Modification of Nylon 6 by Phenol-Containing Polymers

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ABSTRACT: A crystalline polymer, Nylon 6, was selectively blended with various amorphous polymers containing phenolic moieties. It was found that moisture absorption by the amide group in Nylon 6 could effectively be reduced by blending with p-Cl-novolac at ratios as low as 2 phr (part per hundred resin). Blends of Nylon 6 with vinylphenol homopolymer and its copolymer with styrene also showed reduced moisture uptakes, but the effect was less dramatic than that of the p-Cl-novolac blend at all blend ratios. Novolac content in excess of 5 phr shows little additional advantage in moisture reduction. Thermal transitions of blends of Nylon 6 with poly(vinyl phenol), its copolymer, and p-Cl-novolac were also investigated. At a blend ratio of 5 phr, p-Cl-novolac caused a larger increase in glass transition temperature than the other two blends. The melting temperatures of the blends were little influenced by low levels of the amorphous polymer incorporation, but broader melting endotherms in the differential scanning calorimetry scans were observed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 295–300, 1999

Key words: nylon 6; novolac; moisture uptake; glass transition; blend

INTRODUCTION

Many aliphatic nylons are widely used semicrystalline polymers having various desirable properties, such as high melting temperatures, good chemical resistance, and superior mechanical performance.[1] In blends containing crystalline polymers, the presence of a second component may cause structural changes in both the crystalline and amorphous regions. Blends of an amorphous polymer having a high glass transition temperature (T_g) with a crystalline nylon raises the relatively low T_g's of these nylons.[2–5]

A disadvantage of some nylons (e.g., Nylon 6) is that the polymer absorbs a considerable amount of moisture leading to problems of dimensional stability and property changes. Many attempts have been made to overcome this difficulty. A previous study[6] conducted in our laboratory indicated that the moisture sorption by Nylon 6 could be effectively reduced by blending it with a small amount of p-tertiary butyl-phenol-formaldehyde (conventionally called novolac). In this investigation, we have expanded the scope of this observation and study how other phenol-containing polymers influence the moisture uptake of Nylon 6. The phenol-containing polymers studied are p-Cl-novolac, poly(vinyl phenol), and a copolymer of styrene and vinyl phenol.

Upon blending with a second component, the properties of Nylon 6 are expected to change. This article describes preliminary findings of changes in the thermal properties, including T_g and the melting temperature of Nylon 6. Detailed studies of the Nylon 6 crystallization from the melt, either at controlled cooling rates or at a constant

Table I   Moisture Absorption (Wt %) of Nylon 6 and Its Blends at 64% Relative Humidity

phr	0	2	5	10	20
Blended with					
LPVPh	6.59	5.05	4.64	4.27	3.60
PS-*co*-PVPh	6.59	4.54	4.25	3.26	—
p-Cl-Novolac	6.59	3.86	3.61	3.46	3.08

PS, polystyrene; PVPh, poly(vinyl phenol).

temperature (isothermal crystallization) using thermal analytical methods and the small-angle X-ray scattering technique, will be discussed in a separate publication.[7]

EXPERIMENTAL

Nylon 6 pellets with an average molecular weight of 24,000 were purchased from Polyscience Co. Poly(vinyl phenol) synthesized in our laboratory with a molecular weight of $\sim$ 2,300 was designated LPVPh.[8] *p*-Cl-novolac with a molecular weight of $\sim$ 1,400 was synthesized according to the method described by DeRosa et al.[9] A styrene/vinyl phenol copolymer was synthesized by free radical polymerization, giving a random copolymer having a weight ratio of 82/18 and molecular weight of 68,500 (gel permeation chromatography polystyrene equivalent). All the synthesized polymers were characterized by Fourier transform infrared and nuclear magnetic resonance (NMR) spectra.

Polymer blends were prepared by the co-precipitation method. An appropriate amount of the amorphous polymer was first dissolved in 2-butanol. A formic acid solution containing a predetermined amount of Nylon 6 was then added to the 2-butanol solution and stirred overnight. The mixed solution was introduced dropwise into water, and the resulting precipitate was then washed with a large amount of water followed by vacuum-drying at 60°C for 1 week. The blend ratio used in this study is expressed as phr (part per hundred resin).[2b]

Moisture absorption measurements were conducted on films with a thickness of $\sim$ 5 mm. Films were made by melt-blending polymers at the preselected compositions and pressed in a laboratory compression mold at 250°C and 1,000 psi to obtain the desired thickness. The resulting film samples were weighed before and after exposure for 2 weeks at room temperature in an environment maintained at a relative humidity of 64%.

