

Effect of Thermal and Solvent Treatment on the Viscoelastic Behavior of PAN Fiber in the Glass-Rubber Transition Region

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Synopsis

PAN shows two glass transition temperatures. Study of dynamic mechanical properties, especially loss tangent, as a function of temperature enables one to study changes in these temperatures after treatment with a few selected solvents, both for the control as well as thermally treated PAN. Results show that two temperatures behave differently for treatments with different solvents. Aromatic solvents affect lower T_g whereas nonaromatic solvents increase the upper T_g preferentially. Thermomechanical analysis confirms the above results. Such behavior is explained on the basis of interaction of the solvent with two characteristic types of binding types in PAN responsible for two transition temperatures.

INTRODUCTION

Glass transition (T_g) temperature of polyacrylonitrile (PAN) has been determined by various workers using different methods.^{1-4,6} The values of T_g reported varied from 52°C to 180°C. Wiley and Brauer⁵ as well as Howard⁷ determined the value of 100% PAN by extrapolating that for PAN-butadiene or PAN-vinyl acetate copolymer. They reported values of 87° and 100°C, respectively. It has been particularly pointed out by Howard that the value of T_g depends on the initiator in polymerization reaction. Gur-Arich and Ingamells⁸ determined the value of T_g of PAN directly using the thermal expansion method both in air and water and reported these to be 90°C and 50°C, respectively. Peter and Wang¹⁵ also reported that T_g shifts down in carrier solution. Miller¹² and Hoff¹³ have observed that for polymer prepared to low degree of conversion with care to remove all traces of solvent, at the same time avoiding coloration, the value of T_g would be close to 100°C. None of these workers have found any indication of two distinct glass transition temperatures.

The existance of more than one characteristic T_g for PAN has been reported by Andrews and Kimmel.¹ They put forward the theory that solid-state PAN may be considered as a single-phase, double-bonded structure with lower temperature transition arising from interchain Van der Waal forces and a higher one involving dipole-dipole forces between polar interchain CN bonds. Some evidence of the existance of these forces has been observed in the study of associating characteristics in dilute solution.¹⁰ Saum¹¹ also has shown that association of nitriles arises from pronounced dipole-dipole interaction between two nitrile groups. He used the expression "CN dipole pair bond" to

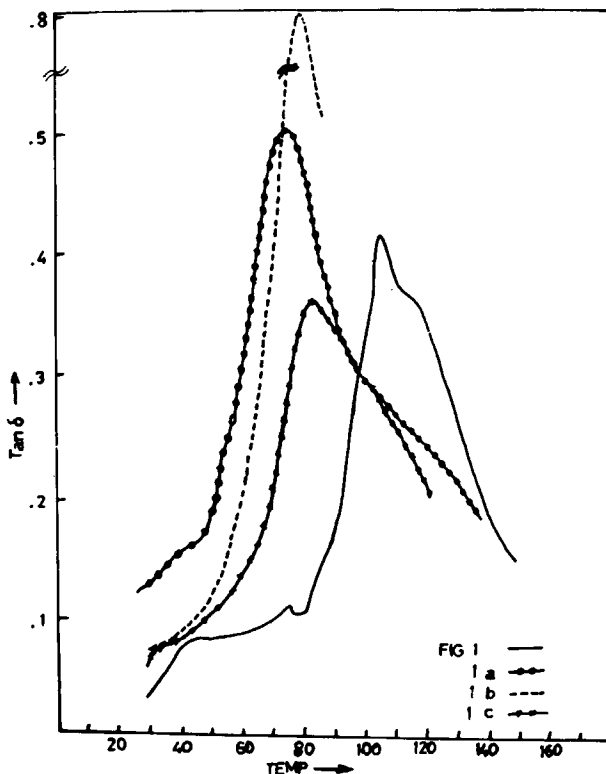


Fig. 1A. Observed $\tan \delta$ with temperature for PAN after solvent treatment. Control: treated with (a) phenol; (b) aniline; (c) resorcinol.

describe such an association and assigned the value of 8 kcal/mol to the interaction energy of such a bond. Recently Asquith and Blair,⁹ using the rheovibron, have reported two maxima in a $\tan \delta$ curve corresponding to two glass transition temperatures both in air and water. The values assigned by them are 56° and 110° for air and 56° and 84°C for water. They, however, have not offered any explanation for these maxima. Gupta and Maiti¹⁴ have only found one glass transition temperature in their dynamic mechanical study and have observed that the T_g is lowered on thermal treatment and reportedly higher crystallinity.

