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Effect of heat treatment on structural changes and dynamic mechanical relaxation of polyacrylonitrile fibers

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Summary

The structural changes of polyacrylonitrile fibers have been studied through the effect of heat treatment on dynamic mechanical relaxation of undrawn and drawn fibers. It is generally accepted that polyacrylonitrile has two transition temperatures. This study showed that the activation energies of the low temperature transition and the high temperature transition were about 53 and 155kcal/mole, respectively. The latter was related to the intermolecular diploe-dipole dissociation of the nitrile groups in the amorphous region and the former was related to the molecular motion in the paracrystalline region.

Introduction

Dynamic mechanical relaxation of polyacrylonitrile(PAN) fibers has been studied by various authors(1-9). It is generally accepted that PAN has two transition temperatures at 100±10℃ and 140±10℃. The interpretation of these two transition temperatures has not been entirely resolved. Andrew and Kimmel(1) explained them in the concept of a heterobonded solid-state structure and suggested that the low transition temperature was corresponded to the loosening of van der Waals bonding, while the high one resulted from the loosening of the dipole-dipole association network.

Minami(4) studied the morphological and mechanical properties of PAN fibers. He proposed a two-phase structure to explain these transitions. He attributed the lower transition to the molecular motion in the paracrystalline region and the higher one to the chain mobility in the amorphous region.

Gupta and coworkers(10-14) studied the effect of heat treatment on the dielectric relaxation of PAN powder. They reported that the heat treatment at a high temperature(160℃) resulted in a smaller number of bound nitrile groups in the structure than the heat treatment at a low temperature(120℃).

In this study, we investigated the effect of heat treatment on structural changes and dynamic mechanical relaxation of undrawn and drawn PAN fibers. The same conditions as in the works of Gupta were used for the heat treatment temperatures and the duration time. The heat treatment was carried out at two temperatures of 120℃ and 160℃ for 8 hours.

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Experimental

PAN homopolymer was prepared in the conventional way by radical polymerization of acrylonitrile(AN) in dimethylformamide(DMF) solution with azobisisobutyronirile(AIBN) as an initiator. Monomers, solvent, and initiator were purified and distilled before use. Polymerization was carried out at 60℃ for 2hr under the nitrogen atmosphere. The polymer was precipitated from DMF solution by using methanol and distilled water, filtered off and dried at 60℃ for 10hr in a vacuum oven. The intrinsic viscosity measured in DMF at 30℃ was 3.6 which corresponded to $M_w=4\times10^5$(15). The polydispersity was 2.16 as measured by Gel Permeation Chromatography(Waters 150C model).

The polymer was dissolved in DMF to give a 13wt% concentration. This solution was subjected to the dry-jet wet spinning through a spinnerette having 0.12mm diameter, with the distance of 10mm between the coagulation bath and the spinnerette. The temperature of the spinning solution at the time of extrusion was kept at 90℃. The coagulation bath contained the solution of 50wt% DMF and 50wt% distilled water at 25℃. The aqueous DMF solution served as a coagulant for the filaments emerging from the spinnerette. This filaments were removed from the coagulation bath continuously at a velocity of 16.6m/min by a rotating bobbin. The fibers were washed with distilled water and dried at 60℃ for 24hr in a vacuum oven and used as samples.

The drawn samples were prepared by stretching a fiber at 160℃ in the air. The heat treatment of PAN fibers was done at a constant temperature for 8hr in a vacuum oven. Characteristics of samples are listed in Table 1.

Table 1

Characterstics of Samples Used in This Study.

sample	draw ratio	Heat Treatment Condition		
		Temperature(℃)	Duration(hr)	Atmosphere
s-1	undrawn	untreated		
s-2	undrawn	120	8	vacuum
s-3	undrawn	160	8	vacuum
s-4	4 times	untreated		
s-5	8 times	untreated		
s-6	8 times	120	8	vacuum
s-7	8 times	120	8	vacuum

Dynamic mechanical relaxation measurements were carried out with a Rheometrics Dynamic Spectometer(RDS-7700). The storage modulus, loss modulus, and loss tangent(tanδ) were measured by testing a bundle of fibers over a temperature range from 40℃ to 170℃. The heating rate for s-1 was approximately 1℃/min at three frequencies, 10, 50, 100rad/sec. The heating rate for the other samples was approximately 3℃/min at the frequency of 100rad/sec.

The wide angle X-ray diffraction patterns of PAN fibers were obtained by using Rigaku D/Max X-ray Diffractometer.

Results and discussion

(a) Activation energy at two transition temperatures.

In this study, two peaks in the transition region were designated as α_{I} (140℃) and α_{II}(100℃). In order to estimate the activation energy of the relaxation process, tanδ of s-1 was measured at three frequencies f of 10, 50, 100rad/sec over a temperature range from 40℃ to 170℃. Transition temperatures of α_{II} and α_{I} are listed in Table 2. The ln(f) shows a good linear relationship to the reciprocal peak temperature, as shown in Figure 1. The α_{II} and the α_{I} at 1rad/sec were estimated by extrapolation. The activation energy of each relaxation process was obtained by the Arrhenius Equation(16), as indicated in Table 2.

