Improvement of Dimensional Stability of Nylon-6 Block Copolymer Using Phenolic Resin by Reaction Injection Molding

M. J. LOZANO-GONZÁLEZ,[1] **E. A. GONZÁLEZ-DE LOS SANTOS,**[1] **A. F. JOHNSON,**[2] **S-W. TSUI**[2]

[1] Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna H. # 140, Saltillo Coahuila, c.p. 25100, Mexico

[2] Interdisciplinary Research Center in Polymer Science and Technology, School of Chemistry, University of Leeds LS2 9JT, United Kingdom

ABSTRACT: In order to decrease moisture uptake and hence provide rigidity and dimensional stability in a nylon-6 block copolymer (NBC), powdered phenolic resin was incorporated into the formulation as a filler and processed by reaction injection molding. A novolac resin was cured with hexamethylenetetramine to produce the phenolic resin, which was modified with diethylamine in order to remplaced the —OH groups by diethylamine groups. 5% by weight of modified and unmodified powdered phenolic resin was used as a filler in the nylon-6 block copolymers, and reinforced-nylon-6 block copolymer plaques were produced by reaction injection molding at 145°C. The materials were characterized by dynamic mechanical thermal analysis (DMTA), and their flexural modulus, impact test, and dimensional stability were evaluated. In unmodified phenolic-resin-reinforced nylon-6 block copolymer, water absorption was decreased by 90% compared with the NBC without filler. Two mechanisms of interaction between the NBC and the phenolic resin have been proposed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1811–1816, 1998

Key words: nylon-6 block copolymer; phenolic resins; nylon-6 block copolymer composite; dimensional stability; reactive fillers

INTRODUCTION

In 1982 nylon-6 block copolymer (NBC), also called NYRIM, was introduced to the market as the first engineering thermoplastic material processed by the reaction injection molding (RIM) technique. With NYRIM, the following two-package system is used: reactive prepolymer and catalyst concentrate. These are dissolved in caprolactam, which make the two reactive streams.[1,2] Elastomer-modified nylon-6 also exists for injection molding; however, they differ from nylon-6 block copolymer because they are a blend of rubber and nylon. In NBC, the chemical bond between the nylon and the rubber phases results in a unique rubber dispersion and have superior properties compared with a straightforward blend.

The effect of moisture uptake on nylon-6 is well known and well documented.[3] The susceptibility of nylon-6 block copolymer to water absorption was expected. Evaluation of applications requiring dimensional stability, such as exterior automotive body panels, indicated that the early NBC formulations would not meet specifications with regards to expansion due to moisture absorption. The dimensional stability of this copolymer appears to be sufficient for most applications when

reinforced with glass fiber. Expansion is reduced to a maximum of 0.3% by reinforcement with 25% of $\frac{1}{16}$ milled glass fiber. This values appear to be acceptable within the parameter for exterior automotive applications and others requiring dimensional stability.[4]

Flexural modulus, impact strength, thermal expansion, and heat sag of reinforced-nylon-6 block copolymer, using various types of reinforcement material, was studied by Gabbert and coworkers.[5] They reported that the most efficient reinforcement was $\frac{1}{16}$-in. precision-chopped dispersible glass fiber.

Zadorecki and Abbas[6] reported the use of cellulose-reinforced nylon-6 block copolymers. Composites were prepared by RIM of nylon-6 system in which one of the reactants contained about 10% by weight of cellulose fibers. He found that the cellulose fibers increased the stiffness of the NBC, that the tensile strength of the composites was slightly decreased, and that the elongation at break and impact strength were reduced compared to glass fiber-reinforced nylon-6.

Phenolic resins are well known as composites binders. However, to date, few studies have been reported relating to phenolic resin suitable for reaction injection molding. In 1983, Brode et al.[7] reported the characterization of glass-reinforced phenolic RIM composites. The material possesses balanced static mechanical properties, which are retained up to 300°C. They also exhibit good room temperature and −35°C damage tolerance, have very good fatigue resistance, and have achieved UL-94 VO flammability rating. Phenolic RIM composites are competitive with polyester or vinyl-ester based material and exhibit superior elevated temperature, flammability, toughness, and fatigue performance.

