

Influence of the Nigrosine Dye on the Thermal Behavior of Polyamide 66

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ABSTRACT: To reveal the effect of the nigrosine dye, that the addition of the dye lowers the crystallization point (T_c) of molten polyamide resins with substantially no shift in the melting point (T_m), thus suppressing the crystallization enhancement of the crystalline nucleation agents, the characteristics of polyamide 66 (PA-66) containing nigrosine dye EX (N-EX) were investigated. Differential scanning calorimetry (DSC) analysis showed that the addition of N-EX reduced the crystallization rate and T_c of molten PA-66 with substantially no shift in T_m and the crystallization enthalpy per unit of weight of PA-66 was substantially constant. T_c of molten PA-66 was lowered with an increase in the amount of N-EX and reached its maximum at 13 wt % N-EX. Dy-

amic mechanical analysis showed that the glass-transition temperature and the secondary glass-transition temperature increased with an increasing amount of the dye. On the other hand, the DSC and X-ray diffraction results indicated that no dye molecule was present in the crystal structure of PA-66. This effect of the nigrosine dye on PA-66 is in contrast to those of crystalline nucleation agents, plasticizers, and antiplasticizers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3270–3274, 2006

Key words: crystallization; nigrosine dye; glass transition; polyamides

INTRODUCTION

To improve the crystallization characteristics of polymers, a variety of additives have been used. Crystalline nucleation agents and plasticizers are most important. Crystalline nucleation agents accelerate the generation of the crystalline nucleus, enhancing the crystallization rate, making the crystal homogeneously fine, and increasing the crystallization point (T_c) of the molten polymer. Plasticizers enhance the polymer mobility, increasing the crystallization rate and decreasing the glass-transition temperature (T_g). On the other hand, antiplasticizers¹ are known to result in mechanical behavior opposite to that observed for plasticizers: the addition of them to polymers increases the tensile modulus and the tensile strength and decreases T_g and the secondary glass-transition temperature (T_{gg}) or eliminates T_{gg} .

Nigrosine,² which is an azine dye used as a coloring agent for polyamide resins, is known to suppress the crystalline nucleation effect.³ The addition of the dye lowers T_c of molten polyamide resins with substantially no shift in the melting point (T_m), thus suppressing the crystallization enhancement of the crystalline nucleation agents. To elucidate this nigrosine effect, we investigated the characteristics and properties of

polyamide 66 (PA-66) containing nigrosine dye EX (N-EX), observing that the addition of the dye reduced the crystallization rate and T_c of molten PA-66 and increased both T_g and T_{gg} . To the best of our knowledge, little has been reported on such a phenomenon, whereas Lin et al.⁴ reported that some metal complex acid dyes reduced T_c of molten PA-66 with substantially no decrease in T_m . They, however, mentioned nothing about the crystallization rate and T_g and T_{gg} .

This article discusses the thermal behavior of PA-66 containing N-EX on the basis of the results of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and X-ray diffraction (XRD) studies.

EXPERIMENTAL

Materials

PA-66 (Zytel 101 L, Dupont Kabushiki Kaisha, Tokyo, Japan) was purified as follows: PA-66 was dissolved in 2,2,2-trifluoroethanol, and then the solution was filtered. After the resulting solution was poured into a large volume of chloroform, the precipitate was collected by filtration, washed with methanol, and dried *in vacuo* at 50°C.

N-EX (Orient Chemical Industries Ltd., Osaka, Japan) was used without further purification. 2,2,2-Trifluoroethanol, chloroform, and methanol were purchased from commercial sources and used without further purification.

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Limiting viscosity in sulfuric acid

After pure PA-66 (100 g) was melted in a Brabender apparatus, N-EX (7.5 g) was added to it. The resulting mixture was then kneaded at 300°C under an N₂ atmosphere. The sampling was started at the end of the N-EX addition and performed at fixed intervals. On the other hand, in the case of pure PA-66 only, sampling was started at the end of the PA-66 addition to the Brabender apparatus, so the heating time of pure PA-66 was 2–3 min shorter.

The viscosities of the various concentrations of the samples in sulfuric acid were measured according to JIS K 6810-1994. The intercept of the axis of the viscosity, namely, the limiting viscosity, was obtained from plots of the viscosity versus the concentration.

DSC measurement

After the prescribed amounts of pure PA-66 and N-EX were dissolved in 2,2,2-trifluoroethanol, the solvent was removed to provide cast films. Cast films containing various amounts of N-EX obtained by the same method were dried *in vacuo* at 80°C.

The DSC analysis of the films was performed with an SDM6200 (Seiko Instruments, Inc., Tokyo, Japan). The analysis conditions were as follows.

