

Effect of Processing Conditions on Compatibility of Nylon 6/Polystyrene Blend

Jin-Hwan Choi,¹ Ho-Gyum Kim,¹ Dong-Hee Han,² Jeong-Cheol Lim,³ Dae-Hee Oh,⁴ Kyung-Eun Min¹

¹Department of Polymer Science, Kyungpook National University, Daegu, Korea

²Advanced Electrical Materials Group, Korea Electrotechnology Research Institute, Changwon, Korea

³Division of Textile Fashion Industry, Yeungnam College of Science and Technology, Daegu, Korea

⁴Division of Chemical Engineering, Pukyong National University, Pusan, Korea

Received 23 February 2005; accepted 21 April 2005

DOI 10.1002/app.22081

Published online 23 March 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The morphology of nylon 6 and polystyrene (PS) blend with styrene-maleic anhydride copolymer (SMA) as a compatibilizing agent was studied. The long-time mixing of blends exhibited slight decrease in storage modulus and larger domain size. This may be caused by imidization between amine end-group of nylon 6, and SMA produce the water, which hydrolyzes an amide group of nylon 6 and results in the decrease of viscosity. As the morphology change in blend influence on physical properties, it is found that modification of nylon 6 by SMA has a better morphology and good physical properties with shorter mixing time.

However, the morphology investigation in nylon 6/PS blends reveals that the effect of mixing time was negligibly small. Addition of small amount of SMA into nylon 6/PS blend has proved to give improvement in physical properties. This behavior is based on the concentration of water derived from imidization. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1–7, 2006

Key words: nylon 6; SMA; imidization; compatibilization; polymer blend

INTRODUCTION

Physical blends of immiscible polymers offer attractive opportunities for achieving unique property combinations and obtaining optimum cost/benefit ratios.^{1,2} Since the most of mixing two or more polymers result in phase separation, the performance of blends depends critically on their phase morphology and the nature of the interface between the phases. The way to overcome most of problems caused by phase separation is compatibilization, which is the addition of appropriate block or graft copolymers that act as interfacial agents.²

Nylon 6 has peculiar properties, which are high strength and modulus, good chemical and abrasion resistance, high melting point, low coefficient of friction, and toughness.³ However, water sorption originated from hydrophilic amide group in structure gives rise to reducing dimensional stability and damages electrical properties. Most of recent interest in nylon 6 blends stems from the possibility of combin-

ing the rubber or thermoplastic resin to reduce moisture sorption and also to improving the processibility.^{4,5} The method of reactive compatibilization is very often used to obtain blends with desirable properties. This method is based on the formation of a block or graft copolymer at the interface between the blend phases during melt mixing. Nylon 6 blends with polypropylene, polystyrene (PS), ABS, and polymethylmetacrylate by the addition of various compatibilizers have been reported.^{5–8} Many studies have been focused on the chemical reaction between nylon 6 and styrene-maleic anhydride copolymer (SMA) during melt mixing and especially the interfacial adhesion between nylon 6 and immiscible components is increased by these reactive groups. However, the current studies have been restricted to the molecular weight, molar ratio, concentration, and properties of compatibilizer in nylon 6 blends. It is necessary to control the mixing parameters that alter the chemical reaction between components to more effective compatibilization.

In this study, we first examine how the mixing sequence affects the properties of SMA-functionalized nylon 6/PS blend. We explore the effect of mixing time and the concentration of SMA on the rheological properties of blends.

Correspondence to: K.-E. Min (minkyek@kmu.ac.kr).

TABLE I
Materials Used in This Study

Material	η_0^a ($\times 10^3$)	T_g^b ($^{\circ}\text{C}$)	T_m^b ($^{\circ}\text{C}$)
Nylon 6	5.86	57	220
Polystyrene	1.79	94	—
SMA	8.67	120	—

^a Measured by DSC on heating rate of $10^{\circ}\text{C}/\text{min}$.

^b Measured by rheometer with radius of 25 mm cone and plate at 230°C .