In 1991, Yoshitaka obtained a patent in which powder phenolic resin used as a filler in nylon-6 block copolymer-RIM system is described.[8] This patent reports the improvement of mechanical properties and dimensional stability, with swelling in water of 1.20% with phenolic resin and 1.95% without phenolic resin.

The present report describes the observation and measurements of the morphology, physical, and mechanical properties of NBC, comparing the dimensional stability with and without the phenolic resin filler, and substantiates the idea that the phenolic resin is a reactive filler, not just an inert filler.

EXPERIMENTAL PROCEDURE

Nylon-6 Block Copolymer

In RIM, the commercial polyesteramide prepolymer (30%) is dissolved in molten ε-caprolactam at 90° (polyol stream A). For the second part of the system (catalyst stream B), anionic polymerization catalyst was also dissolved in molten ε-caprolactam at 110°C. Once the catalyst was fully dissolved, both solutions were mixed and poured into the preheated mold at 140°C for 10 min, where polymerization occurred. The final NBC polymer properties are developed in this time, and the molded plaques did not require a post-cure. The mold was cooled down to 25°C, and the nylon-6 block copolymer plaque was released from the mold (NBC plaque).

Phenolic-Resin-Reinforced Nylon-6 Block Copolymer

Pulverized novolac resin was cure with 15% by weight of hexamethylenetetramine at 170°C for 10 min and cooled to room temperature.[9] The phenolic resin obtained was also pulverized in a ceramic ball mill until an average particle size of approximately 100 μm was achieved. They were then dried in a vacuum oven at 100°C for 48 h. Also, modified phenolic resin was prepared. The powder phenolic resin obtained was refluxed for 3 h at 95–100°C with diethylamine in the presence of sodium bisulfite.[10,11] Subsequently, the solid was filtered and dried in a vacuum oven at 100°C for 48 h.

To produce the unmodified and modified phenolic-resin-reinforced NBC, the polymerization procedure was similar to that used for the synthesis of NBC. In this case, it was necessary to add 5% by weight of phenolic resin, an excess of catalyst (20% or 30%), and to modify the temperature of mixing (100°C), mold temperature (145°C), and reaction time (25 min.) (compare to 10%, 90 and 140°C, and 10 min, respectively). The formulations of NBC, unmodified phenolic-resin-reinforced NBC (PHR-R-NBC), and modified phenolic-resin-reinforced NBC (MPHR-R-NBC) are summarized in Table I.

Characterization and Testing Methods

Flexural Modulus and Impact Test

Standard test methods ASTM D 790M-86, Method I-A, and ASTM D 256-87, Method B, Charpy-type were used to determined the flexural modulus and impact strength, respectively.

Table I   Formulation Used to Obtain the Nylon-6 Block Copolymer With and Without Reactive Filler

Sample ID	NBC	PHR-R-NBC	MPHR-R-NBC
Prepolymer[a]	30	30	30
ε-Caprolactam[a]	70	70	70
Catalyst[b]	10	20	20
Phenolic resin[a]	—	5	5[e]
Mixing temp[c]	90	100	100
Mold temp[c]	140	145	145
Reaction time[d]	10	25	25

[a] Percentage by weight.
[b] Percentage by total weight.
[c] In degrees Celsius.
[d] In minutes.
[e] Phenolic-resin-modified.

Measurement of Dimensional Stability

The samples were cut as rectangular bars (40 × 15 × 5 mm) in the flow direction. The dimensions were measured with a vernier micrometer just before immersion (time 0) and during the test. All the samples were immersed in a hot water bath (40°C), and the dimensional changes, as well as the weight of each samples, were measured after several days of immersion in the bath. This procedure was repeated several time over a period of 1 month.