The three amorphous additives were blended with Nylon 6 for the study of thermal transition properties. A TA 2920 MDSC^{TM} equipped with liquid nitrogen cooling accessory was used to measure T_g and melting temperatures. The sample was first heated to 250°C and kept at that temperature for at least 5 min to remove the previous thermal history, then quenched to the subambient. A rate of 10°C min^{-1} was used in the second heating scan, and the inflection point of the heat capacity step change was chosen as the T_g. T_g's of *p*-Cl-novolac, LPVPh, and the copolymer were 98°, 133°, and 125°C, respectively. Peak endotherm temperatures in the heating scans of the quenched specimens were used for reporting melting temperatures.

RESULTS

Moisture Absorption

It has been well documented that the properties of nylons are influenced by the amount of water/moisture absorbed.[10-12] Therefore, it is of great interest to study how the moisture absorption can be reduced by blending Nylon 6 with other polymers. In this study, Nylon 6 was blended with the three phenol-containing additives previously described.

As seen in Table I, the moisture sorption of Nylon 6 blended with these amorphous polymers decreased. A particularly significant reduction, 41%, was found for the novolac-containing blends at a blend ratio as low as 2 phr. The moisture sorption continues to decrease, but less precipitously, as the blend ratio increases. Similar observations were obtained for the Nylon 6/LPVPh and Nylon 6/copolymer blends, except that the reduction in moisture sorption was less dramatic.

Table II   Thermal Transitions (°C) of Nylon 6 and Its Blends

	T_g	T_m
Nylon 6	47	223
5 phr LPVPh	50	222
20 phr LPVPh	60	219
5 phr *p*-Cl-novolac	55	223
20 phr *p*-Cl-novolac	56	223
5 phr copolymer	50	221
20 phr copolymer	56	222

It is interesting to note that the copolymer exhibits a more efficient reduction in moisture absorption, compared with the vinyl phenol homopolymer.

Thermal Transitions of Polymer Blends

Although the 5 phr *p*-Cl-novolac film is the most promising blend from the point of view of moisture absorption, differences in the structural features of the novolac *versus* poly(vinyl phenol) blends are not obvious. For this reason, we have included in our study of thermal transitions of blends containing higher amounts of phenolic groups in hopes that the various transitions, T_g and T_m, provide some insight to the states of mixing of the different blends.

The differential scanning calorimetry heating scans of Nylon 6 blended with 5 phr of LPVPH displayed a glass transition at 50°C, which was 3°C higher than that of Nylon 6. A cold crystallization exotherm appeared at 76°C, followed by a melting endotherm peak at 222°C. As the blend ratio increased to 20 phr, the T_g increased by 13°C compared with Nylon 6, but the melting point remained almost the same. In comparing the T_g values of the LPVPh and copolymer blends, the values are the same at 5 phr (i.e., 50°C). At 20 phr, however, the T_g of the LPVPh blend is 4°C higher, at 60°C. Blending with the copolymer also did not change the melting temperature of Nylon 6.

Although *p*-Cl-novolac has a lower T_g than that of LPVPh, it enhanced the T_g of the blend most effectively at 5 phr, from 47°C to 55°C. However, the increase in T_g did not continue with additional *p*-Cl-novolac. The melting temperatures of the *p*-Cl-novolac blends were the same as that of Nylon 6. The thermal transitions of these nylon blends are compiled in Table II. It should be pointed out as a reminder that only a single T_g

was observed for each of the polymer blends investigated, indicating miscibility of Nylon 6 with these phenol-containing amorphous polymers.

DISCUSSION

Moisture Absorption

The sorption of moisture by Nylon 6 has been extensively studied.[13] A similar investigation in this area was also conducted in our laboratory, and the results showed that the amount of absorbed moisture could be markedly reduced by blending Nylon 6 with *t*-butyl-novolac.[6] It is generally believed that the amide groups in Nylon 6 are responsible for the moisture uptake. In principle, the absorbed moisture will be reduced if the amide groups in Nylon 6 are bonded to other polymers through specific interactions (e.g. hydrogen bonding interaction). Therefore, it seems reasonable that the moisture sorption of Nylon 6 can be reduced by blending with polymers that are categorized as hydrogen-bond donors.

