

Studies on Novel Composites of Polyoxymethylene/Polyamide 6

Yulin Li,^{1,2} Tingxiu Xie,³ Guisheng Yang^{1,3}

¹Joint Laboratory of Polymer Science and Technology, Institute of Chemistry, Chinese Academy of Sciences, Beijing, People's Republic of China

²Graduate School of the Chinese Academy of Sciences, Beijing, People's Republic of China

³Shanghai Genius Advanced Materials Co., Ltd, Shanghai, People's Republic of China

Received 9 March 2005; accepted 26 April 2005

DOI 10.1002/app.22146

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

ABSTRACT: A series of new composite of polyoxymethylene/polyamide 6 (POM/PA 6) were synthesized by using ϵ -caprolactam as a reactive solvent with POM soluble in it. Incorporating a small content of POM (1–4 wt %) into PA 6 led to a great improvement of impact resistance POM/PA 6. The effects of POM content on the mechanical, morphological, and thermal properties of the composites were investigated. Incorporating minor POM (1 wt %), disposed in finely dispersed level (about 1 μ m), into PA 6 matrix can greatly reduce the crystallization rate and crystallinity of PA 6. Scanning electron microscopy measurements indicated that

much microfibers with aspect ratio about 10 appeared with the addition of 3 wt % POM because of the change of phase separation mechanisms. As a result, with a small content of PA 66 (1–4 wt %) incorporated, the impact strength and elongation of POM/PA 6 were improved markedly, with retention of good tensile strength. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 335–339, 2006

Key words: impact resistance; polyamide; polymerization-induced phase separation; polyoxymethylene; spinodal decomposition

INTRODUCTION

It is a very common and often effective way to produce new substances with various properties by blending current polymers. The fact that most polymer blends have low miscibility has led to extensive research into their thermodynamic and kinetic properties.^{1–3}

Thermodynamically, introduction of functional groups with specific interactions into corresponding polymer chains or addition of a compatibilizer to a blend are two common methods to enhance the poor miscibility.

On the other hand, *in situ* polymerization technique is another effective way to control morphologies of polymer blends, mainly from the angle of kinetics of phase separation. As for this method, much attention has been paid to rubber or thermoplastic-modified thermosetting polymer systems, such as epoxy resins/thermoplastic systems.^{4–12} As reported, such types of morphologies can be controlled by the dissolution/diffusion of thermoplastic in reactive solvent and the

thermodynamics combined with the kinetics of reaction of the systems.¹³

However, few studies have been investigated on the thermoplastic/reactive thermoplastic systems.^{14,15} It can be expected that such more mobile systems may assume some new features in their morphologies and properties because of different reaction kinetics and phase separation.

In our previous studies,¹⁶ a series of polyamide 6 (PA 6) molecular composites with PA 66, PA 66/PA 6, were synthesized. Differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) measurements indicated that PA 66 macromolecules can be inserted, disposed in molecular level, into PA 6 matrix via *in situ* anionic polymerization of ϵ -caprolactam with soluble in it PA 66. The mechanical properties of the composites were superior to those of pure PA 6, particularly, as far as the tensile strength and impact resistance were concerned. It was found that the improvement in toughness might be attributed to decrease in crystallinity of PA 6 and the special morphology found in the composites. It was because of the strong hydrogen bonding interactions in the mixture that PA 66 did not crystallize and phase separate out in *in situ* polymerization process. PA 66 macromolecules in a molecular level dispersion in PA 6 matrix interfered with the arranging order of hydrogen bonding of PA 6, changed its crystalline structure, and reduced its crystallization rate and crystallinity. This

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

Contract grant sponsor: MOST Program 973; contract grant number: 2003CB615602.

comprehensive change generated by changing the arranging order of hydrogen bonding structure of PA 6 led to the improvement of impact resistance of PA 6.

