

Dynamic Viscoelastic Behavior of Styrene-Grafted Nylon 6 Fiber

TOSHIO HAGA and HIROSHI ISHIBASHI, *Textile Research Institute of Osaka Prefecture, Izumiotsushi, Osaka, Japan*

Synopsis

Styrene-grafted nylon 6 fibers which had been prepared by the UV irradiation method were investigated by dynamic-viscoelasticity and dilatometry. It was found that nylon 6 is relaxed and polystyrene is simultaneously plasticized by nylon 6 during grafting. These phenomena are interpreted as follows. The grafting process causes nylon 6 to have a lower glass transition temperature and increases grafting frequency of polystyrene to nylon 6 by increasing the chemical junctions between the two components, so that they necessarily become more compatible.

INTRODUCTION

There are many studies¹ that discuss the mixture state of both components in binary polymer system by grafting or blending from dynamic viscoelastic behavior and glass transition temperature (T_g) by dilatometry. In many of these studies, the temperatures of dynamic loss peaks or T_g by dilatometry of both components are far away from each other, and it has been recognized that these temperatures of the system vary systematically with the ratio of both components. However, in a system such as polystyrene-nylon 6 where these temperatures of both components are near each other, shifts of them are considered to be difficult to be secured. In the present study, the authors found very interesting phenomena in dynamic viscoelastic and dilatometric behavior of styrene-grafted nylon 6 fibers which had been prepared by UV light irradiation of nylon 6 fibers in styrene methanol solution.²

In general, grafting reaction to solid polymer proceeds in a heterogeneous system, and grafting occurs only in amorphous regions of polymer substrate. Furthermore, since polystyrene homopolymer is also a by-product of the present grafting method, the styrene-grafted nylon 6 fiber obtained is practically considered to consist of unreacted nylon 6, styrene homopolymer, and truly grafted copolymer. The purpose of this paper is essentially to study the change in mixture state of each component in the amorphous region of nylon 6 fiber during the grafting process by dynamic viscoelasticity and dilatometry.

EXPERIMENTAL

Materials

Nylon 6 fiber (bright, 210 denier/24 filaments, by Unitica Ltd.) was purified by extraction with ethyl ether and ethanol in a Soxhlet apparatus for 10 hr, respectively. Commercial styrene monomer was washed with 10% sodium hydroxide and distilled water, then dried over night with anhydrous calcium chloride, and distilled under reduced pressure. First, reagent-grade methanol was dried with calcium oxide and then distilled.

Grafting Reaction²

After nylon 6 fiber (0.5 g) was absolutely dried at 70°C under reduced pressure, it was immersed in 50 ml styrene-methanol solution at a volume ratio of 30:70 within a transparent quartz testing tube (internal diameter 2.4 cm, length 15 cm). Then, the testing tube containing sample and solution was tightly closed with silicone rubber in the presence of air. Nylon 6 fiber was kept in contact with the solution within the testing tube for 1 hr in order that styrene monomer sufficiently penetrated into the fiber, and was then irradiated by UV light at 25°C at a distance of 9 cm from the light source while the testing tube being rotated with a pulley. As light source, a Japan Storage Battery 100-watt high-pressure mercury lamp H-100 was used. After the irradiation, the product was soaked several times in benzene to eliminate polystyrene homopolymer in the outside solution and on the surface of the fiber, and was extracted with the same solvent in a Soxhlet apparatus for more than 50 hr. Per cent grafting was obtained from the following equation:

$$\text{per cent grafting} = 100(W_2 - W_1)/W_1$$

where W_1 and W_2 are the weights of the fiber before and after grafting, respectively.

Apparatus and Procedure for Viscoelasticity and Dilatometry

The measurement of dynamic viscoelastic properties was done using a Vibron DDV-II (Toyo Measuring Instrument Co. Ltd.) at a frequency of 110 cps. Dilatometry was carried out using mercury. The rate of temperature increase was 0.5°C/min for the measurements of dynamic viscoelasticity and dilatometry.