EXPERIMENTAL

Materials

Nylon 6 used in this study was KN170, supplied from Kolon (Gumi, Korea). Polystyrene (PS; $M_w = 230,000$, $M_n = 140,000$) and the reactive compatibilizer SMA ($M_w = 224,000$) containing 7 wt % of anhydride were also obtained from Aldrich Korea (Seoul, Korea). Some properties of materials used are shown in Table I. The antioxidant Irganox 1010 and Irgafos 168 were the products of Ciba Geigy (Toms River, NJ). Dichloromethane and formic acid obtained from Aldrich Korea were used to confirm the reactivity of compatibilizer.

Blend preparation

All polymers were dried in a vacuum oven at 80°C for 10 h to remove the moisture before mixing. The blends were prepared by melt mixing at 230°C with rotor speed of 60 rpm with Brabender plasticoder (PLE 331) under inert atmosphere. To investigate the effect of mixing sequence on the properties of blends, two kinds of mixing methods were employed. In the first method, the sequential mixing, nylon 6 was blended with SMA first

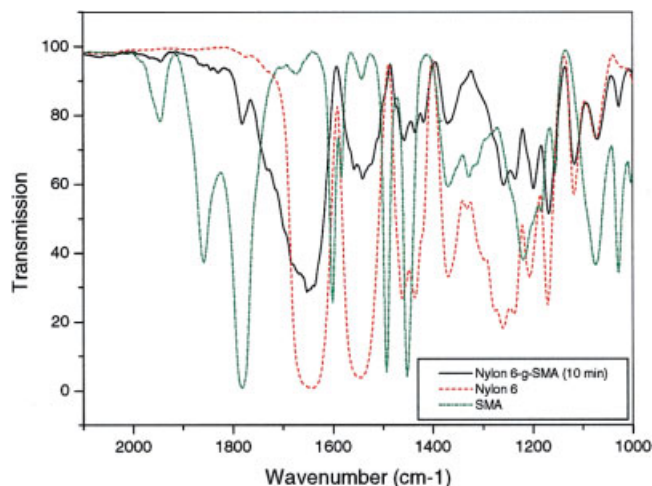


Figure 1 FTIR spectrums of nylon 6, SMA, and nylon 6/SMA blend. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

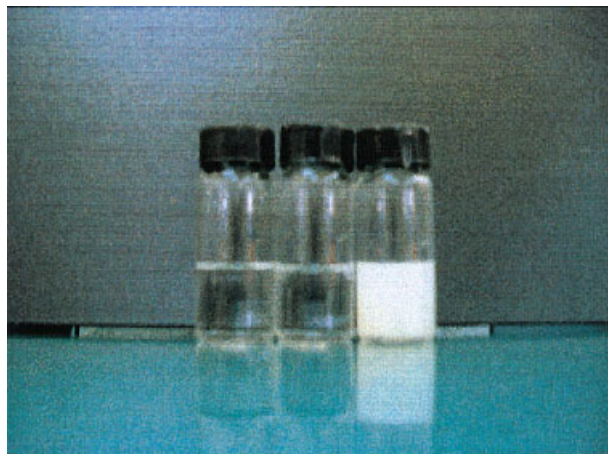


Figure 2 Solvent test for (a) nylon 6, (b) SMA, and (c) nylon 6/SMA blends in formic acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and then with PS in the second step. In the second method, simultaneous mixing method, all three components were simultaneously introduced to Brabender. The composition of the blends was 80/20 (wt %) for nylon 6/PS with 1.3 and 5 phr of SMA, according to experimental condition.

Characterization of blends

The functionalization of nylon 6 by SMA was determined by using JASCO V620 Fourier transform infrared spectroscopy (FTIR). The solubility of nylon 6 treated in formic acid was examined to identify the modification.

