

Studies on the Glass Transition of Blends of Nylon-6 and Polyacrylic Acid

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Synopsis

The glass transition temperatures (T_g) of blends of polyacrylic acid (PAA)–Nylon 6 in various proportions used as membrane material in pervaporation separation of acetic acid–water and ethanol–water mixtures were determined using differential scanning calorimetry (DSC). All the samples examined showed a single T_g which lay between the T_g of Nylon 6 and PAA, indicating that complete miscibility was achieved in these polymer blends. Further evidence of complete miscibility was obtained by scanning electron microscopy (SEM) of cross sections of the blended films which showed a uniform structure. An interesting phenomenon was observed during the DSC measurements which showed a shift in T_g of the blended samples with scanning time. Infrared and thermogravimetric measurements were conducted to further investigate this phenomenon and the results were explained as the change in T_g being caused by the elimination of water molecules and the formation of anhydrides in the polyacrylic acid portion of the polymer blends.

INTRODUCTION

In previous publications from this laboratory, the synthesis of polyacrylic acid (PAA)–Nylon 6 blended membranes for the pervaporation separation of acetic acid–water^{1,2} and ethanol–water systems^{3,4} has been reported. These membranes were shown to possess high selectivity and good flux rates for these separation processes.

In an attempt to obtain an effective membrane, the components to be blended should be miscible, that is, the various components should have thermodynamic ability to be mixed at the molecular level. For proving the miscibility of the blending components one of the most useful methods is to observe the glass transitional behavior of the blends utilizing a variety of experimental techniques; results of volume dilatometry,⁵ dynamic mechanical analysis,⁶ thermal optical analysis and differential scanning calorimetry (DSC),⁷ and electron scanning microscopy have been reported. Experimental methods for establishing criteria for determining polymer–polymer miscibility have been summarized by Olabisi, Robeson, and Shaw.⁸ In this study we used DSC to measure the transition glass temperatures of the blends and scanning electron microscopy (SEM) to examine the cross-sections of the blended film.

During the process of determining the T_g , we found that the T_g of the Nylon 6 and PAA blends was variable. It increased with the time of running in DSC. Thus the research work was focused on the factors which influence the T_g of the blend.

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TABLE I
Characteristics of the Polymers and the Chemical Solvent

Chemical	State	MW	BP
Polyacrylic acid ^a	25% aq.	150,000	
Nylon 6 ^a	solid	35,000	
Formic acid ^b	90% aq.		106°C

^aPAA and Nylon 6 were obtained from Polysciences Inc., Philadelphia, Pa.

^bFormic acid was obtained from Fisher Scientific, Toronto, Ontario, Canada.

Through thermogravimetric analysis and infrared spectra measurements we found that the T_g change of Nylon 6 and PAA blends is caused primarily by dehydration of the carboxyl groups which join the PAA macromolecular chains.

EXPERIMENTAL

Reagents

The polymers and chemical solvent used in this study were obtained from commercial sources and no additional purification was used. Their characteristics are listed in Table I.

Preparation of Polymer-Blended Films

A series of Nylon 6 and PAA blends were prepared according to different weight ratios as shown in Table II. The mixtures were kept stirring for 24 h to form a homogeneous blending solution. The mixed solution was cast onto a glass plate with the aid of a Gardner casting knife to obtain a film with appropriate thickness; it was then dried in a drying oven at 60°C for 50 min. After separating the film from the glass plate they were dried at 50°C under vacuum for 7 days. The thickness of films was about 60 μm .

Differential Scanning Calorimetry Measurements (DSC)

The glass transition temperatures were measured by a Perkin-Elmer DSC-4 differential scanning calorimeter with a Perkin-Elmer thermal analysis data

TABLE II
Description of Casting Solution

No.	Nylon 6 (g)	Formic acid (g)	25% PAA aq. (g)	Nylon 6 : PAA (weight ratio)
0	0	10	10	
1	0.48	12	7.7	2 : 8
2	0.60	10	5.6	3 : 7
3	1.20	15	7.2	4 : 6
4	1.20	12	4.8	5 : 5
5	1.20	10	3.2	6 : 4
6	2.40	18	4.1	7 : 3
7	2.40	18	2.4	8 : 2
8	2.40	18	0	

station model TADS-101. All the samples were initially heated from 20°C to 160°C at a heating rate of 20°C min⁻¹ followed by programmed cooling immediately after heating at the cooling rate of 320°C and min⁻¹. The sample weight was 7–10 mg. The sample was surrounded by a helium atmosphere. All glass transition temperatures were measured by the midpoint method. Because there is some annealing peak in the first running in DSC which would disturb the T_g value, we chose the data of the second running as the experimental value of T_g .