To gain insight to the nature of the specific interaction, ^{13}C NMR experiments were devised to study the model compounds *N*-methyl acetamide and *p*-cresol representing nylon and polymers containing phenol groups, respectively. Various types of possible specific interactions could be proposed in accordance with Scheme 1.

As shown in Figure 1(a), the carbonyl carbon (C2) shifts from 170.9 ppm for *N*-methyl acetamide to 172.0 ppm for the mixture of *N*-methyl acetamide and *p*-cresol, indicating a newly formed H-bond occurring at the C=O group. In addition, the changes in chemical shifts of C1 and C3 [Figure 1(b)] rule out, as a significant factor, the possibilities of (b) and (c), in which the nitrogen atom in the amide group participates in the H-bonding formation in the mixture. From an energetic point of view, the interaction between the C=O and the phenol hydrogen results in the most stable conformation.[8]

Based on the above, the reduction in moisture uptake in the blends can be interpreted as the result of a decrease in the available amide groups of Nylon 6, which is caused by the strong interaction of phenolic groups with the free amide groups (not hydrogen-bonded to another amide moiety) of Nylon 6. Although the replacement of the already existing amide–amide by the amide–phenol interactions undoubtedly also takes place, the number of free amide groups is unaltered in the replace-

Scheme 1 Possible specific interactions between amide and phenol groups.

ment reaction. Therefore, it is believed that mechanism (a) is the most important factor in moisture reduction. However, the relationship between the degree of moisture reduction and the blend ratio is not linear. In fact, the phenol group content in excess of 5 phr does not seem to further reduce moisture absorption to any significant extent. Possibly, some amide groups are inaccessible to phenol groups for geometrical or other reasons.

We have already shown in Table I that the blends containing novolacs had a more prominent effect in reducing moisture sorption than their LPVPh counterparts. If the interpretation of NMR results is correct, then the finding suggests that the novolac resin has a more efficient interaction with the carbonyl moiety of the amide group in Nylon 6 and results in a lower moisture uptake. The more efficient reduction of moisture absorption by the copolymer, compared with LPVPh, is most likely due to the hydrophobic character of the styrene units. The result also carries the implication that only a minor amount

of vinyl phenol units suffices for the purpose of interacting with the amide groups.

In a recent paper by Murthy and coworkers,[14] it was shown that water diffuses into two distinct domains, one in the interlamellar regions inside the lamellar stack and the other outside the lamellar stack. Vergelati and colleagues[15] showed earlier that only a small amount of water was located in the interlamellar regions, in which the segments are more constrained and the remaining water molecules resided in the less constrained amorphous phase. Without further specifying whether the less constrained amorphous chains are located between lamella bundles,[16] the term amorphous phase will be used hereafter for

Figure 1 (a) ^{13}C NMR spectrum of N-methyl acetamide (bottom) and its 1 : 1 mole ratio mixture with p-cresol (top) in the C=O region. (b) ^{13}C NMR spectrum of N-methyl acetamide (bottom) and its 1 : 1 mole ratio mixture with p-cresol (top) in the C=O region.

convenience. If we follow the conclusions of Murthy and Vergelati, the reduction of water absorption by the three additives must be caused by the interaction between the phenol and amide groups in the amorphous phase of Nylon 6.

Thermal Transitions

The conclusion derived from moisture uptake studies that the novolac resin interacts more effectively than LPVPh with the carbonyl group of Nylon 6 in the amorphous phase is supported by the results of T_g measurements. At 5 phr, the novolac-containing blend has a T_g of 55°C, which is higher than that of the corresponding LPVPh blend, 50°C. The interpolymer hydrogen bonds discussed in the previous section can be regarded as physical crosslinks that raise the T_g's. At a higher blend ratio (20 phr), the T_g's of the three blends all increase, although the enhancement in T_g is only marginal for the novolac blend. The reason for the observation will be discussed in a separate paper.[7]

