wt % exhibit a good filmability. With increasing the loading of Na⁺-MMT up to 4 wt %, the filmability of PMMA/Na⁺-MMT composites

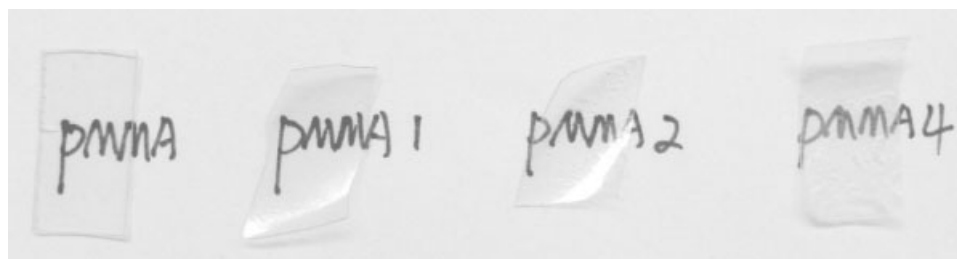


Figure 1 Films of PMMA/Na⁺-MMT composites.

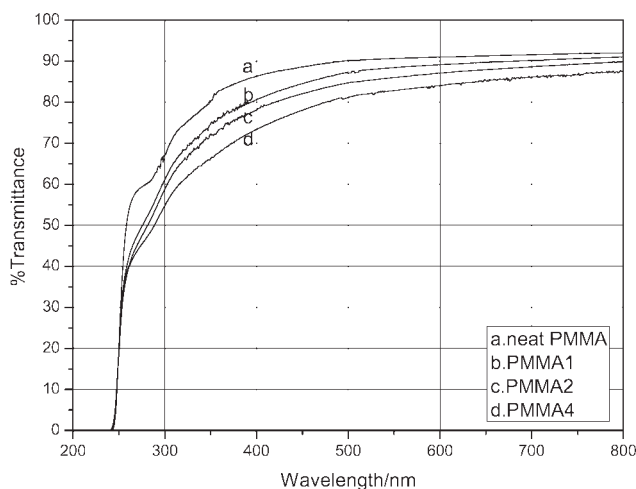


Figure 2 Transmittance UV-vis spectra of PMMA/Na⁺-MMT composites and neat PMMA, scanned from 200 nm to 800 nm.

becomes poor. PMMA4 film is roughened, which could be due to the large viscosity and poor fluidity in the final stage of solvent evaporation caused by adding excess silicate layers and influenced the optical clarity. The UV-vis spectra are shown in Figure 2 for the transparency of PMMA/Na⁺-MMT composite films in comparison to neat PMMA film. PMMA/Na⁺-MMT composite films exhibit transmittances of 50% and higher at or above 300 nm. The percent transmittances at 300 nm, 400 nm, and 500 nm are tabulated in Table I. With increasing the loading of Na⁺-MMT, the percent transmittances decrease slowly and PMMA/Na⁺-MMT composite films show high transparency with a loading of Na⁺-MMT below 4 wt %. For UV wavelengths and the near-UV visible light, there is some scattering and/or absorption from the Na⁺-MMT layers with lateral sizes from 100 nm to 1000 nm,³⁹ resulting in a moderate loss transmission in this waveband for nanocomposites.

Nanocomposites structure characterization of PMMA/Na⁺-MMT nanocomposites

The studies on the Na⁺-MMT layers structure of PMMA/Na⁺-MMT nanocomposites were imple-

TABLE I
UV-Vis Transmittances of Composites at 300 nm, 400 nm, and 500 nm

Sample	Transmittance/%		
	300 nm	400 nm	500 nm
Neat PMMA	67.5	86.1	90.3
PMMA1	61.3	80.9	87.4
PMMA2	59.5	79.1	85.6
PMMA4	56.6	71.8	81.3