The SEM was used to study the morphology of the microtomed surfaces of nylon 6/PS blends. The cryogenically fractured samples were prepared by soaking in liquid nitrogen for a few minutes. The samples were then treated with dichloromethane to dissolve the minor PS domain presents at the sur-

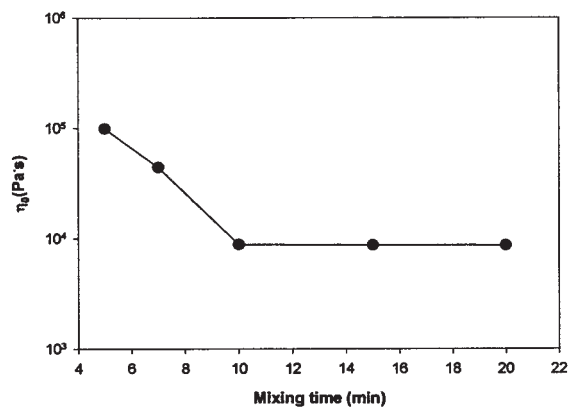


Figure 3 Effect of mixing time on zero shear viscosity of nylon 6/SMA (5 phr) blends at 230°C .

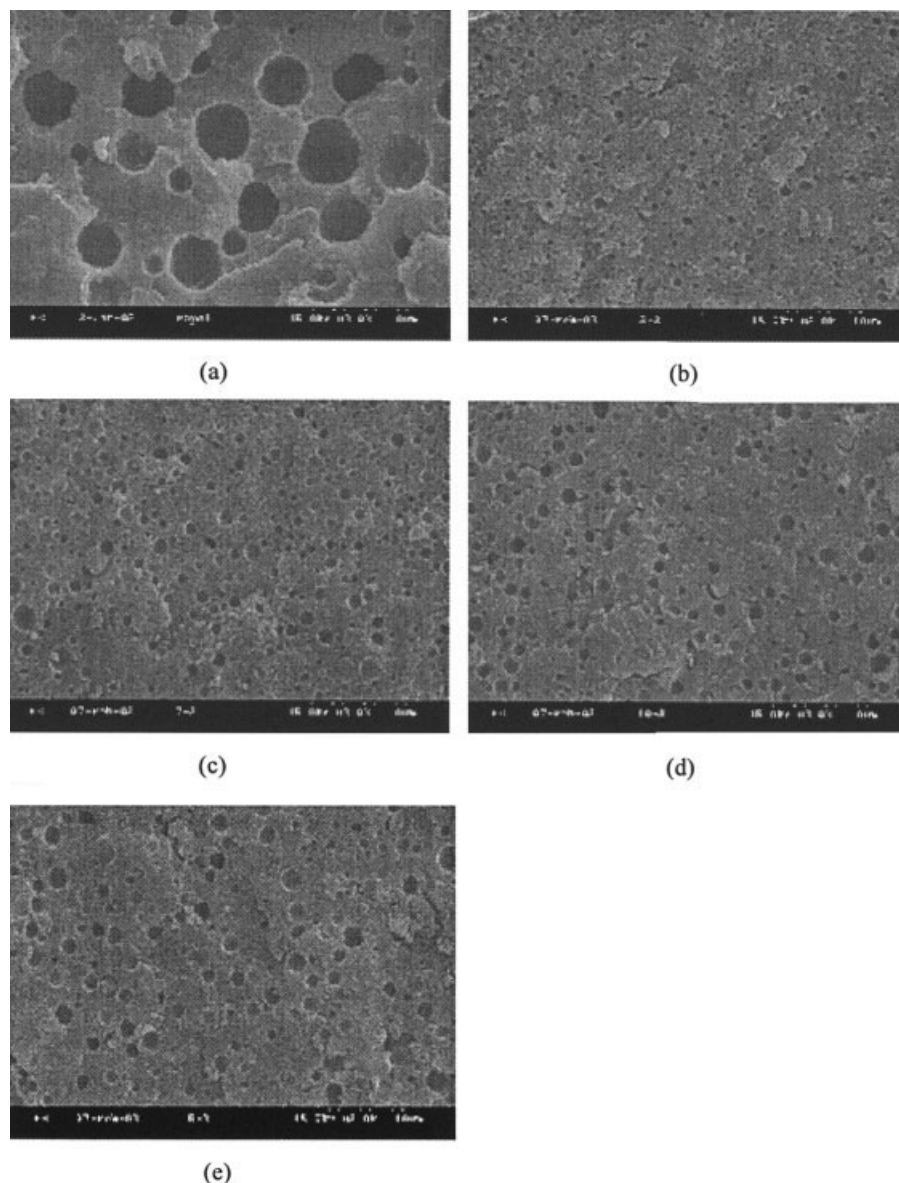


Figure 4 SEM micrographs of blends by sequential mixing (a) 0 min, (b) 5 min, (c) 7 min, (d) 10 min, and (e) 15 min for SMA mixing time.

face of the specimens. The samples were dried in vacuum oven for 24 h, followed by dissolution.