The next question we wish to address is whether all the additives are located in the amorphous phase at low levels of additive incorporation. The conventional thought is that some of the additives are likely to be trapped in the interlamellar region, because they are excluded by the lamella during crystallization. Because moisture absorption data suggest that the additives reside, at least to a significant extent, in the amorphous domains, we have conducted preliminary small-angle X-ray scattering studies to see whether the interlamellar spacings have changed. The details of this study will be presented in a separate paper.[7] Only the results obtained for LPVPh and novolac blends at 5 phr will be cited herein. In Table III, values are listed for the average thickness of the lamella, l_c, and that of interlamellar region, l_a, for Nylon 6 and the two 5 phr blends (Figure 2). The lamella thickness is essentially

Figure 2 Schematic representation of the amorphous and crystalline phases in a blend.

identical for the three materials. The l_a values of 58 Å for the 5 phr LPVPh blend is nearly the same as that of Nylon 6, but the small l_a value of 51 Å for the 5 phr novolac blend is surprising. (The difference is believed to be outside the range of experimental error.) We are tempted to speculate that, in the 5 phr blend, most if not all of the novolac resin resides in the amorphous phase, thereby causing a significant increase in T_g and a decrease in moisture absorption.

We have reported previously that the melting temperatures of Nylon 6 in t-butyl-novolac blends remain unchanged at low additive levels. In the present study, the melting points also did not change materially in all the blends. In the context of the Nishi–Wang equation, the interaction parameter between the two components must be quite small at T_m.[17] This is not surprising because hydrogen bonds between the two have dissociated, to a large extent, at temperatures near the melting point of Nylon 6. At ambient temperatures, however, the effect of hydrogen bonding is reflected in reduced moisture absorption and T_g.

CONCLUSIONS

Nylon 6 was blended with various amorphous polymers containing phenolic groups. Moisture absorption was effectively reduced even at a low blend ratio of 2 phr. T_g's of these blends also increased upon blending, but the melting temperatures were essentially unchanged. In comparing the three types of blends, p-Cl-novolacs showed the best results in moisture reduction and T_g

Table III   Layer Thickness by Small-Angle X-Ray Scattering of Nylon 6 and Its Blends (Å)

	l_a	l_c
Nylon 6	56	31
5 phr LPVPh	58	34
5 phr p-Cl-Novolac	51	31

l_a and l_c represent the thickness of amorphous and crystalline phases, respectively.

enhancement at low levels of incorporation than vinyl phenol homopolymer and its copolymer with styrene.

REFERENCES

1. Welgos, R. J. Encyclopedia of Polymer Science and Engineering, 2nd ed., Vol. 11; John Wiley and Sons: New York, 1988; p. 445.
2. Chiba, K. Int Polym Sci Technol 1989, 16, 25.
3. Cortazar, M.; Irvin, J. J. Br Polym J 1989, 21, 47.
4. Gittiflia, E.; Truturro, A. J Appl Polym Sci 1990, 41, 1411.
5. Zimmerman, J.; Pearce, E. M.; Miller, I. K.; Epstein, I. G.; Hosegood, E. A. J Appl Polym Sci 1973, 17, 849.
6. Huang, M. W.; Zhu, K. J.; Pearce, E. M.; Kwei, T. K. J Appl Polym Sci 1993, 48, 563.
7. Huang, P. T.; Kwei, T. K.; Groeninckx, G.; Pearce, E. M. in preparation.
8. Huang, P. T. Ph.D. Dissertation, Polytechnic University, Brooklyn, NY, 1996.
9. DeRosa, T. F.; Pearce, E. M.; Charton, M. Macromolecules 1985, 18, 2277.
10. Boyd, R. H. J Chem Phys 1959, 30, 1276.
11. Wiebusch, K.; Richter, R. J. J Mater Sci 1986, 21, 3302.
12. Kohan, M. I. Nylon Plastics; John Wiley and Sons: New York, 1973.
13. Auerbach, I.; Carnicom, M. L. J Appl Polym Sci 1991, 42, 2417.
14. Murthy, N. S.; Akkapeddi, M. K.; Orts, W. J. Macromolecules 1998, 31, 142.
15. Vergelati, C.; Imberty, A.; Perez, S. Macromolecules 1993, 26, 4420.
16. Sauer, B. B.; Hsiao, B. S. Polymer 1995, 36, 2553.
17. Nishi, T.; Wang, T. T. Macromolecules 1975, 8, 909.