Similar to the approach to synthesize PA 66/PA 6 molecular composites, the composites of polyoxymethylene/polyamide 6 (POM/PA 6) have been synthesized via *in situ* anionic ring opening polymerization of ϵ -caprolactam POM with soluble in it, instead of PA 66. The purpose of this study is to investigate that whether a crystalline polymer POM without strong hydrogen bonding with PA 6 can improve impact resistance of PA 6. The effect of the POM modifier content on the mechanical properties was studied. The corresponding morphological and thermal characteristics of the obtained composites were characterized by means of DSC and SEM. The effect of POM content in POM/PA 6 composites on the mechanisms of phase separation was also discussed.

It was found that by this approach a slight content of POM, such as PA 66, can also markedly improve the impact strength and elongation of POM/PA 6.

EXPERIMENTAL

Materials

POM was supplied by Yunnan Yuntian Chemical Company (Commercial Grade, Yunnan province, China). ϵ -Caprolactam was obtained from Nanjing Oriental Chemical Company (Commercial Grade, Jiangsu province, China). Sodium hydrate (NaOH) and toluene diisocyanate (TDI) used in this study were purchased from Shanghai Chemical Reagents Company and China National Medicines and were used without further purification.

Preparation of POM/PA 6 composites

POM was dissolved in melted ϵ -caprolactam monomer at 180°C under nitrogen, and a homogeneous transparent polymer–monomer solution was observed. It was vacuumed at 170°C for about 20 min for removing water. Then 0.2 wt % NaOH was added under stirring and continuously vacuumed for another 10 min. After this, 0.4 wt % TDI was added with stirring. The mixture was then immediately poured into a mold preheated to 180°C, and polymerized in oven at 180°C for 20 min. After polymerization, the products were cooled to room temperature and extracted with boiling water to eliminate the residual monomer. As a result, the POM/PA 6 composites of various POM contents were obtained.

Measurements

The tensile testing was performed on Instron 1122 according to ASTM D638, with crosshead speed of 50

mm/min. The Izod notched impact strength was measured with an impact testing machine (CSI-137C) according to ASTM D256.

SEM images were taken from the impact-fractured surfaces of specimens at room temperature, using JSM-6360LV SEM.

DSC measurements were carried out on a Perkin-Elmer Pyris-1 DSC calibrated with indium. All the DSC measurements were performed from room temperature to 300°C at a heating rate of 20°C/min under nitrogen atmosphere for 10 min to eliminate residual crystals. T_m was determined in the second scan.

RESULTS AND DISCUSSION

It is well known that anionic ring opening polymerization of ϵ -caprolactam generally proceeds faster (several minutes) than the step growth polymerization or radical polymerization.¹⁷ Therefore, it is more easier for thermoplastic/ ϵ -caprolactam systems via *in situ* polymerization to manipulate morphological structure than common thermoplastic/thermosetting system.

To study polymerization-induced phase separation (PIPS), POM with different content (1–4 wt %) was dissolved in ϵ -caprolactam. Clear POM solutions were obtained by heating the mixtures for about half an hour at 180°C under a nitrogen atmosphere. For comparison, pure PA 6 was prepared under the same conditions.

After polymerization for 20 min at 180°C, the sheets were yellowish, translucent, and a little elastic. With cooling at 20°C for about 10 min, they were gradually crystallized into yellow, opaque material.

To characterize the morphology of the composites, SEM measurements of the impact-fractured surfaces were performed (Fig. 1). The SEM micrographs indicated that for POM/PA 6 containing 1 and 2 wt %, the POM phase as the minor phase was dispersed as small droplets in a continuous matrix of the PA 6 phase. The size of the droplets obviously increased with increasing amounts of POM. For POM/PA 6 with 3 wt % POM, besides the appearance of particles with larger size, semicontinuous microfiber-like structure was found. The microfibers were less than 100 nm wide and about 1 μ m long, with an aspect ratio about 10.