The dynamic mechanical analysis was performed with a parallel plate mode rheometer (UDS 200, Paar Physica, Korea) at 230°C, the frequency of tests ranged from 0.1 to 150 rad/s at the fixed strain rate.

RESULTS AND DISCUSSION

Determination of functionalized nylon 6

The existence of imide group at the nylon 6/SMA mixtures was confirmed by FTIR and the results were shown in Figure 1. For nylon 6, strong characteristic absorbance peak of amide group was observed at 1645 cm^{-1} , and a new absorption band at

1779 cm^{-1} indicated the imidization between amine end group of nylon 6 and maleic anhydride of SMA. The carboxylic stretching in maleic anhydride (MA) unit in SMA seemed to be negligible, which means the most of MA is consumed during the reaction with amine group of nylon 6. It can be easily found from the previous reports that the reaction of MA units with amine is more favorable than with amide group in nylon 6.⁹⁻¹¹

The disintegration of blends in etching solution (formic acid) was evaluated. As the chemical bond exists between nylon 6 and SMA, the etching solvent does not dissolve modified nylon 6, so a milky solution may be obtained. As can be seen in Figure 2, they are not disintegrated by formic acid and this

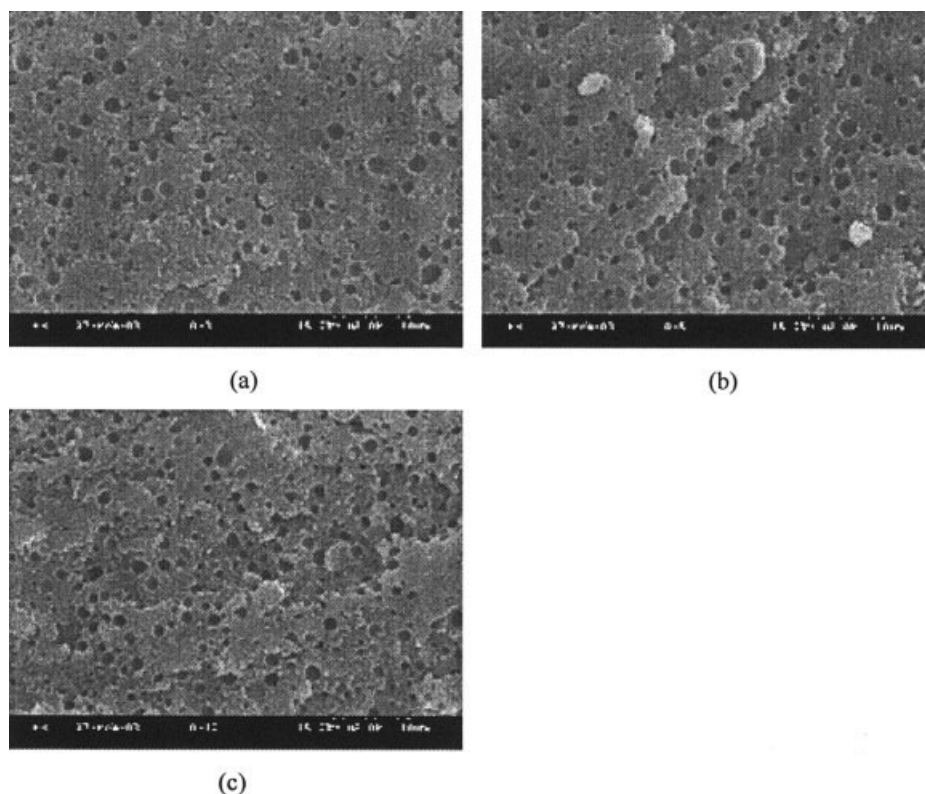


Figure 5 SEM micrographs of blends by sequential mixing (a) 3 min, (b) 5 min, and (c) 10 min for PS mixing time.

result is quite evident that nylon 6 was effectively modified by SMA.