RESULTS

Figure 1 shows the data on the dynamic viscoelastic properties of the original nylon 6 fiber and fibers at several grafting levels. Nylon 6 fiber shows a gradual decrease of dynamic modulus, which is unique to a crystalline polymer, while the dynamic modulus of the grafted fibers is generally lower than that of nylon 6 fiber and decreases more intensely at lower temperature with increasing grafting levels. Nylon 6 fiber has a dynamic

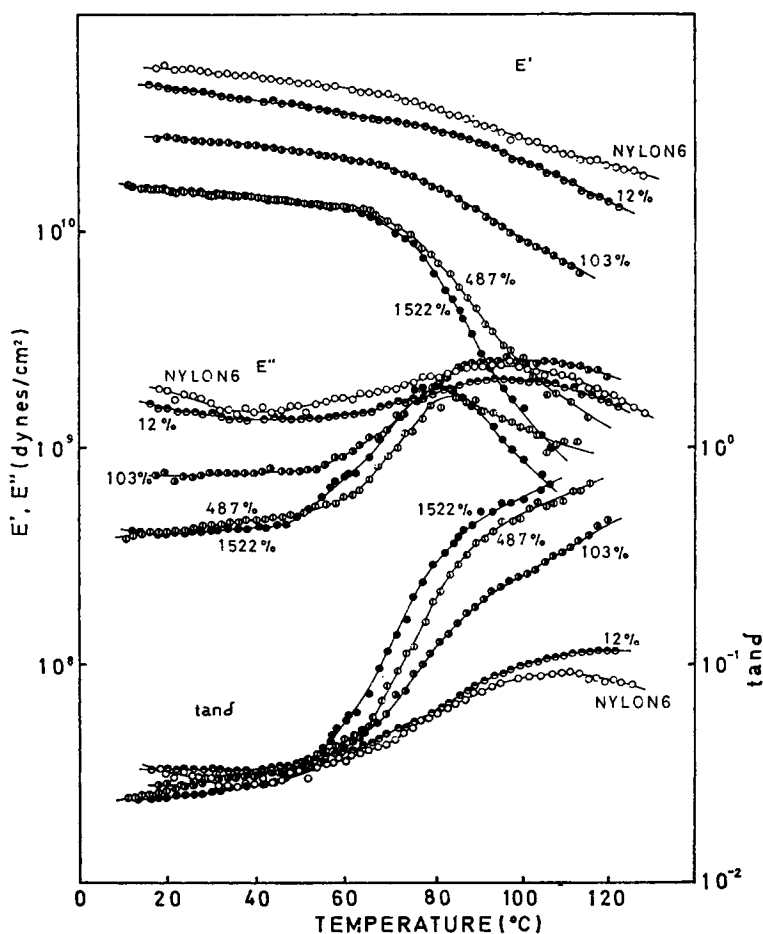


Fig. 1. Dynamic viscoelastic properties of the original nylon 6 fiber and the grafted fibers. Figures show per cent grafting.

loss peak at 96°C. In the 12% grafted fiber, a very broad peak of dynamic loss appears in the vicinity of that of nylon 6 fiber. The 103% grafted fiber has as broad a peak as the 12% grafted fiber. The 487% grafted fiber has a relatively sharp peak at 84°C. In the 1522% grafted fiber, this peak appears more sharply. These peaks of dynamic loss gradually shift to lower temperature and become stronger and narrower with the increasing grafting levels. They clearly reflect polystyrene in the grafted fiber. Concerning $\tan \delta$, the original nylon 6 fiber has a peak at 110°C, while those of the grafted fibers increase monotonously in this temperature range.

Dilatometric behavior of the original nylon 6 fiber and the grafted fibers is shown in Figure 2. The grafted fibers at 51%, 161%, 487%, and 1522% grafted levels are represented. In the case of nylon 6 fiber,