This observation can be explained by the higher rate of reaction of ϵ -caprolactam, compared with that of conventional thermosetting precursors. This fast reaction rate led to a more intense increase of viscosity and an earlier vitrification. Moreover, the length scale on which phase separation took place was mainly influenced by the extent of aggregation of POM and the mechanisms of phase separation, before POM was trapped in the PA 6 matrix.

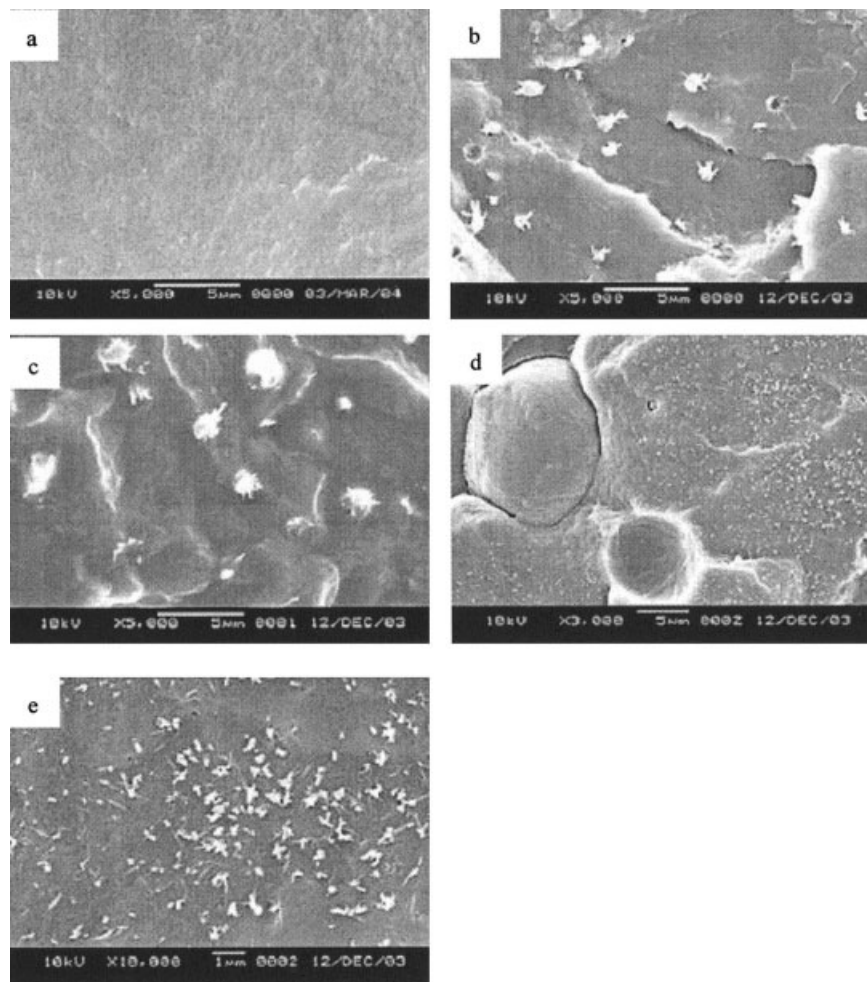


Figure 1 SEM micrographs of fractured surfaces of POM/PA 6 containing (a) 0 wt % POM, (b) 1 wt % POM, (c) 2 wt % POM, and (d, e) 3 wt % POM.

The phase graph of PIPS was showed in Figure 2. In PIPS, polymer is dissolved in a reactive monomer, which is subsequently polymerized to cause phase separation, resulting in two polymeric phases

with certain morphology. The region above the binodal curve corresponds to the homogeneous one-phase solution condition. The region inside the spi-

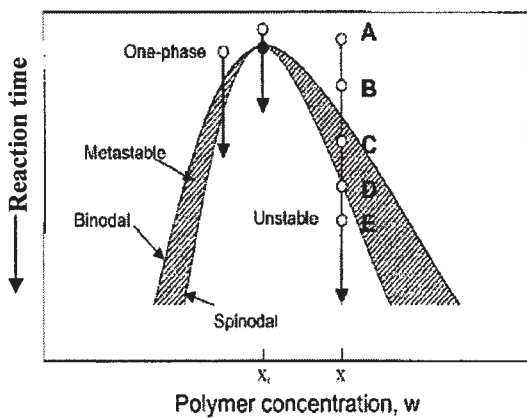


Figure 2 Schematic representation of the PIPS.