A sample was heated at a 20°C/min rate to 300°C, held at this temperature for 3 min, and then cooled at 10°C/min to 20°C under an argon atmosphere. After this heating cycle was repeated five times, T_m and T_c of molten PA-66 and the crystallization enthalpy of molten PA-66 were determined with the arithmetic average of four data points (the second time to the fifth time). Because the first data point was considered to contain thermal hysteresis, it was omitted. The standard deviations of the T_m , T_c , and crystallization enthalpy measurements were relatively small, namely, <0.2, <0.1, and <0.4, respectively. This fact indicates that the number of heating cycles, that is, the heating time, does not affect these properties.

XRD analysis

The measuring sample sheet was obtained as follows. A cast film obtained in the same way used for DSC was charged in an aluminum mold (ca.400 μm thick). After the entire sheet was pressed at 300°C for 5 min, it was allowed to stand at room temperature. The analysis was performed with an MXP-18 [MAC Science Co., Tokyo, Japan; 18 kW, 1.54050 Å (Cu); sampling width = 0.020°; scanning speed = 4.000°/min).

DMA measurement

A sample about 200 μm thick was obtained by a method similar to that for the XRD analysis. The mea-

surement was performed with an SDM5600 (Seiko Instruments, Tokyo, Japan; tensile mode; 2.0°C/min rate from -120 to 200°C; 1 Hz).

RESULTS AND DISCUSSION

Influences of the N-EX concentration on T_m , T_c , and the crystallization rate

A typical result of the DSC analysis of PA-66 containing N-EX is shown in Figure 1. Similarly to literature reports,³ the addition of the dye drastically lowered T_c with only a slight drop in T_m . Furthermore, the exothermic peak was gradually broadened with an increase in the addition concentration. This fact indicates that the addition of N-EX reduces the crystallization rate.

The changes in T_m and T_c of molten PA-66 were examined after various amounts of N-EX were added to PA-66. Figure 2 shows plots of T_m and T_c of molten PA-66 versus the N-EX concentration. Substantially no drop in T_m was observed for the addition of a 10% concentration by weight, and furthermore, the drop was only 3° even when the N-EX addition concentration was 33.3 wt %. It is clear that the influence of the addition is very small on T_m . On the other hand, for T_c of molten PA-66, a drop of 15° was observed when the N-EX addition concentration was only 3.3 wt %. The concentration of 13 wt % gave the maximum drop (ca. 24°). In contrast to T_m , the effect of the addition is extremely significant for T_c of molten PA-66.

Thermal stability of PA-66 containing N-EX

As the cause for such a phenomenon, it was suspected that the molecular weight of the polymer was changed by the addition of N-EX. To examine the relation between the change in the molecular weight and the drop in T_c of molten PA-66, PA-66 containing 7.0% N-EX by weight and that without any additive were then compared with respect to the limiting viscosity of a sulfuric acid solution after heat treatment. Figure 3 shows the relation between the kneading time at 300°C under N₂ and the limiting viscosity. The limiting viscosities are similar to each other at every kneading time, and the changes in the limiting viscosity are very small. This result indicates that the change is negligible for the molecular weight by the degradation and condensation of the polymer during heat treatment for a relatively short time in both PA-66 containing N-EX and that without N-EX. This drop in T_c is therefore not due to the change in the molecular weight.

Crystallinity and crystal structure of PA-66 containing N-EX

Figure 4 shows the relation between the addition concentration of N-EX and the crystallization enthalpy of