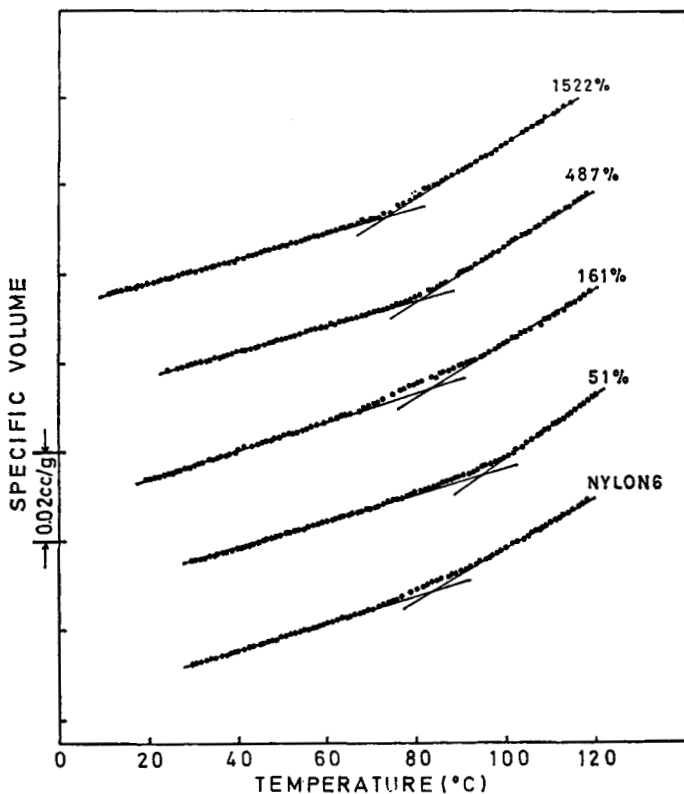


Fig. 2. Dilatometry of the original nylon 6 fiber and the grafted fibers. Figures show per cent grafting.

a bend of the expansion slope is observed from 70°C to 95°C, and 84°C is considered as T_g . This value of T_g is valid, since it is near the temperature of dynamic loss peak, 96°C, and close to the data reported in the literatures.³⁻⁶ The 51% grafted fiber gives a bend of the expansion slope from 73°C to 99°C; 95°C is considered as T_g . In the 161% grafted fiber, a similar bend is observed and 83°C is considered as T_g . In the case of larger polystyrene content, the 487% grafting level, a sharper bend of the expansion slope is observed and 81°C is considered as T_g . T_g of the 1522% grafted fiber is also clearly observed at 77°C. It is well known that T_g of polystyrene appears at about 100°C⁷⁻⁹ and that it undergoes little change according to its molecular weight¹⁰⁻¹² and its hysteresis.¹³ In order to measure the temperature of dynamic loss peak and T_g by dilatometry of polystyrene in the grafted fiber, the grafted fibers were immersed in concentrated hydrochloric acid at 98°C for more than 50 hr to remove the nylon 6 content by hydrolysis. It was ascertained by infrared spectra that the nylon 6 in the grafted fibers was completely removed by this treatment. The isolated polystyrene still retains a fibrous form, but its

strength is not great enough to be measured by Vibron DDV-II. Therefore, its dynamic viscoelasticity was measured by casting film from benzene solution without the case of the highly grafting levels, where polystyrene cannot be dissolved in benzene by crosslinking. Polystyrene from the highly grafted fibers was measured by dilatometry. Dynamic viscoelastic properties of polystyrene isolated from the 103% grafted fiber is shown in Figure 3. The temperature of dynamic loss peak is