Scanning Electron Microscopy (SEM)

The morphology of the cross-section of the films for all the blends was examined by scanning electron microscopy in a JOEL Model JSM-840 SEM microscope at 25 kV acceleration voltage after 500 Å gold sputter coating.

Thermogravimetric Analysis

All the prepared films were examined by a Perkin-Elmer TGS-2 thermogravimetric analyzer Model TADS-101. The samples were surrounded by nitrogen atmosphere and initially heated from 30 to 180°C at a scanning rate of 10°C min⁻¹. The sample weight was about 6 mg.

Infrared Analysis

Infrared spectra were measured with a Perkin-Elmer Model 1330 Infrared Spectrophotometer. All the samples were cast on sodium chloride plates, then dried at 60°C under vacuum for 3 days. Before the next measurement, all the samples were heated in 160°C for 10 min in an air oven.

RESULTS AND DISCUSSION

The glass transition temperatures of all samples were determined using DSC and the results throughout the entire composition range are presented in Figure 1. As can be seen, the samples measured all showed a single T_g and the values were between those of Nylon 6 and polyacrylic acid. Figure 2 presents the relationship of the T_g and the composition of the blends.

Reasonable agreement between the experimental T_g value and calculated T_g value is indicated in Table III. The calculated T_g values were obtained by the Fox equation:⁹

$$\frac{W}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}}$$

where T_g is the glass transition temperature of the miscible blend, T_{g_1} , T_{g_2} are the glass transition temperatures of component 1 and component 2, W_1 , W_2 are the weight fractions of component 1 and component 2, respectively.

Further evidence of the miscibility was obtained by the micrographs of the cross-section surfaces of the Nylon 6- and PAA-blended films (Fig. 3). When the amplifications were (a) 2000 times PAA, (b) 9500 times, phase separation was not visible. All the micrographs showed that the blended films consisted of a uniform amorphous structure.

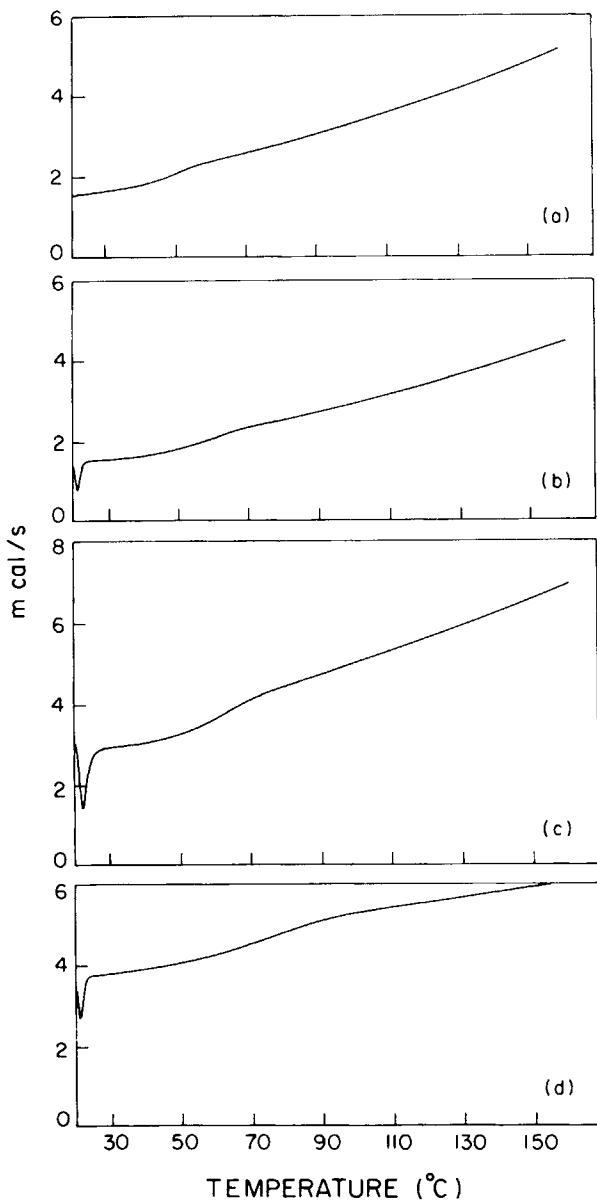


Fig. 1. Thermograms showing the single glass transition temperatures of various compositions of blends of Nylon 6 and polyacrylic acid (PAA). (a) Nylon 6: PAA = 8:2; (b) Nylon 6: PAA = 6:4; (c) Nylon 6: PAA = 4:6; (d) Nylon 6: PAA = 2:8 (weight ratio composition).