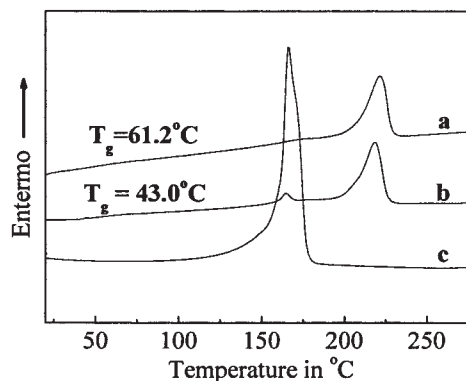


Figure 3 The second heating run DSC thermograms of (a) PA 6, (b) POM/PA 6 containing 3 wt % POM, and (c) pure POM.

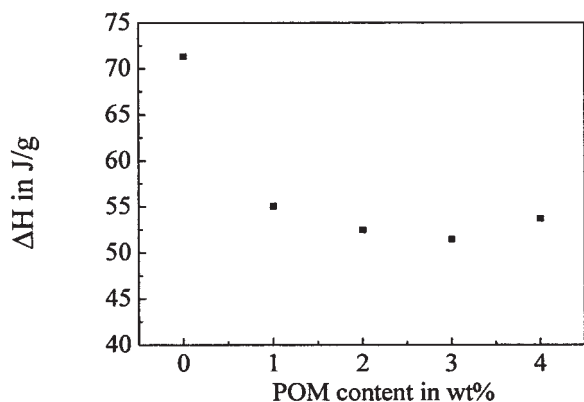


Figure 4 The plots of melting enthalpy versus POM content (wt %).

nodal curve represents the thermodynamically unstable region where all the concentration fluctuations result in a decrease of free energy and lead to a spontaneous phase separation. In the metastable region between the binodal and the spinodal region, the solution is stable to small fluctuations, but undergoes phase separation for large concentration fluctuations. When metastable regions are entered, phase separation is expected to proceed by the nucleation and growth mechanism (NG). When unstable regions are entered, the mechanism of phase separation is that of spinodal decomposition (SD). Whether the phase separation should proceed by NG or SD will depend on the depth of penetration (the magnitude of concentration fluctuations) into the region of immiscibility. With the addition of 1–2 wt % POM, phase separation proceeded only by the NG mechanism, resulting in only the appearance of droplet particles dispersed in PA 6 matrix. With further increasing POM content, SD mechanism combined with NG mechanism proceeded because of local large concentration fluctuations caused by the intense reaction of ϵ -caprolactam. Therefore, larger particles and semicontinuous microfiber-like structure were found.

Further investigation of the extent of phase separation was performed by DSC. As seen from Figure 3,

the T_g of PA 6 of the POM/PA 6 was quite lower than that of pure PA 6, which revealed that part of POM was well dispersed in PA 6 matrix. The T_m 's of PA 6 and POM in the composites were lower than those of pure PA 6 and pure POM, respectively, also indicating partial/good interdispersion of them due to the fast polymerization rate.

When the values of the melting enthalpy of PA 6 (ΔH) were compared, it was clear that the crystallinity of PA 6 in the composites markedly reduced (as shown in Fig. 4). This further indicated that part of POM was well dispersed in the PA 6 matrix. Nevertheless, the values of ΔH varied slightly with more than 1 wt % POM added.