The effect of mixing sequence

Blends prepared by sequential mixing

The modification of nylon 6 by SMA was done with a sequential mixing and then nylon 6/PS blends were prepared. The results of the variation of zero shear viscosity in nylon 6 reacted with SMA show that the viscosity of nylon 6-g-SMA was higher than that of the original two components. This may be due to the chemical reaction between nylon 6 and SMA. In Figure 3, the zero shear viscosity data with various mixing times are presented. The viscosity was gradually decreased with the mixing time, and this result corresponds to torque value in Brabender. The viscosity of nylon 6-g-SMA mixture is increased in the early mixing stage. The moisture formed by imidization between amine end group in nylon 6 and MA in SMA may cause the hydrolysis of amide group in nylon 6.^{9–12} This is thought to reduce the viscosity of the blend in subsequent mixing stage. Interestingly, there disappears to be decreasing in viscosity after 10 min. We assumed that the most of moisture was consumed for hydrolysis of amide group.

Morphology. To have an insight into the dependence of nylon 6-g-SMA melt viscosity in mixing stages on the blend morphology, PS was melt-blended with modified nylon 6 with the same mixing time. From Figure 4, it is clear that the viscosity of modified nylon 6 apparently affects the morphology of the blends, espe-

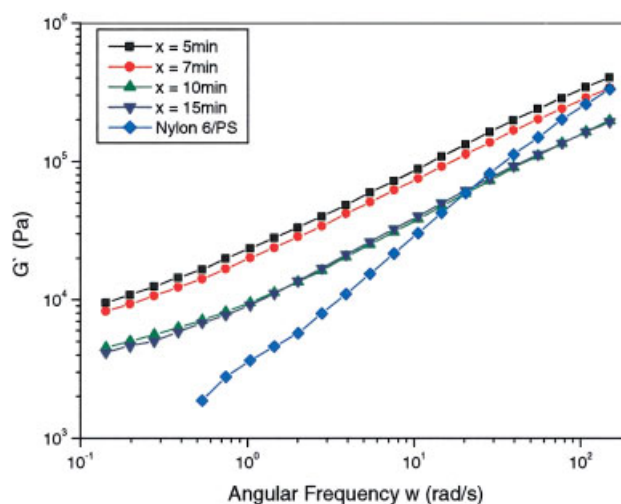


Figure 6 Effect of SMA mixing time (x) on storage modulus of blends by sequential mixing at 230°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

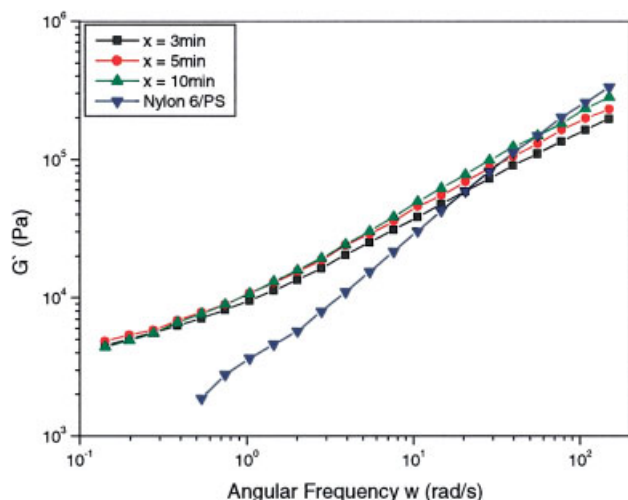


Figure 7 Effect of PS mixing time (x) on storage modulus of blends by sequential mixing at 230°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cially the most of small PS domain was observed at 5 min of mixing time. However, the difference of morphology was negligible up to 10 min mixing time and this situation is identical to the change of viscosity.

We expected only the effect of PS mixing time on the blends morphology, because the influence of viscosity

of nylon 6 and SMA might be zero even in 10 min mixing time. Only the effect of PS mixing time on the blend morphology was examined for nylon 6-g-SMA, in which the nylon 6 was mixed with SMA during 10 min, because the melt viscosity became constant after 10 min of mixing time.