Dynamic Mechanical Thermal Analysis

The apparatus used was a Polymer Laboratories Model MK II DMTA with dedicated computer software. A power head clamping frame and dual cantilever mode was used to run all the samples. The temperature range used was set from −100 to 150°C at 2°C/min, and the frequency used was 10 Hz. The samples of nylon-6 block copolymer (NBC = JL-10), phenolic-resin-reinforced nylon-6 block copolymer (PHR-R-NBC = JL-1) and modified phenolic-resin-reinforced nylon-6 block copolymer (MPHR-R-NBC = JL-2), were cut as rectangular bars (30 × 8 × 3 mm).

RESULTS AND DISCUSSION

Figure 1 shows the balance of the flexural modulus and impact test results, obtained for plaques of PHR-R-NBC, MPHR-R-NBC, and NBC. The impact properties decrease when the phenolic resin or modified phenolic resin is added to the NBC, and, consequently, the flexural modulus in the samples with phenolic resin increased somewhat more than the unreinforced NBC. When samples of PHR-R-NBC and MPHR-R-NBC were examined by optical microscopy, some agglomerates were easily visible in the fracture surface, probably because of the poor mixing (hand mixing), the poor distribution of the phenolic resin into the NBC matrix, and the subsequent formation of agglomerates, producing impaired impact property.

If it is assumed that the phenolic resin forms some kind of association with the amide groups, and that this association does cause some disruption in the packing of the hard block (nylon-6), it would be expected that the flexural modulus would decrease. If there is no association, as in the modified phenolic resin case, an increase would be observed because the influence of the filler reinforcement. The above rationalization is in agreement with the flexural modulus observations for both materials.

One of the most important properties to evaluate was the linear expansion (%) in the NBC material with and without phenolic resin, as well as the NBC with modified phenolic resin. Figure 2 exhibits the effect of absorption on linear expansion (%) for the plaques NBC, PHR-R-NBC, and MPHR-R-NBC. The NBC exhibiting maximum expansion (about 2%), and the incorporation of a simple unreactive filler (MPHR-R-NBC) produces a decrease in water absorption. Moreover, the incorporation of a reactive filler, such as the phenolic resin PHR-R-NBC, is reflected in a consid-

Figure 1   Effect of the phenolic resin (5 wt %) on impact and modulus in NBC.

Figure 2 Effect of phenolic resin on water absortion in NBC.

erable decrease in water absorption and improvement of linear expansion.

The linear expansion for samples (PHR-R-NBC) that contained the reactive filler phenolic resin was diminished from 2.2 to 0.2%. This improvement was not observed in the blocked phenolic resin, where a reduction from 2.2 to 1.4%

only was observed. As was mentioned earlier, the phenolic resin may form an association (hydrogen bond) with the NBC amide group (Fig. 3), which obstruct the attack of the water to the amide groups in the NBC material.

It is possible that a second mechanism could be involved. The phenolic resin —OH groups could

(a)

(b)

Figure 3 Postulated mechanisms of how the phenolic resin help to prevent the moisture uptake by NBC: (a) the association of the phenolic resin with amide groups in the NBC; (b) association of the phenolic resin with water.

Figure 4 Dynamic modulus of NBC and phenolic resin as filler.

associated with the water (as depicted in Fig. 3); such an association would prevent or retard the absorption of water into the NBC material. However, when the phenolic resin becomes saturated with water, then it is possibility that it will start to interact with the NBC amide groups. After a 50-day dimensional stability test, no change was observed once equilibrium in dimension after 8 days had been reached.

Measurement of dynamic modulus (E') and loss factor (tan δ) were obtained by DMTA. Figure 4 illustrate the dynamic modulus (E') curves as a function of temperature for the three plaques, NBC, PHR-R-NBC, and MPHR-R-NBC. The incorporation of the phenolic resin as an unreactive

filler (MPHR) results in a decrease in the dynamic modulus, unfortunately, as a reactive filler (PHR) the decrease is greatest. The strong change in behavior occurs at about -25 to 65°C.