Therefore, it can be concluded from the above experimental results that under the conditions of this study the Nylon 6 and polyacrylic acid are miscible. However, an interesting phenomenon appeared during the procedure of the determination. The value of T_g shifted up as running times of the same sample increased, for example, for sample No. 1, the T_g of the second run was 70.80°C, the third run was 73.08°C, and the fourth run was 75.29°C. The T_g s of the samples at different running times are indicated in Table IV.

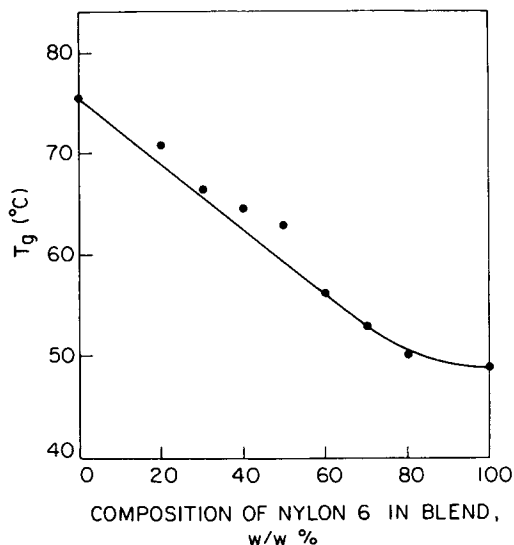


Fig. 2. Effect of blend composition on T_g for Nylon 6 and polyacrylic acid (PAA).

It is now generally recognized that the glass transition behavior represents a change in the motional freedom of main chain segments in the amorphous phase of a polymer which results in significant changes in thermal, dielectric, and mechanical responses of the macroscopic specimen. The temperature at which this change in the motional freedom occurs is affected by the very local environment of the segments. From this viewpoint, the T_g changes with the DSC running times could be viewed as caused by the structure of the blends changing under the thermal action during running in DSC.

Considering the T_g of Nylon 6 and polyacrylic acid, respectively, Gordon¹⁰ and Greco et al.¹¹ found the transition to be present in the initial heating cycle, but then disappeared in the subsequent cooling and also in an immediate rerun, it began to reappear only after a few hours rest of the samples but at a lower temperature than the initial one. Only after about a week of rest did the transition appear again at the initial temperature. On the other hand, Eisenberg and Yokoyama¹² reported the glass transition temperature of

TABLE III
Comparison of Experimental T_g and Calculated T_g

No.	Composition (wt% of Nylon 6)	Experiment T_g (°C)	Calculated T_g (°C)
0	pure PAA	76	
1	20	71	68
2	30	66	65
3	40	64	62
4	50	63	59
5	60	56	57
6	70	52	55
7	80	50	53
8	pure Nylon 6	49	