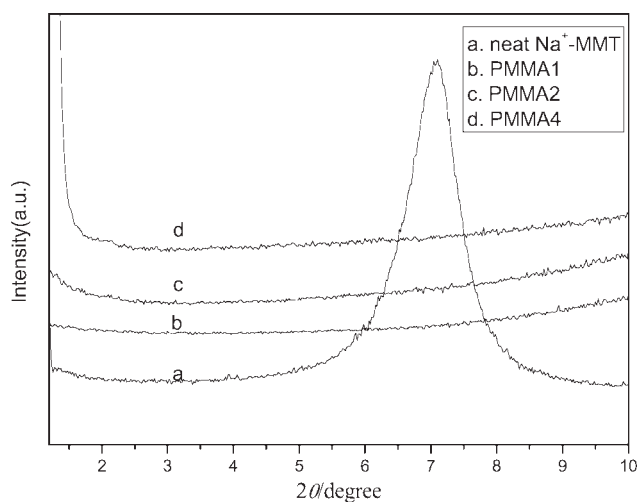


Figure 3 XRD for various samples.

mented by XRD shown in Figure 3. The XRD pattern shows primary silicate diffraction at about 7.0° for the neat Na⁺-MMT. However, there are hardly any visible reflection peaks for PMMA/Na⁺-MMT nanocomposites, which demonstrates that the Na⁺-MMT layers are exfoliated.⁶ TEM is also used to investigate the separation of Na⁺-MMT layers in the exfoliated state at two magnifications of ×30 k and ×75 k. Figure 4 shows micrographs PMMA/Na⁺-MMT composite films with a Na⁺-MMT loading of 1 wt%, 2 wt%, and 4 wt %. The dark lines are the silicate layers dispersed within the matrix of PMMA, which demonstrates a fully exfoliated structure of silicate layers in nanocomposites. This TEM result also confirms that silicate layers are well exfoliated in DMF solution. DMF is a good organic medium for Na⁺-MMT dispersed in nano-scale, which could attribute to the effective stabilizing ability from the strong molecular polarity of DMF and the heat of mixing with water. Because of the absence of the stack of silicate layers with high degree of order, their composite films are isotropic and have an optically clear appearance in visible light.

Thermal properties

The glass transition temperature (T_g) for PMMA determined by DSC is shown in Figure 5. The values of T_g were 106.0°C, 116.5°C, 130.5°C, and 151.5°C for neat PMMA, PMMA1, PMMA2, and PMMA4, respectively. The significant increase of T_g for PMMA/Na⁺-MMT nanocomposites is probably due to the suppression of the molecular mobility by the good adhesion between polar silicate layers and the PMMA matrix.³⁹⁻⁴¹

The thermal stabilities of PMMA/Na⁺-MMT nanocomposites with a Na⁺-MMT loading of 1 wt% and 2 wt % were studied by TGA under nitrogen