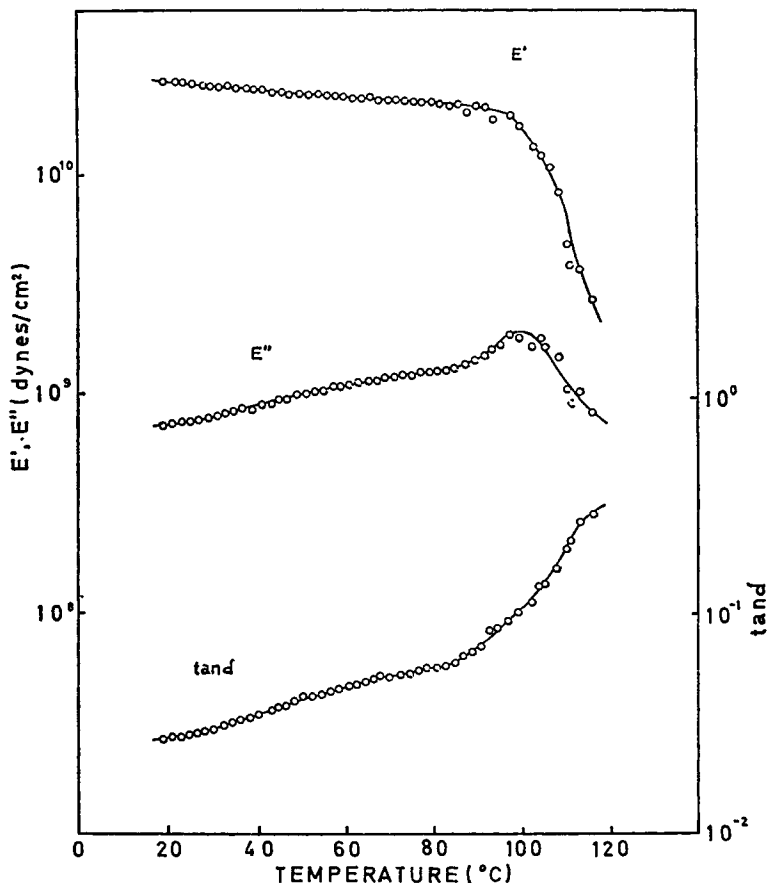


Fig. 3. Dynamic viscoelastic properties of polystyrene isolated from the 103% grafted fiber. Film cast from benzene solution.

100°C. In dilatometric results, the specific volume of polystyrene isolated from the grafted fiber remarkably decreases from about 90°C in the first heating run and it became impossible to observe T_g . However, in the second heating run, after cooling to room temperature, a definite bending of the expansion slope appeared at a higher temperature than for the grafted fiber before hydrolysis. Figure 4 shows dilatometric behavior of polystyrene isolated from the 986% grafted fiber in the second heating

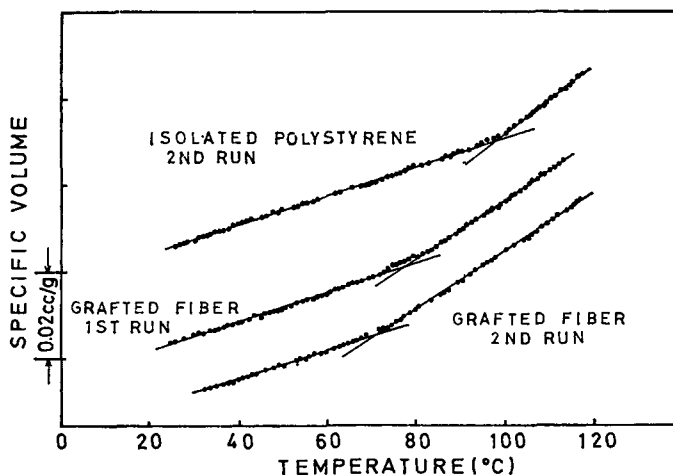


Fig. 4. Dilatometry of polystyrene isolated from the 986% grafted fiber and the original 986% grafted fiber.

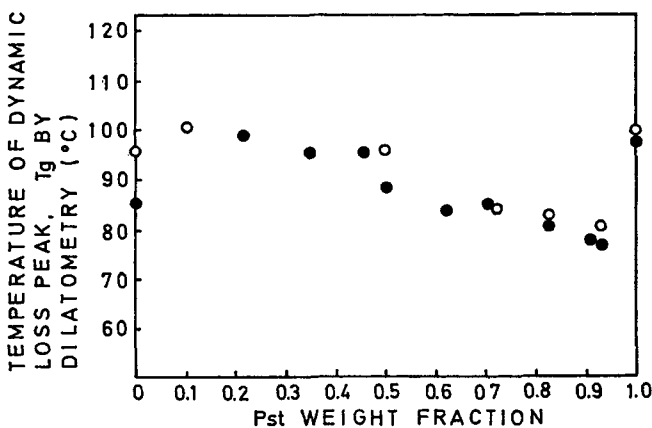


Fig. 5. Temperature of dynamic loss peak and T_g by dilatometry vs. polystyrene weight fraction in the grafted fiber: (○) temperature of dynamic loss peak; (●) T_g by dilatometry.