Also, the loss factor (tan δ) for these three materials is plotted as a function of temperature in Figure 5. This figure shows that there is a downward shift of the nylon-6 T_g (from 75 to 25°C) and an upward shift of the polyol T_g (from -50 to -45°C) with the addition of the modified phenolic resin (postulated as an unreactive filler) MPHR-R-NBC, compared with the control sample of NBC.

When the unmodified phenolic resin (postulated as a reactive filler) PHR-R-NBC was incor-

Figure 5 Tangent δ of NBC with phenolic resin as filler.

porated into the NBC, the 2 T_g peaks (polyol and nylon-6) converge to give a broad peak at about 20°C. These results suggest that the phenolic resin is likely to act as a compatibilizer between the soft block (polyol) and the hard block (nylon-6), with the subsequent modification of the mechanical properties.

Additionally, when the reactive phenolic resin filler (PHR-R-NBC) was combined with the NBC, the dynamic modulus (E') for the hard block at high temperatures was decrease significantly (about 6.9 Pa) compared with the control (about 8.3 Pa). Less of a decrease was observed for the unreactive phenolic filler (about 8.0 Pa). It is suggested that the association of the phenolic resin with the amide groups disrupts the packing efficiency of the hard block material, reducing its ability to bond with hydrogen bonds, which act as reinforcement tie points.

CONCLUSIONS

The poor distribution of the phenolic resin in the nylon-6 block copolymer decreased the flexural modulus and impact properties of the material. Nevertheless, this decrease is not significant and could be improved by using a proper RIM mixing machine, and then the phenolic resin can be used as a reactive filler in NBCs. The DMTA analysis suggest that the phenolic resin is likely act as a bending agent between the soft-block (polyol) and the hard-block (nylon-6) components.

The NBC exhibiting maximum expansion (about 2.2%), the linear expansion for samples (PHR-R-NBC) that contained the reactive filler phenolic resin, was diminished from 2.2 to 0.2% (90% of decrement). This improvement was not observed in the blocked phenolic resin, where a reduction from 2.2 to 1.4% (64% of decrement) only was observed. As was mentioned earlier, the phenolic resin forms an association (hydrogen bond) with the NBC amide group, which obstructs the attack of the water to the amide groups in the NBC material.

Two possible mechanisms of interaction between the nylon-6 block copolymer and the phenolic resin have been proposed, as follows: (1) hydrogen bond association with the amide group, and (2) hydroxyl group association with the water molecule. Also, it is possible that both mechanisms could be acting in concert.

REFERENCES

1. J. D. Gabbert and R. M. Hedrick, *Proceedings of the 91st National AIchE Meeting,* Detroit, MI, Aug. 1981.
2. R. M. Hedrick and J. D. Gabbert, *Proceedings of the 91st National AIChE Meeting,* Detroit, MI, Aug. 1981.
3. I. Melvin, *Nylon Plastics SPE Monographs,* M. I. Kohan, Ed., John Wiley and Sons, New York, 1973.
4. J. D. Gabbert, *Polym. Proc. Eng.,* **4,** 359 (1986).
5. J. D. Gabbert, A. Y. Garner, and R. M. Hedrick, *Polym. Comp.,* **4,** 196 (1983).
6. P. Zadorecki and K. B. Abbas, *Polym. Comp.,* **6,** 162 (1985).
7. G. L. Brode, M. J. Michno, and S. W. Chow, *Abstr. Pap. Am. Chem. Soc.,* **186,** 192 (1983).
8. O. Yoshitaka, Jpn. Pat. JP 03-114810, (1991).
9. W-Y Chiang and S-Y Yang, *J. Appl. Polym. Sci.,* **37,** 499 (1989).
10. J. March, *Advanced Organic Chemistry Reactions, Mechanisms and Structure,* 4th ed., Wiley-Interscience, 1992.
11. R. T. Morrison and R. N. Boyd, *Organic Chemistry,* 3rd ed., Allyn and Bacon, Needham Heights, MA, 1973.