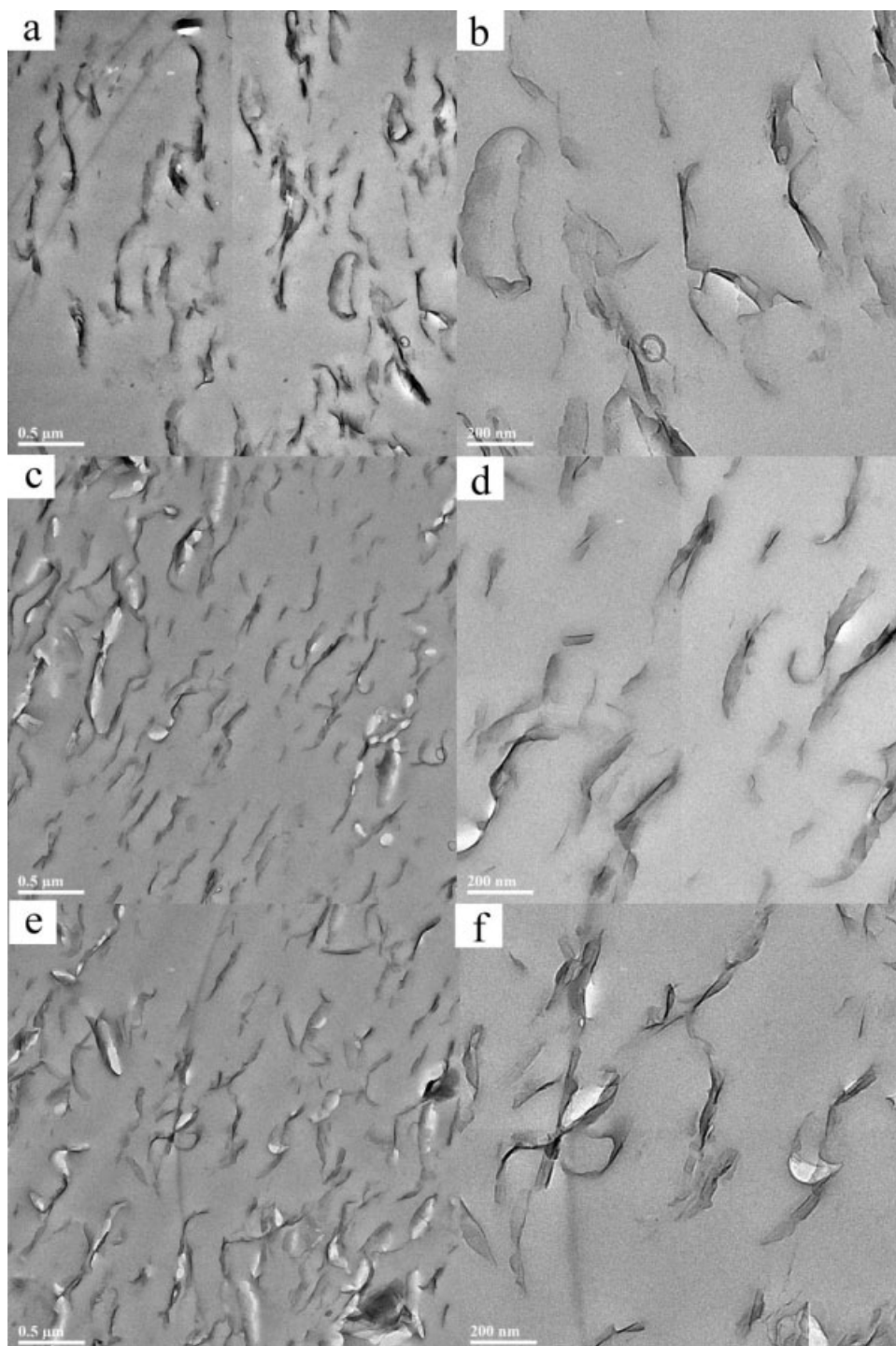


Figure 4 TEM of PMMA/Na⁺-MMT composites (a, b: PMMA1; c, d: PMMA2, and e, f: PMMA4).

flow in comparison with neat PMMA are shown in Figure 6. The TGA parameters are tabulated in Table II. The neat PMMA started to decompose at a temperature around 170°C and was completely combusted at approximately 500°C. The DTG of neat PMMA shows three steps at 209°C, 335°C, and 393°C. The thermogram agrees with the earlier published data.^{42,43} The first minor peak at 209°C is

attributed to thermal decomposition initiated from these vinylidene chain ends that results from disproportionation termination of propagating radicals, which is the principal termination in the MMA free radical polymerization at 60°C.⁴⁴ The two major peaks at 335°C and 393°C refer to decomposition initiated by random scission of the polymer backbone. Compared with neat PMMA, the DTGs of PMMA/

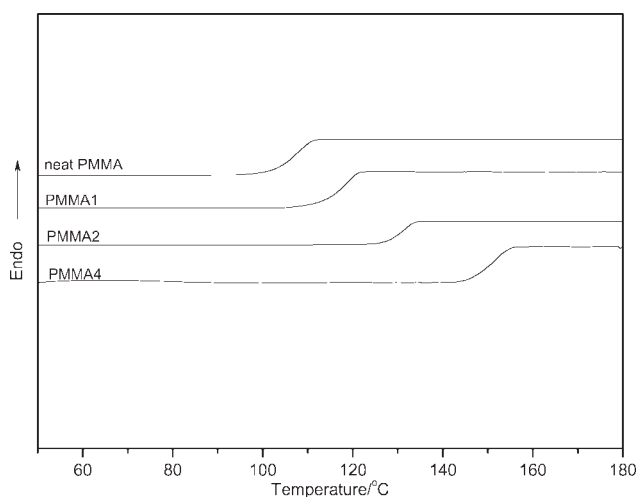


Figure 5 DSC of various samples.