run, behavior of the 986% grafted fiber before hydrolysis in the first and second heating runs is also shown. In the second heating run of the isolated polystyrene, a sharp bend of expansion slope appears and 97°C is considered to be T_g . From these results, the remarkable decrease of specific volume of the isolated polystyrene in the first heating run is considered to be due to relaxation in the vicinity of T_g . The heat treatment by the first heating run gives a definite bend to the expansion slope due to T_g in the second heating run. On the other hand, the 987% grafted fiber shows T_g at 77°C in the first heating run and 72°C in the second heating

TABLE I
Temperature of Dynamic Loss Peak and T_g by Dilatometry of Polystyrene Isolated from the Fibers at Several Grafting Levels

| Grafting, % | Temp. of dynamic loss peak, °C ^a | T_g by dilatometry, °C |
|-------------|---|--------------------------|
| 103 | 96 | — |
| 261 | 96 | — |
| 587 | — | 97 |
| 986 | — | 98 |
| 1522 | — | 98 |

^a Casting film from benzene solution.

run, where T_g decrease by heat treatment. The temperature of dynamic loss peak and T_g by dilatometry of polystyrene isolated from the grafted fibers are shown in Table I. The data on polystyrene from the 103% and 261% grafted fibers are the temperatures of dynamic loss peak and those of polystyrene from the 587%, 986%, and 1522% grafted fibers are T_g by dilatometry. The results of Table I show that the temperature of dynamic loss peak and T_g by dilatometry are constant regardless of the grafting level.

From the above-mentioned results, the temperature of dynamic loss peak and T_g by dilatometry versus polystyrene weight fraction in the grafted fibers are shown in Figure 5. The results of polystyrene isolated from the grafted fiber are shown at the polystyrene weight fraction 1. The values obtained by each method correspond well with each other. They shift to lower temperature with an increasing polystyrene weight fraction in the grafted fiber. Moreover, they gradually deviated from those of polystyrene isolated from the grafted fiber.

DISCUSSION

The temperature of dynamic loss peak and T_g by dilatometry of polystyrene isolated from the grafted fiber are near to those of the original nylon 6 fiber. At the early stage of grafting, a very broad peak of dynamic loss corresponds to a mild bend of expansion slope in dilatometry. This phenomenon is considered to be due to the fact that two near peaks or bends of nylon 6 and polystyrene cannot be separated from each other and outwardly form only one very broad peak or mild bend. On the other hand, with increasing grafting level, the temperature of dynamic loss peak and T_g by dilatometry clearly shift to the lower temperature. In the higher grafting level, at a polystyrene weight fraction above 0.6, it is clear that the temperatures are lower than those of the original nylon 6 fiber and reflect increasing polystyrene content, specially as shown in dynamic loss peak (see Fig. 1). From these results, it is assumed that polystyrene in the grafted fiber is gradually plasticized by nylon 6 matrix as grafting proceeds.

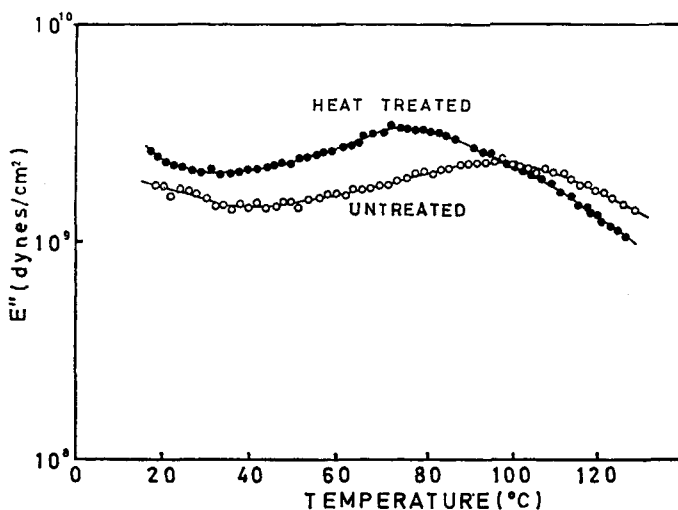


Fig. 6. Dynamic loss of nylon 6 fiber before and after heat treatment at 150°C for 2 hr in vacuo.