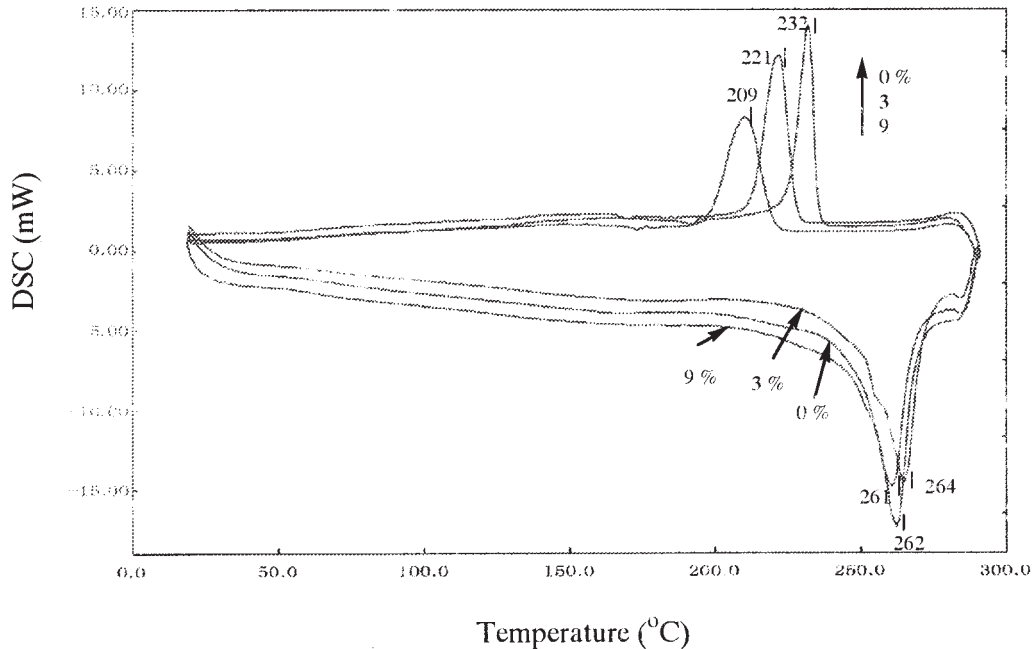


Figure 1 DSC analysis of PA-66 samples containing different amounts of N-EX.

molten PA-66. Although the crystallization enthalpy decreased with an increase in the addition concentration, the crystallization enthalpy per unit of weight of PA-66 was substantially constant over a wide range (from 0 to 50%) of N-EX addition concentrations. This result indicates that the addition of N-EX over a wide range does not change the crystallinity of PA-66; the reason for this cannot be determined at this time.

To elucidate how changes occur in the crystal structure of PA-66 with the addition of N-EX, XRD of PA-66 samples containing various amounts of N-EX was measured. PA-66 is well known to have two types (α and β forms) of crystal structures.⁵ Changes in the crystal structure were examined through a compari-

son of the peaks of the 100 plane and the 010 + 110 plane of the α form, which are the strongest reflections (Fig. 5).⁵ Substantially no shift was observed with the addition of N-EX. This result indicates that the change in the crystal structure does not occur in the presence of N-EX. This finding shows that the N-EX molecule exists not in the crystal structure but in the amorphous phase. This fact is quite consistent with the fact that the addition of N-EX does not change T_m .

On the other hand, the peak intensity ratio of the 100 plane to the 010 + 110 plane appears to widely vary. This is thought to be due to the fact that the

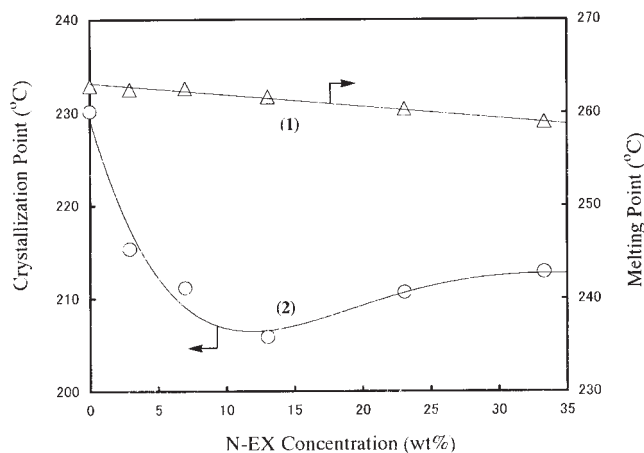


Figure 2 Plots of the N-EX concentration versus (1) T_m and (2) T_c .

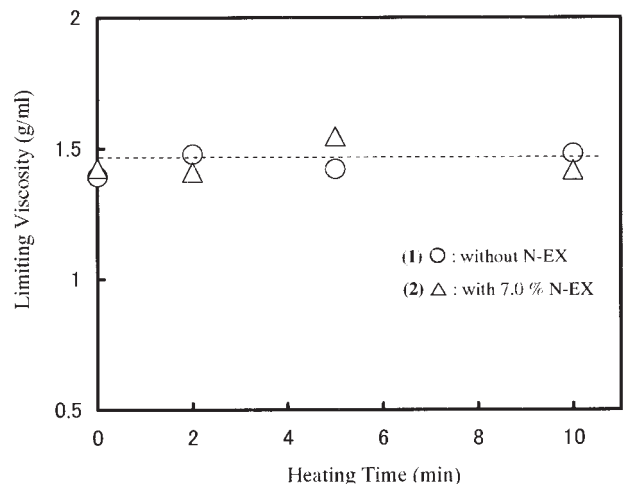


Figure 3 Plots of the kneading time at 300°C under N_2 versus the limiting viscosity of PA-66 (1) without N-EX and (2) with 7.0 wt % N-EX.