Na⁺-MMT nanocomposites only show two steps. The minor peak that originate from the decomposition started at vinylidene end groups have practically disappeared, and the onset of decomposition is retarded from 170°C to 300°C for PMMA in the presence of Na⁺-MMT, which indicates that the decomposition step has been significantly suppressed. It has been demonstrated that vinylidene end groups are less stable for an efficient chain-transfer process in which the end group reacts with a radical to form an active chain end, which can depolymerize.⁴⁵ The enhanced thermal stability of vinylidene end groups in this case is probably due to the radical trapping by the structural iron in Na⁺-MMT,^{46,47} which suppressed the efficient chain-transfer process and stabilize the vinylidene end groups.

The maximum decomposition temperature of two major peaks at lower temperature ($T_{\max 2}$) for nanocomposites almost has no shift in comparison with that of neat PMMA, which indicates that the presence of Na⁺-MMT layers did not influence the onset decomposition temperature initiated by random scission of the polymer backbone. In contrast to $T_{\max 2}$, $T_{\max 3}$ of the nanocomposites shift to higher temperature by 19°C and 32°C for PMMA1 and PMMA2, respectively. This result is in good agreement with the earlier reports.^{37,40} Evidently, the decomposition rates of those nanocomposites become slower compared with that of neat PMMA, indicating the enhancement of overall thermal stability of PMMA,

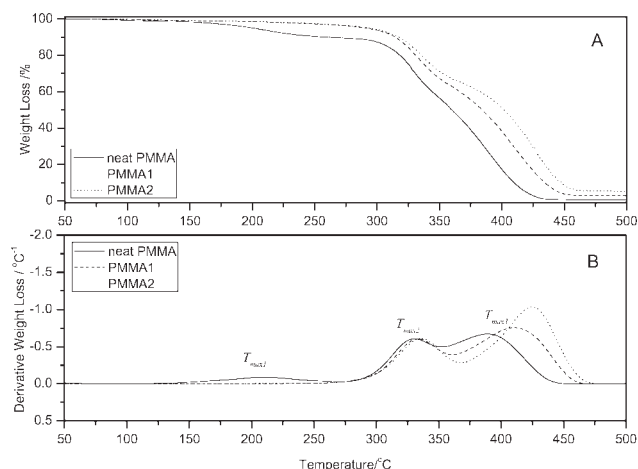


Figure 6 (A) TGA and (B) DTG curves of neat PMMA, PMMA1, and PMMA2.

as well as assistance in the formation of char after thermal decomposition. This enhancement could be attributed to the heat barrier properties of Na⁺-MMT nanolayers dispersed in the matrix and the suppression of the PMMA molecular mobility, preventing the heat to transmit quickly and limiting the continuous decomposition.³⁹

Mechanical properties

Here, we focus on the change in glassy modulus, as most potential applications of Na⁺-MMT nanocomposites rely on enhanced glassy behavior. DMA results are shown in Figure 7 for temperature sweeps of PMMA2 in comparison with neat PMMA. It can be seen that both the storage modulus E' of the samples decreases with increasing temperature and that the values for PMMA2 are much higher than the neat PMMA in the whole glassy plateau zone. An approximately 81% increase in modulus results from the addition of 2 wt % silicate layers. The substantial enhancement of the storage modulus at temperatures below T_g could be explained by the creation of a three-dimensional network of interconnected long silicate layers, strengthening the material through mechanical percolation.^{2-4,39} It is also observed from Figure 4 that the value of $T_{g'}$, which was taken to be at the location of the $\tan\Delta$ peak, increases by 31.9°C from 100.2°C in neat PMMA to

TABLE II
TGA Parameters for Neat PMMA, PMMA1, and PMMA2

Sample	$T_{10\text{wt}\%}/^{\circ}\text{C}$	$T_{30\text{wt}\%}/^{\circ}\text{C}$	$T_{50\text{wt}\%}/^{\circ}\text{C}$	Char yield/%	T_{\max}
Neat PMMA	257	330	359	0.5	209;330;393
PMMA1	314	345	384	3.0	335;412
PMMA2	316	351	401	5.5	335;425