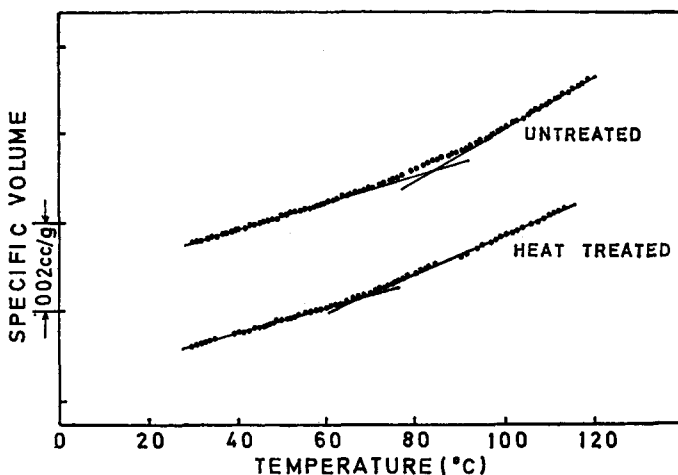


Fig. 7. Dilatometry of nylon 6 fiber before and after heat treatment at 150°C for 2 hr in vacuo.

In general, in binary polymer system, one polymer can be plasticized by another having a lower glass transition temperature when both are compatible with each other, and that of plasticized one changes between independent values of both.¹⁴ Since the temperature of dynamic loss peak and T_g by dilatometry reflecting polystyrene in the highly grafted fiber are lower than those of the original nylon 6 fiber and since polystyrene is considered to be incompatible with nylon 6, it is apparently difficult to consider that polystyrene is plasticized by nylon 6. However, as shown in Figures 6 and 7, the temperature of dynamic loss peak of nylon 6 fiber treated at

150°C for 2 hr in vacuo appears at 72°C and T_g by dilatometry at 67°C, while the corresponding values of the untreated nylon 6 fiber are 96°C and 84°C, respectively. These values of nylon 6 fiber after heat treatment are lower than those of the 1522% grafted fiber, which is the highest grafting level in this study. Accordingly, it can be assumed that nylon 6 is gradually relaxed to have lower glass transition temperature as grafting proceeds from a consideration that the grafting reaction has the same effect on nylon 6 fiber as does heat treatment. Secondly, it is probable that grafting frequency of polystyrene to nylon 6 is gradually increased as true graft copolymer increases during the grafting process. This has been verified previously.¹⁵ In consequence, as grafting proceeds, this system would necessarily be more compatible and more homogeneous with increase in chemical junctions between nylon 6 and polystyrene, although both components are originally incompatible.

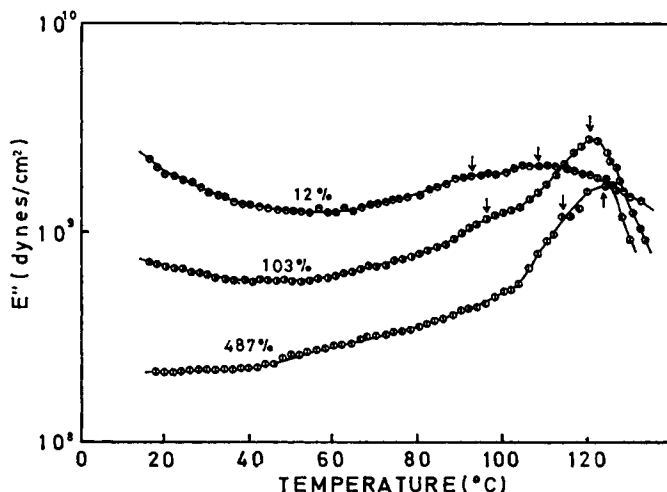


Fig. 8. Dynamic loss of the grafted fibers solvent exchanged from benzene to methanol. Figures show per cent grafting.