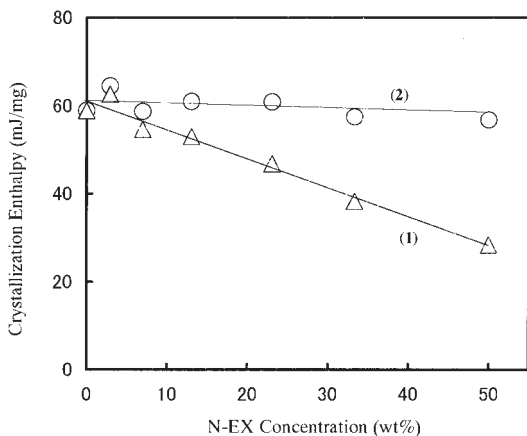


Figure 4 Plots of the addition concentration of N-EX versus (1) the crystallization enthalpy and (2) the crystallization enthalpy per unit of weight of PA-66.

degree of orientation could not be constant in all the measured sample sheets. Furthermore, it appears that the peak drops are larger than expected even for the amounts of added N-EX; that is, the crystallinity decreases with increasing amounts of N-EX. This result seems to significantly conflict with the preceding DSC result, that the addition of N-EX over a wide range does not change the crystallinity of PA-66. That such a result has been obtained is thought to be due to the fact that the amorphous part is increased during rapid cooling for the preparation of a sample sheet.

T_g and T_{gg} of PA-66 containing N-EX

T_g and T_{gg} were obtained by DMA of PA-66 containing N-EX. Figure 6 shows the relation between the N-EX concentration and T_g and T_{gg} . Both T_g and T_{gg} increase with an increase in the N-EX concentration. This fact

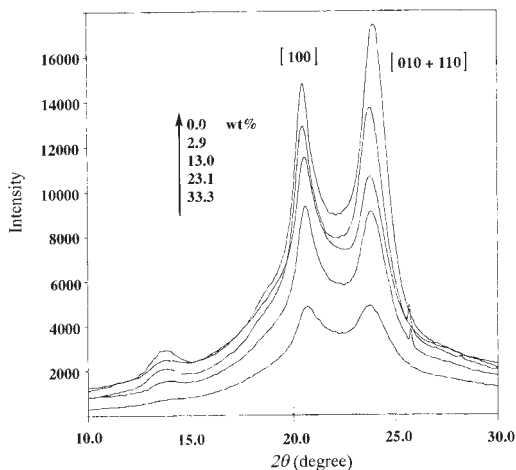


Figure 5 XRD patterns of PA-66 containing various concentrations of N-EX.

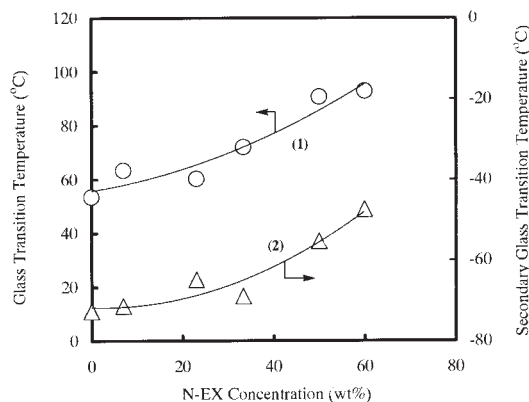


Figure 6 Plots of the N-EX concentration versus (1) T_g and (2) T_{gg} .

shows that the motion of the PA-66 polymer chain is inhibited by the addition of N-EX in the amorphous state and that the effect is increased with an increase in the addition concentration. The result, in which the addition of the dye increases T_g and T_{gg} and reduces T_c and the crystallization rate, is in contrast to those for crystalline nucleation agents, plasticizers, and antiplasticizers.

As mentioned previously, the change in the molecular weight is negligible by degradation and condensation of the polymer during heat treatment for relatively short times in both PA-66 containing N-EX and pure PA-66. Therefore, the elevation of T_g is not caused by the change in the PA-66 molecular weight. On the other hand, because an increase in crystallinity is known to elevate T_g ⁶ and in this sample sheet the amorphous phase is increased by the addition of N-EX, the lowering of T_g should be expected as N-EX increases. Contrary to expectations, however, T_g increases as N-EX increases. These results strongly suggest that the increase in T_g and T_{gg} is not caused by the change in the PA-66 property itself but is caused by the inhibition of the molecular motion of PA-66 due to a relatively large interaction between the PA-66 polymer chain and the N-EX molecule.

CONCLUSIONS

The addition of the dye reduces the crystallization rate and T_c of molten PA-66 and increases T_g and T_{gg} . This effect of nigrosine dye is in contrast to those of crystalline nucleation agents, plasticizers, and antiplasticizers.

The fact that the addition of the dye increases T_g and T_{gg} strongly suggests that there is a large interaction between the PA-66 chain and N-EX molecule, which inhibits the PA-66 molecular motion in the amorphous phase. Although the essentials of the interaction are not clear, it is easy to presume that this interaction

plays an important role in generating the unique effect of N-EX on PA-66.

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