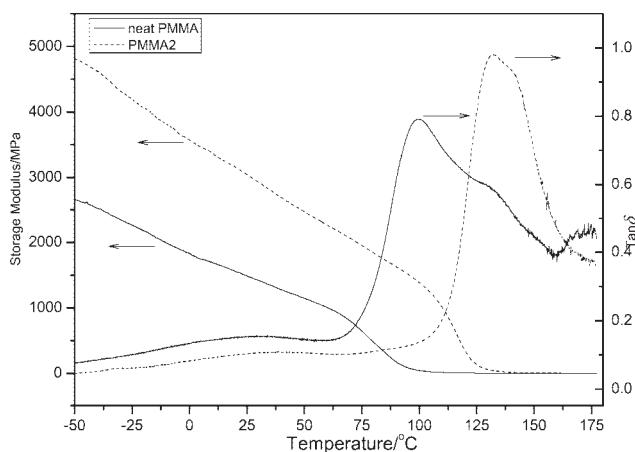


Figure 7 DMA of PMMA2 and neat PMMA.

132.1°C for PMMA2, which is in good agreement with DSC results.

CONCLUSION

Films of poly(methyl methacrylate)/Na⁺-MMT nanocomposites have been successfully prepared utilizing preformed PMMA and pristine sodium montmorillonite by DMF solution casting and show high transparency. The high transparency of the films was investigated by UV-vis spectra. The uniformity of dispersion of Na⁺-MMT layers was investigated by XRD and TEM. Our result confirms that pristine silicate layers can be well exfoliated in DMF solution. TGA and DMA results demonstrate an enhanced thermal resistance and mechanical properties of PMMA developed by adding sodium montmorillonite in comparison with the neat polymer film.