Figure 5 shows that there is no distinguishable difference in morphology, which suggests that nylon 6-g-SMA does not cause viscosity change in blending with PS any more.

Rheological behaviors. Figure 6 presents the dependence of SMA mixing time on shear storage modulus (G') with sequential mixing in Brabender. For the modified nylon 6/PS blends, more apparent increase of modulus than the unmodified blends was observed at the low frequency region, which obviously revealed the formation of nylon 6-g-SMA. The highest modulus value was observed in 5 min for mixing time, but with more mixing time, modulus was rather decreased. Over 10 min, however, there was no significant difference in modulus.

The storage modulus of modified nylon 6/PS blends is presented as a function of the PS mixing time in Figure 7.

Blends prepared by simultaneous mixing

Morphology. Figure 8 shows how the morphology of nylon 6/PS blends prepared by simultaneous mixing

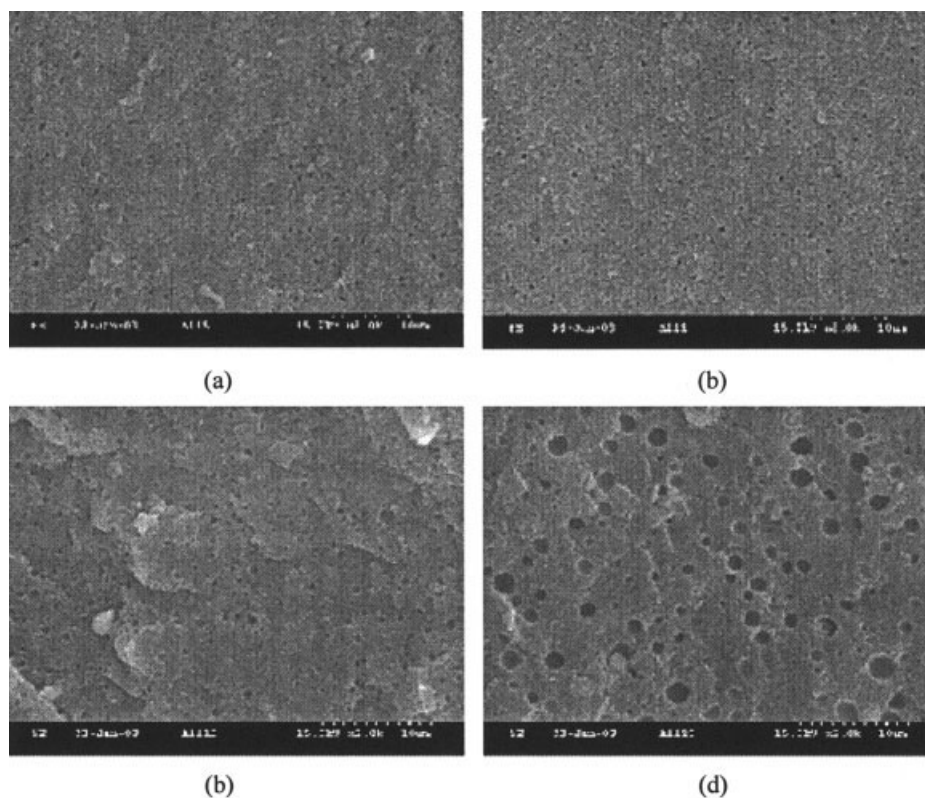


Figure 8 SEM micrographs of blends by simultaneous mixing (a) 5 min, (b) 10 min, (c) 15 min, and (d) 20 min for mixing time.