The activation energies of α_{II} and α_{I} are about 53 and 155 kcal/mole, respectively, and these value are in good accord with the value in the literature(3).

(b) Structural changes of thermally treated PAN fibers.

The transition data for samples are summarized in Table 3. The storage modulus and loss tangent are plotted as a function of temperature.

In Figure 2, α_{I} peak of s-2(treated thermally at 120℃) is slightly decreased, while α_{I} peak of s-3(treated themally at 160℃) is drastically decresed. This phenomenon can be interpreted similarly to Gupta's works. He had studied the effect of heat treatment on the dielectric relaxation of PAN powder(10-14). He reported that owing to the segmental mobility above the glass transition temperature, possibility of nitrile groups coming in close proximity of other nitrile groups would become higher, which might result in the formation of bound nitrile group pairs through their dipole-dipole interactions. As the temperature increased, the segmental motion became active by the increased thermal energy and tended to break the bound nitrile group pairs. Thus, the heat treatment at the higher temperature(160℃)

Table 2
Transition Points for s-1
Measured at Three Frequencies.

Frequency(rad/sec)	α_{II}(K)	α_{I}(K)
10	364	412
50	372	415
100	376	417
1	353	405
Activation energy (kcal/mole)	53	155

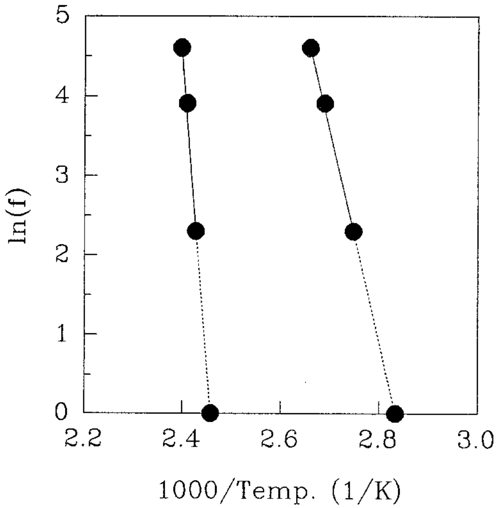

Fig.1 Plots of ln(f) vs. peak temperature

Table 3
Values of Loss Peak Temperatue(T_{max}) and Peak Height ($\tan\delta_{max}$) for Samples Measured at a Frequency of 100rad/sec.

sample	α_{II}		α_{I}	
	T_{max}(℃)	$\tan\delta_{max}$	T_{max}(℃)	$\tan\delta_{max}$
s-1	103	0.2396	144	0.2237
s-2	104	0.1900	151	0.2116
s-3	102	0.1831	149	0.1774
s-4	104	0.2118	144	0.1701
s-5	102	0.2150	-	-
s-6	94	0.2023	-	-
s-7	95	0.1990	-	-

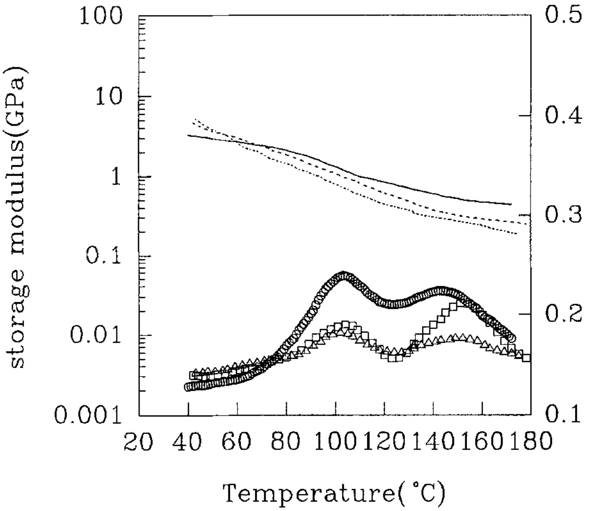

Fig.2 Effect of Temperature on the storage modulus and loss tangent for the undrawn PAN fibers treated thermally.

(——),(○):s−1;
(-------),(□):s−2;
(··········),(△):s−3.

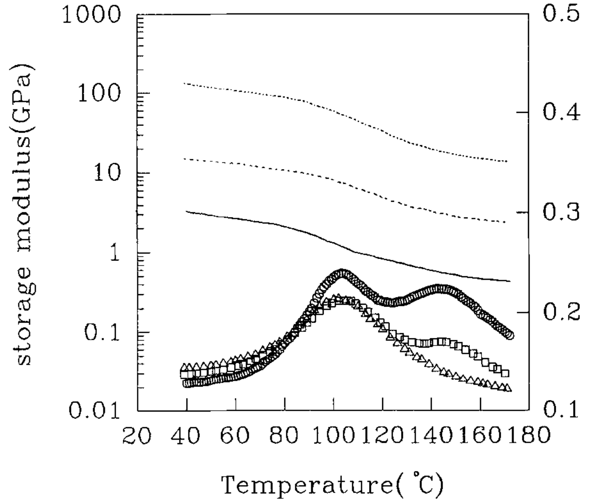

Fig.3 Effect of Temperature on the storage modulus and loss tangent for the drawn PAN fibers.