References

- Okada, A.; Kawasumi, M.; Usuki, A.; Kojima, Y.; Kurauchi, T.; Kamigaito, O. Synthesis and Properties of Nylon-6/Clay Hybrids. In *Polymer Based Molecular Composites*; Schaefer, D. W.; Mark, J. E., Eds.; MRS Symposium Proceedings, Pittsburgh, 1990; 171, p 45.
- Giannelis, E. P. *Adv Mater* 1996, 8, 29.
- Giannelis, E. P. *Adv Polym Sci* 1999, 138, 107.
- LeBaron, P. C.; Wang, Z.; Pinnavaia, T. J. *Appl Clay Sci* 1999, 15, 11.
- Giannelis, E. P. *Appl Organomet Chem* 1998, 12, 675.
- Xu, R.; Manias, E.; Snyder, A. J.; Runt, J. *Macromolecules* 2001, 34, 337.
- Bharadwaj, R. K. *Macromolecules* 2001, 34, 9189.
- Messersmith, P. B.; Giannelis, E. P. *J Polym Sci, Part A: Polym Chem* 1995, 33, 1047.
- Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci, Part A: Polym Chem* 1993, 31, 2493.
- Kojima, Y.; Usuki, A.; Kawasumi, M.; Fukushima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
- Gilman, J. W.; Kashiwagi, T.; Lichtenhan, J. D. *SAMPE J* 1997, 33, 40.
- Gilman, J. W. *Appl Clay Sci* 1999, 15, 31.
- Bourbigot, S.; LeBras, M.; Dabrowski, F.; Gilman, J. W.; Kashiwagi, T. *Fire Mater* 2000, 24, 201.
- Gilman, J. W.; Jackson, C. L.; Morgan, A. B.; Harris, R. Jr.; Manias, E.; Giannelis, E.; Wuthenow, M.; Hilton, D.; Phillips, S. H. *Chem Mater* 2000, 12, 1866.
- Du, J.; Zhu, J.; Wilkie, C. A.; Wang, J. *Polym Degrad Stab* 2002, 77, 377.
- Wang, D.; Zhu, J.; Yao, Q.; Wilkie, C. A. *Chem Mater* 2002, 14, 3837.
- Zhu, J.; Start, P.; Mauritz, K. A.; Wilkie, C. A. *Polym Degrad Stab* 2002, 77, 253.
- Su, S.; Wilkie, C. A. *J Polym Sci Part A: Polym Chem* 2003, 41, 1124.
- Su, S.; Jiang, D. D.; Wilkie, C. A. *Polym Adv Technol* 2004, 15, 225.
- Du, J.; Wang, J.; Su, S.; Wilkie, C. A. *Polym Degrad Stab* 2004, 83, 29.
- Qu, X.; Guan, T.; Liu, G.; She, Q.; Zhang, L. *J Appl Polym Sci* 2005, 97, 348.
- Jash, P.; Wilkie, C. A. *Polym Degrad Stab* 2005, 88, 401.
- Salem, N.; Shipp, D. A. *Polymer* 2005, 46, 8573.
- Stadtmueller, L. M.; Ratinac, K. R.; Ringer, S. P. *Polymer* 2005, 46, 9574.
- Meneghetti, P.; Qutubuddin, S. *Thermochim Acta* 2006, 442, 74.
- Zhao, Q.; Samulski, E. T. *Polymer* 2006, 47, 663.
- Costache, M. C.; Wang, D.; Heidecker, M. J.; Manis, E.; Wilkie, C. A. *Polym Adv Technol* 2006, 17, 272.
- Leszczynska, A.; Njuguna, J.; Pielichowski, K.; Banerjee, J. R. *Thermochim Acta* 2007, 453, 75.
- Hwu, J. M.; Jiang, G. J.; Gao, Z. M.; Xie, W.; Pan, W. P. *J Appl Polym Sci* 2001, 83, 1702.
- Su, S.; Jiang, D. D.; Wilkie, C. A. *J Vinyl Additive Technol* 2004, 10, 44.
- Manninen, A. R.; Naguib, H. E.; Nawaby, A. V.; Day, M. *Polym Eng Sci* 2005, 45, 904.
- Kim, S. J.; Wilkie, C. A. *Polym Adv Technol* 2008, 19, 496.
- Kumar, S.; Jog, J. P.; Natarajan, U. *J Appl Polym Sci* 2003, 89, 1186.
- Laachachi, A.; Leroy, E.; Cochez, M.; Ferriol, M.; Cuesta, J. M. *Polym Degrad Stab* 2005, 89, 344.
- Zheng, X.; Jiang, D. D.; Wilkie, C. A. *Thermochim Acta* 2005, 435, 202.
- Si, M.; Goldman, M.; Rudomen, G.; Gelfer, M. Y.; Sokolov, J. C.; Rafailovich, M. H. *Macromol Mater Eng* 2006, 291, 602.
- Yeh, J. M.; Liou, S. J.; Lin, C. Y.; Cheng, C. Y.; Chang, Y. W. *Chem Mater* 2002, 14, 154.
- Brandrup, J.; Immergut, E. H. *Polymer Handbook*, Wiley-VCH: New York, 1989.
- Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
- Zhang, W.; Li, Y.; Wei, L.; Fang, Y. *Mater Lett* 2003, 57, 3366.
- Lee, D. C.; Jang, L. W. *J Appl Polym Sci* 1996, 61, 1117.
- Manring, L. E. *Macromolecules* 1991, 24, 3304.
- Kashiwagi, T.; Inaba, A.; Brown, J. E.; Hatada, K.; Kitayama, T.; Masuda, E. *Macromolecules* 1986, 19, 2160.
- Allock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, Prentice Hall: New Jersey, 1981; p 61.
- Manring, L. E. *Macromolecules* 1989, 22, 2673.
- Zhu, J.; Uhl, F. M.; Morgan, A. B.; Wilkie, C. A. *Chem Mater* 2001, 13, 4649.
- Chen, K.; Susner, M. A.; Vyazovkin, S. *Macromol Rapid Commun* 2005, 26, 690.
- Delville, A. *Langmuir* 1992, 8, 1796.
- Hensen, E. J. M.; Smit, B. *J Phys Chem B* 2002, 106, 12664.