The mechanical properties were measured with tensile and impact tests (see Table I). From the mechanical data, it can be seen that the impact resistance and elongation of POM/PA 6 were greatly improved compared with those of pure PA 6, while the tensile strength only slightly reduced. The obvious improvement of toughness of POM/PA 6 with 3 wt % POM, compared with that of POM/PA 6 with 2 wt % POM, might mainly be ascribed to the existence of local semicontinuous phase due to spinodal decomposition, besides the decrease of crystallinity of PA 6.

CONCLUSIONS

We have shown that a series of novel POM/PA 6 composites were formed *via* a simple polymerization. A finely dispersed phase was obtained due to the short time available before solidification set in—; in this way decreasing the crystallinity of PA 6 in POM/PA 6 with quite small POM (1 wt %) added. The variation of POM content can manipulate the morphological change of POM/PA 6 by changing the mechanisms from nucleation and growth mechanism to the coexistence of nucleation and growth mechanism as well as spinodal decomposition mechanism. The latter led to the appearance of microfiber-like structure. It was the decrease of crystallinity and the special morphology that resulted in the marked tough improvement with tensile strength maintenance.

TABLE I
Mechanical Properties of POM/PA 6 with Different POM Content

POM content (wt %)	Elongation at break (%)	Tensile strength (MPa)	Notched impact strength (J/m)	Flexural strength (MPa)	Flexural modulus (MPa)
0	67	67.4	42	78.1	2302
1	136	66.9	59	64.5	1796
2	142	62.9	70	59.2	1644
3	141	56.1	120	48.1	1316
4	200	53.8	120	49.1	1394
100	50	56.5	110	74.4	2304

This work was supported by 973 program of MOST (No.2003CB615602).

References

1. Paul, D. R.; Bucknall, C. B. *Polymer Blends*; Academic Press: New York, 1999.
2. Curro, J. G.; Schweizer, K. S. *Macromolecules* 1991, 24, 6736.
3. Reichart, G. C.; Graessley, W. W.; Register, R. A.; Krishnamoorti, R.; Lohse, D. J. *Macromolecules* 1997, 30, 3363.
4. Rajagopalan, G.; Immordino, K. M.; Gillespie, J. W., Jr.; McKnight, S. H. *Polymer* 2000, 41, 2591.
5. Girard-Reydet, E.; Sautereau, H.; Pascault, J. P.; Keates, P.; Navard, P.; Thollet, G.; Vigier, G. *Polymer* 1998, 39, 2269.
6. Bonnet, A.; Pascault, J. P.; Sautereau, H.; Taha, M.; Camberlin, Y. *Macromolecules* 1999, 32, 8517.
7. Ishii, Y.; Ryan, A. J. *Macromolecules* 2000, 33, 158.
8. Girard-Reydet, E.; Riccardi, C. C.; Sautereau, H.; Pascault, J. P. *Macromolecules* 1995, 28, 7608.
9. Oyanguren, P. A.; Riccardi, C. C.; Williams, R. J. J.; Mondragon, I. *J Polym Sci Phys Ed* 1998, 36, 1349.
10. Alig, I.; Jenninger, W. *J Polym Sci Phys Ed* 1998, 36, 2461.
11. Cui, J.; Yu, Y.; Chen, W.; Li, S. *Macromol Chem Phys* 1997, 198, 3267.
12. Cui, J.; Yu, Y.; Li, S. *Macromol Chem Phys* 1998, 199, 1645.
13. Lestriez, B.; Chapel, J. P.; Gerard, J. F. *Macromolecules* 2001, 34, 1204.
14. Lipatov, Y. S.; Kosyanchuk, L. V.; Nesterov, A. E.; Antonenko, O. I. *Polym Int* 2003, 52, 664.
15. Lipatov, Y. S.; Kosyanchuk, L. F.; Nesterov, A. F. *Polym Int* 2002, 51, 772.
16. Yu, L. L.; Yang, G. S. *Macromol Rapid Commun* 2004, 25, 1714.
17. Chorvath, I.; Mertens, M. D. M.; van Greenen, A. A.; Meijer, H. E. H.; Lemstra, P. J. *Polym Prepr* 1996, 37, 2, 726.