(——),(○):s−1;
(-------),(□):s−4;
(··········),(△):s−5.

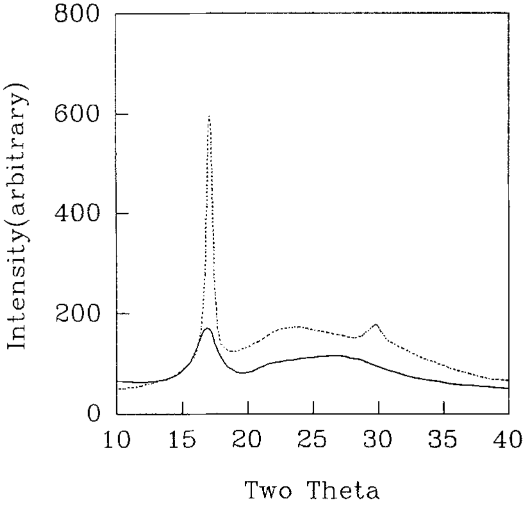

Fig.4 Wide angle X-ray diffraction patterns of the PAN fibers.
(——):s-1;
(·········):s-5.

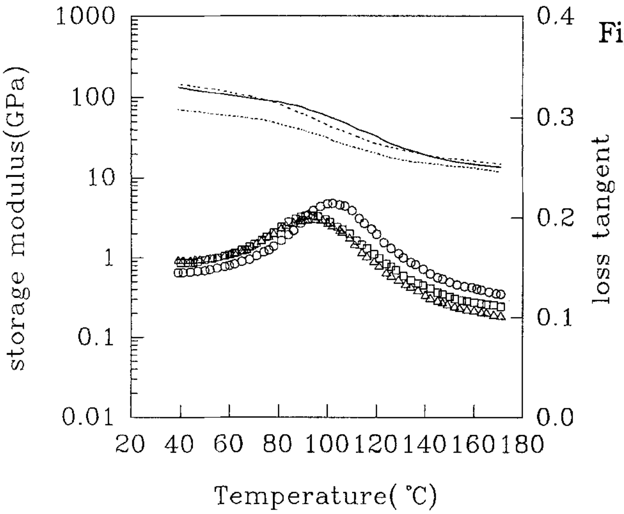

Fig.5 Effect of Temperature on the storage modulus and loss tangent for the drawn PAN fibers treated thermally.
(——),(○):s-5;
(·······),(□):s-6;
(·········),(△):s-7.

resulted in less bound nitrile groups in the structure than that at the lower temperature(120℃). Therefore, it is found from Figure 2 that α_I peak is related to the dissociation of dipole-dipole association network as Andrew suggested because the α_I peak of s-2 decreases slightly but the α_I peak of s-3 decreases drastically by the heat treatment.

In Figure 3, α_I peak decreases with increase of draw ratios, while α_{II} peak is nearly constant up to 8 times stretch. In this regard Minami suggested that α_I peak was due to the molecular motion in the amorphous region. He synthesized amorphous PAN and investigated its relaxation behavior. The amorphous PAN gave only one peak at 165℃, which implied that α_{II} peak orginated from the molecular motion in paracrystalline region.

From the above results, it is known that α_I peak results from the dipole-dipole dissociation of the nitrile groups and is affected by stretching. Thus, we propose that α_I peak is related to the intermolecular dipole-dipole dissociation of the nitrile groups in the amorphous region.

Figure 4 shows the wide angle X-ray diffraction patterns of s-1 and s-5. The peakwidth at half maximum(17) is a measure of crystallite size(i), and/or imperfections in the ordered phase(ii). In Figure 4, the undrawn fiber s-1 has a smaller crystallite size according to the Scherrer(18) line-broadening formular because it has a broader peakwidth at $2\theta=17^{\circ}$ than the drawn fiber s-5. That is, the drawn fiber has a more closely packed and perfect region. It is recognized from Figure 2 and 5 that the α_{II} peak of the undrawn fiber is much affected by the heat treatment but that of the drawn fiber very little. Thus α_{II} peak is related to the molecular motion in the paracrystalline region(ordered region) like Minami's suggestion.

Conclusion

This work shows the effect of heat treatment on structural changes and dynamic mechanical relaxation of undrawn and drawn PAN fibers. From the above results, it is concluded that : (i) The activation energies of α_{II} and α_{I} are about 53 and 155kcal/mole, respectively. (ii) The transition at the higher temperature(α_{I}) results from intermolecular dipole-dipole dissociation of the nitrile groups in the amorphous region. (iii) The transition at the lower temperature(α_{II}) is due to the molecular motion in the paracrystalline region.

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