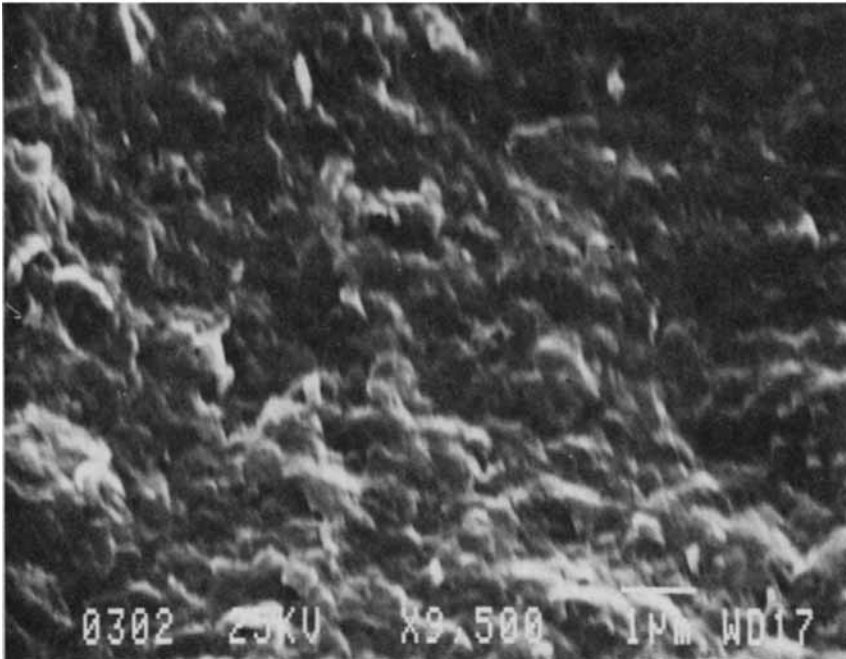
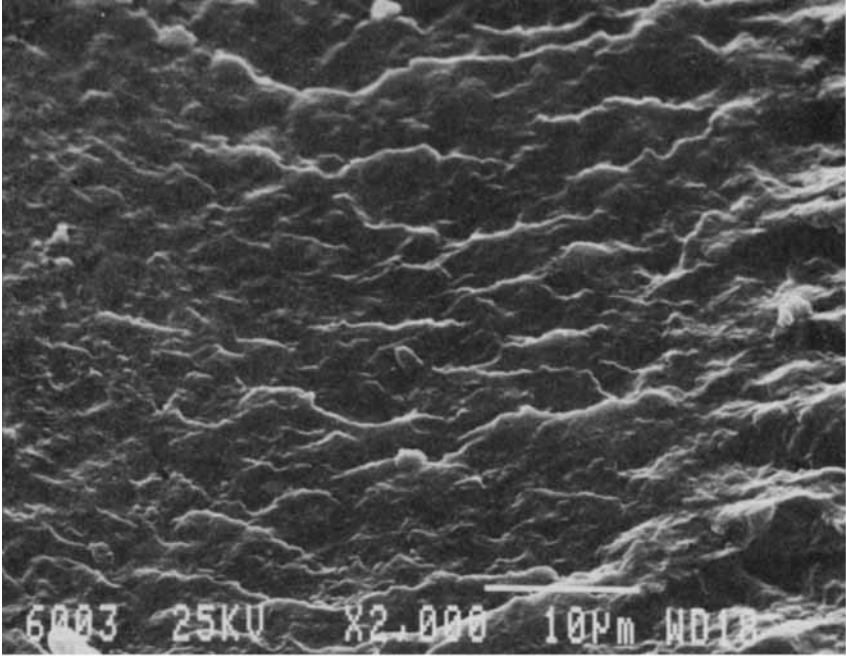


Fig. 3. Scanning electron micrographs of cross-section surfaces of Nylon 6 and polyacrylic acid (PAA) blended films. (Magnification 2000 \times and 9500 \times). (a) Nylon 6: PAA = 3:7; (b) Nylon 6: PAA = 6:4 (weight ratio composition).

TABLE IV
 T_g Data at Different Running Times

No.	Composition (wt% of Nylon 6)	T_g in R2 (°C)	T_g in R3 (°C)	T_g in R4 (°C)
0	Pure PAA	75.77	77.75	78.19
1	20	70.80	73.08	75.29
2	30	66.37	67.98	70.75
3	40	64.48	65.89	66.92
4	50	63.20	65.65	66.67
5	60	56.04	56.52	57.35
6	70	53.10	56.66	58.13
7	80	50.11	53.49	58.17

polyacrylic acid to be a function of percentage weight loss and they considered the glass transition of PAA increased with increasing anhydride concentration, which, in turn, was raised with the dehydration and/or decarboxylation by intramolecular reactions.

Combining these phenomena, the T_g increase of Nylon 6 and PAA blends conceivably could be due mainly to the dehydration of the polyacrylic acid, since in the continuous running of the blending samples in DSC, the Nylon 6 should not cause the T_g to increase.

In order to pursue this point we proceeded with the thermogravimetric analysis and infrared spectra measurements under conditions similar to the procedure of the T_g determination.