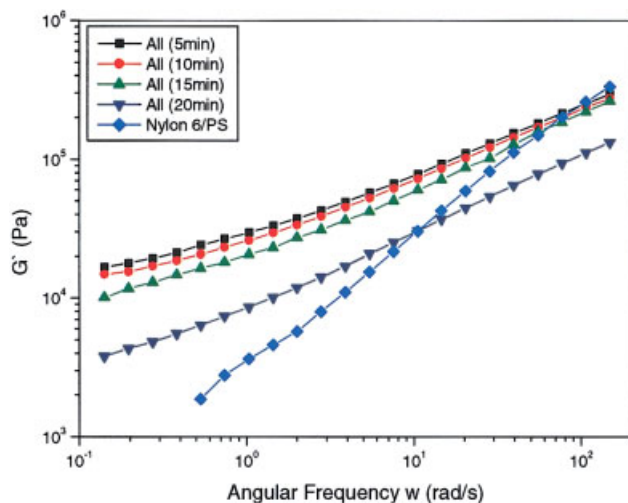


Figure 9 Effect of mixing time on storage modulus of blends by simultaneous mixing at 230°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

changes as a function of mixing time. Average PS particle diameters suggest that the smaller size can be obtained with the shorter mixing time. The results shown in Figure 8 are also due to the water that came from the imidization between nylon 6 and SMA that may hydrolyze the amide group of nylon 6, and these behaviors are quite analogous to the sequential mixed blends results.

Rheological behaviors. The rheological behavior of nylon 6/PS blends prepared by simultaneous mixing is shown in Figure 9. By comparing the results of the previous blends, it can immediately be seen that the mixing sequence does not influence on the rheological behaviors

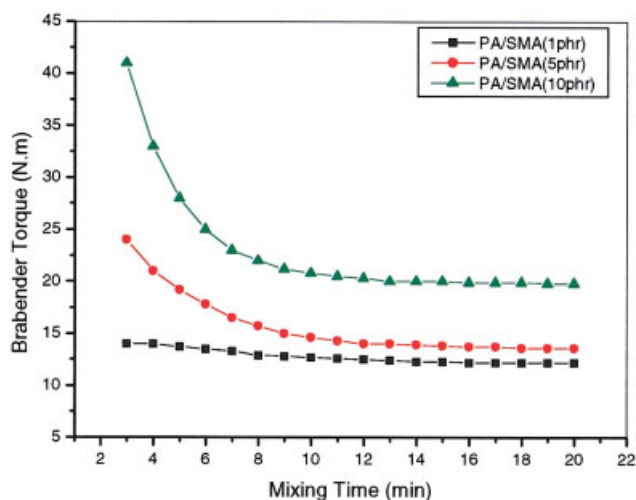


Figure 10 Torque as function of mixing time for nylon 6/SMA blends at various SMA contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

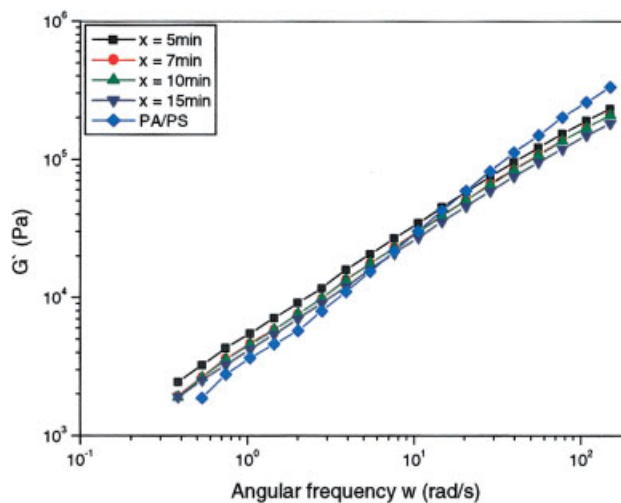


Figure 11 Effect of SMA mixing time (x) on storage modulus of blends by sequential mixing at 230°C (SMA content = 1 phr). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of blends. The moisture formed in the blends also may react with the amide group in nylon 6, this cause the viscosity decrease in nylon 6 matrix, whereas the viscosity of PS domain was relatively increased.

The effect of SMA concentration on blend properties

To investigate the effect of SMA content on blends properties, we introduced 1 and 10 phr of SMA. In Figure 10, the torques of blends as a function of time show that the reduction of torques was not so much pronounced in blend with 1 phr SMA compared with existing blend with 5 phr SMA. However, the torque was remarkably reduced in blend with 10 phr SMA in early stage. This may be related to the fact that the formation of the water is dependent on the concentration of SMA, which reduces the torque of blend in various mixing time. The results also indicate that the torque in blend with 10 phr SMA is entirely higher than the blend with 5 phr SMA, and this may due to the addition of highly viscous SMA besides the moisture existence.