From the above-mentioned discussion, it can be reasonably explained that polystyrene is plasticized by nylon 6 in the grafted fiber. At the early stage of grafting, grafting frequency of polystyrene to nylon 6 would be smaller and polystyrene would be nearly phase separated from nylon 6. Therefore, in this stage, the aggregate state of polystyrene in the grafted fiber would be similar to that of polystyrene which polymerized outside the nylon 6 fiber substrate, that is to say, similar to that of polystyrene being isolated from the grafted fiber and having no effect on the nylon 6 matrix.

In order to elucidate the mixture state of nylon 6 and polystyrene in the grafted fiber from another standpoint, the 12%, 103%, and 487% grafted fibers were gradually solvent exchanged from benzene to methanol. Dynamic loss behavior of these treated fibers is shown in Figure 8. A dynamic

loss peak appears in the vicinity of 120°C in every case of them. Moreover, another peak appears in the vicinity of 96°C in the 12% and 103% grafted fibers, the magnitude of this peak in the latter being smaller than in the former. However, in the 487% grafted fiber, another independent peak does not appear, but a shoulder appears at the lower temperature side of the strong peak of 120°C.

In general, polystyrene grafted onto the fiber forms a hard granular structure by methanol, which is a poor solvent for polystyrene, so that the dynamic loss peak shifts to a higher temperature, about 120°C.¹⁶ It must follow that two independent dynamic loss peaks of nylon 6 and polystyrene appear if nylon 6 and polystyrene do not affect each other, because these peaks are fairly far away. The results of Figure 8 show that, in the highly grafted fiber, the two peaks of nylon 6 and polystyrene are difficult to separate from each other, and therefore the two components are more compatible. These results support the foregoing assumption that polystyrene is gradually plasticized by nylon 6 as grafting proceeds.

CONCLUSIONS

In general, different kinds of polymers are considered to be incompatible with each other. Nylon 6 would be completely phase separated from polystyrene without the chemical junctions created by grafting. Styrene-grafted nylon 6 fibers prepared by the UV irradiation method are a mixture consisting of the unreacted nylon 6, the entrapped polystyrene homopolymer, and the truly grafted copolymer. In this study by dynamic viscoelasticity and dilatometry, it was found that, as grafting proceeds, nylon 6 is relaxed and polystyrene in the grafted fiber is simultaneously plasticized by nylon 6. It is concluded that the grafting process causes nylon 6 to have a lower glass transition temperature by relaxation and increases grafting frequency of polystyrene unto nylon 6 to increase the truly grafted copolymer content in the mixture, so that they necessarily become more compatible.

References

1. T. Kuroda, M. Nagasawa, and Y. Yamashita, *Syntheses and Physical Properties of Copolymers*, Kagaku Zokan, 27, Kagaku Dojin, Kyoto, 1967.
2. H. Ishibashi, *Kobunshi Kagaku*, **23**, 620 (1966).
3. E. Nagai, *Kobunshi Kagaku*, **8**, 407 (1951).
4. R. Yamada and R. Stein, *J. Appl. Phys.*, **36**, 10, 300 (1965).
5. J. Seki, *Sen-i Gakkaishi*, **25**, 151 (1969).
6. T. Shibusawa and T. Iijima, *J. Appl. Polym. Sci.*, **14**, 1553 (1970).
7. R. Wall, J. Sauer, and A. Woodward, *J. Polym. Sci.*, **35**, 281 (1951).
8. S. Newman and W. Cox, *J. Polym. Sci.*, **36**, 29 (1960).
9. T. Holt and D. Edward, *J. Appl. Chem.*, **15**, 223 (1965).
10. T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1951).
11. K. Ueberreiter and G. Kanig, *J. Colloid Sci.*, **7**, 569 (1952).
12. K. Kanamaru, I. Uematsu, and Y. Toyota, *Kogyo Kagaku Zasshi*, **55**, 610 (1952).

13. T. Hatakeyama and S. Ogawa, *Kobunshi Kagaku*, **26**, 431 (1968).
14. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962.
15. H. Ishibashi, M. Okahisa, and M. Oku, 12th Meeting of the Society of Polymer Science, Kobe, Japan, 1966.
16. T. Honjo, S. Ogawa, and H. Obata, *Bull. Text. Res. Inst.*, **No. 73**, 47 (1965).

Received September 7, 1971

Revised February 8, 1972