As mentioned above, Eisenberg and Yokoyama suggested that the weight loss and the changes in T_g of the PAA samples upon heating are due to the formation of the anhydride. In this study, if the T_g increase after heating was caused by the same factor, a weight loss also should be found. The plot of weight loss versus temperature obtained by thermogravimetric analysis is shown in Figure 4. We can see there was no obvious weight change below

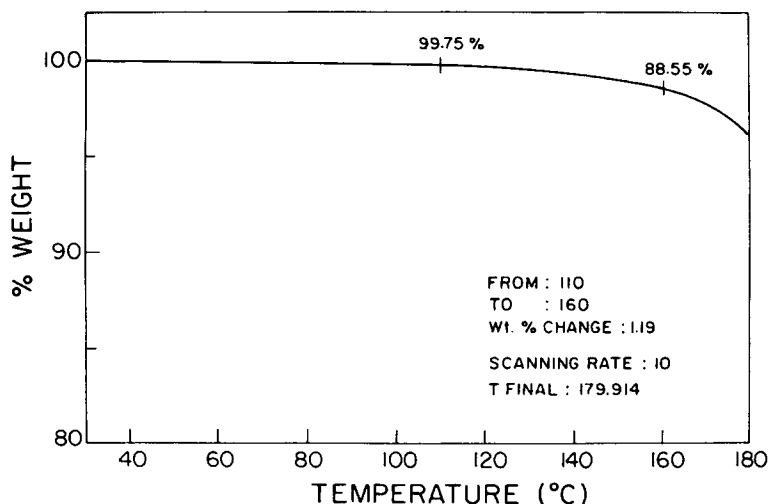


Fig. 4. Thermograms of the thermogravimetric analysis of blends of Nylon 6 and polyacrylic acid (PAA) in the weight ratio composition of 3:9.