Figures 11 and 12 explain the effect of SMA concentration and mixing time on the rheological behavior of blends. In Figure 11, when 1 phr of SMA was added, the difference of storage modulus was not observed compared with the blend with no SMA. In fact, this tendency corresponds to the results of torques in blends.

Addition of 10 phr SMA into the blend gives rise to further difference of modulus changes comparing with the result of blend with 5 phr SMA as a function of mixing time shown in Figure 12. From these results, it is inferred that the concentration and mix-

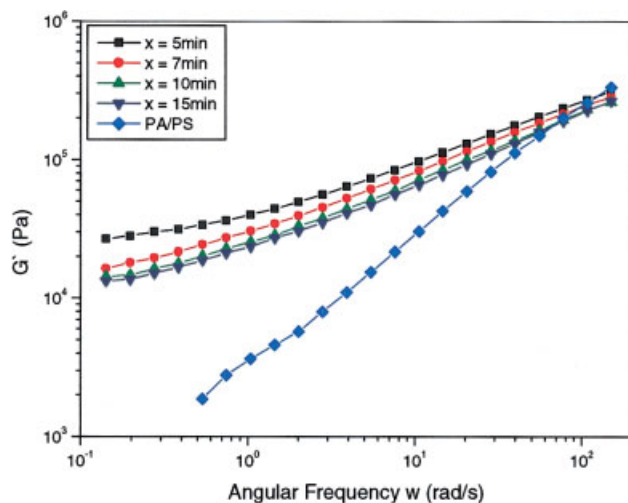


Figure 12 Effect of SMA mixing time (x) on storage modulus of blends by sequential mixing at 230°C (SMA content = 10.phr). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ing time of SMA also influence on the properties of blend.

CONCLUSIONS

The experiments studied here were designed to gain insight into the improvement of miscibility in nylon 6/PS blends using the reactive compatibilizer. It is confirmed that the imidization occurred between SMA and nylon 6, as observed from FTIR and disintegration

of samples in etching solution. This indicates that nylon 6 was functionalized.

Regardless of mixing sequence, increasing the mixing time of nylon 6 with SMA produces the larger PS domain sizes and causes the decrease of storage modulus in blend. These can be attributed to the hydrolysis of amide group in nylon 6 originating from the water formed during in imidization, and this hydrolysis may reduce the nylon 6 viscosity.

It was also shown that the mixing time of PS domain has no significant effect on the rheological properties of blend. Additionally, the concentration of SMA was obviously influenced on the properties of the blends.

References

1. Utracki, L. A. *Commercial Polymer Blends*; Chapman & Hall: London, 1998.
2. Paul, D. R.; Bucknall, C. B. *Polymer Blends*; Wiley-Interscience: New York, 1999.
3. Melvin, I. K. *Nylon Plastics Handbook*; Hanser/Gardner: Cincinnati, OH, 1995.
4. Okada, O.; Keskkura, H.; Paul, D. R. *Polymer*, 2001, 42, 8715.
5. Okada, O.; Keskkura, H.; Paul, D. R. *Polymer* 1999, 40, 2699.
6. Kudva, R. A.; Keskkura, H.; Paul, D. R. *Polymer* 2000, 41, 225.
7. Kudva, R. A.; Keskkura, H.; Paul, D. R. *Polymer* 2000, 41, 239.
8. Oderkerk, J.; Groeninckx, G. *Polymer* 2002, 43, 2219.
9. Marechal, P.; Coppens, G.; Legras, R.; Dekoninck, J. M. *J Polym Sci Part A: Polym Chem* 1995, 33, 757.
10. De Roover, B.; Devaux, J.; Legras, R. *J Polym Sci Part A: Polym Chem* 1997, 35, 901.
11. Al-Malaika, S. *Reactive Modifiers for Polymers*; Chapman & Hall: London, 1997.
12. Kim, B. K.; Park, S. J. *J Appl Polym Sci* 1991, 43, 357.