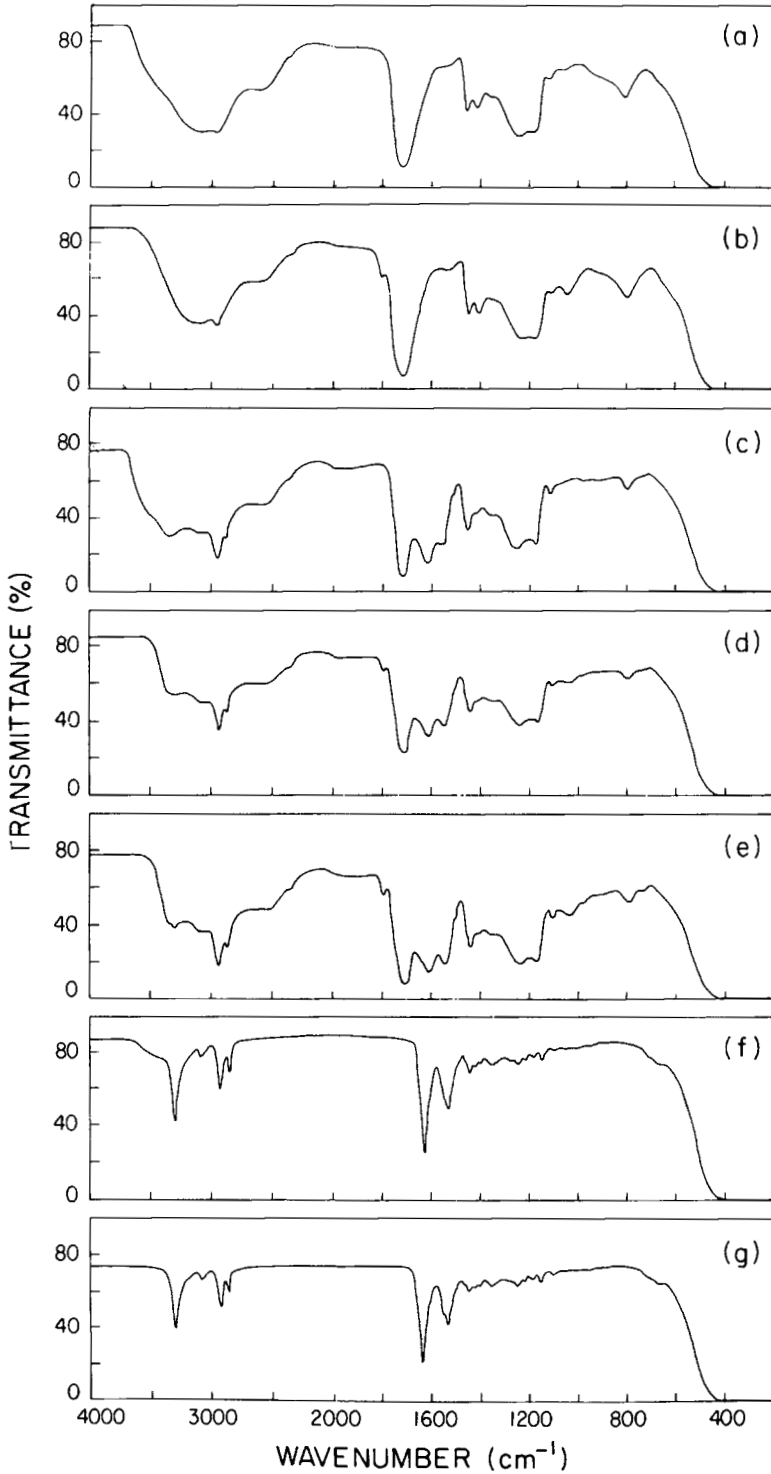


Fig. 5. Infrared spectra of (a) pure polyacrylic acid (PAA) before heating, (b) pure PAA after 10 mins heating, (c) 50% PAA and Nylon 6 blend before heating, (d) the blend after 10 mins heating, (e) the blend after 20 mins heating, (f) pure Nylon 6 during heating, (g) pure Nylon 6 after 10 mins heating.

TABLE V
Frequencies of Anhydride Bands of PAA

Sample heating temperature (°C)	Anhydride frequencies (cm ⁻¹)
150	1740–1750, 1803
200	1740–1760, 1803
250	1745–1760, 1803
300	1750–1760, 1803
350	1760, 1803

120°C, but from 120°C to 160°C there was a continuous weight loss from 0.4–1.2%. As the samples were dried sufficiently, we can consider the weight loss by heating was the result of the elimination of water between the neighboring carboxyl groups and the formation of the anhydrides on the polyacrylic acid macromolecule.

Further evidence of the formation of the anhydride was obtained from the infrared (IR) spectra measurements. All the IR spectra of the samples are shown in Figure 5. From Figure 5 we find that a new absorption band appeared at about 1800 cm⁻¹ after the samples, except for the sample of pure Nylon 6, were heated for 10 min at 160°C in the oven. The change in the infrared spectra of polyacrylic acid upon heating has been reported in the literature.¹³ Eisenberg and Yokoyama found that when the sample of PAA was heated at 155°C for 43 h, the carbonyl bands of the original PAA (1700 cm⁻¹) became weak and new bands appeared at 1750 and 1800 cm⁻¹. These new absorption bands can be assigned to the carboxylic anhydride group.

McGaugh and Kottle¹⁴ reported that after the sample of PAA was heated in air for 5 min from 25–150°C, the anhydride frequencies appeared at 1740–1760 and 1803 cm⁻¹. They studied PAA heated at different temperatures and found the anhydride frequencies shown in Table V.

All these data are consistent with our results and we also examined the IR spectra of the samples heated continuously in an interval of 10 min at 160°C in an air oven. We found the appearance of a new peak at 1800 cm⁻¹ upon heating. This indicated that the dehydration between the carboxyl groups took place each time the sample was heated. Thus, it is not unexpected that the T_g depended on the running time in DSC, since each running time corresponded to a different state of the formation of anhydride.

Comparing the IR spectra of pure Nylon 6 samples before and after heating, it is clear from Figure 5 that both absorption bands are the same; this means that the structure change of Nylon 6 did not happen after heating. There is no doubt that the T_g increase of the Nylon 6 and polyacrylic acid blend upon heating is caused by the PAA and not the Nylon 6.

CONCLUSIONS

With the aid of T_g measurements and scanning electron microscopy examination, it has been shown that blends of Nylon 6 and PAA in the entire weight ratio range are a miscible system. This indicates that, by using an appropriate method, a uniform membrane can be prepared for use in membrane separation processes.

The studies of T_g of the blends through the thermal procedure showed that when the blends were heated above 120°C, an elimination of water between the neighboring carboxyl groups occurs and the formation of the anhydrides on the polyacrylic acid macromolecules will restrict the motional freedom of the chain segments and lead to the increase of T_g . It also indicates that, under different thermal conditions, the Nylon 6 and PAA blends membrane T_g s may appear different.

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