EXPERIMENTAL

Viscoelastic properties, as a function of temperature were measured on a Rheovibron model DDVII apparatus, in the temperature range 30–150°C and frequency of 11 Hz. The readings were taken from the meter and plotted. The graph for various samples are given in Figures 1 and 2.

Thermomechanical analysis study of some samples was carried out on a Stanton Redcroft TMA 691 apparatus. The range of temperature selected was again 30°–150°C. Weight applied on probe was 70 g and probe cross-section was 1 mm². The samples were cast in the form of thick pellets from the same fibers used earlier.¹⁶

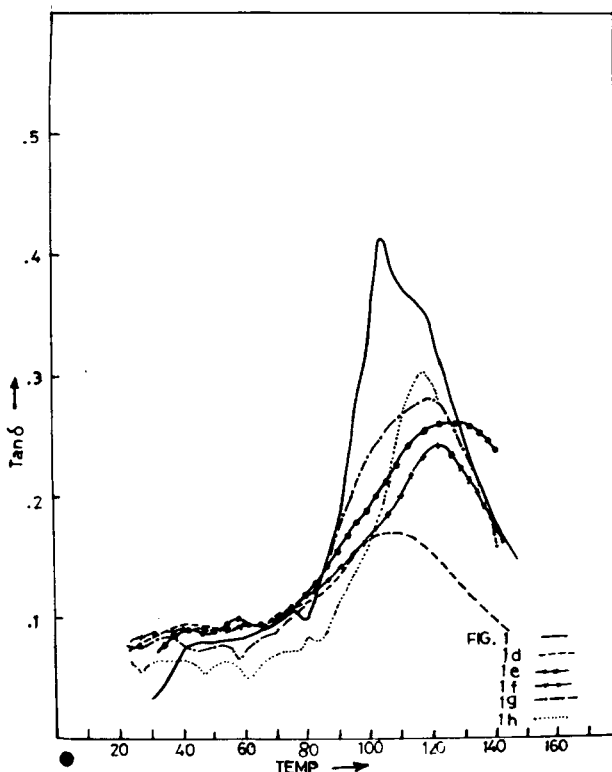


Fig. 1B. Observed $\tan \delta$ with temperature for PAN after solvent treatment. Control: treated with (d) methanol; (e) amyl amine; (f) dimethyl amine; (g) ethylene glycol; (h) acetonitrile.

Material and Solvents

PAN from Bayer Germany is used. Type characteristics as given by company of fiber are "nicht texturized, detex 133, f 488, z120". Solvents which are selected are all AR grade from SD chemicals and were used without further purification. It is a homopolymer as shown by infrared (IR) spectrum.

Heat treatment is given in an oven at 150°C for 24 h in air. Both thermally treated and control fibers were selected for solvent treatment. Solvent treatment is carried out as described by Gur-Arich and Ingamells.⁸ Following solvents were selected for study, aniline, phenol, resorcinol, methanol, amyl amine, dimethyl amine, ethylene glycol, and acetonitrile. Solvent treatment on PAN, control, and thermally treated fibers, was carried out in aqueous solutions of the above selected solvents at 95°C for 24 h. Concentration of solvents used was 1 mol in all cases. About 1 g of fiber was taken for study, keeping the liquor to fiber ratio 100 : 1. After completion of solvent treatment, PAN fibers from different solvents were taken out and solvent was allowed to drain out and the samples washed in running water. Afterward, fibers were allowed to dry completely in air at room temperature and then kept in a vacuum desiccator for 24 h thus, accomplishing complete removal of solvent. Samples were stored in a desiccator.

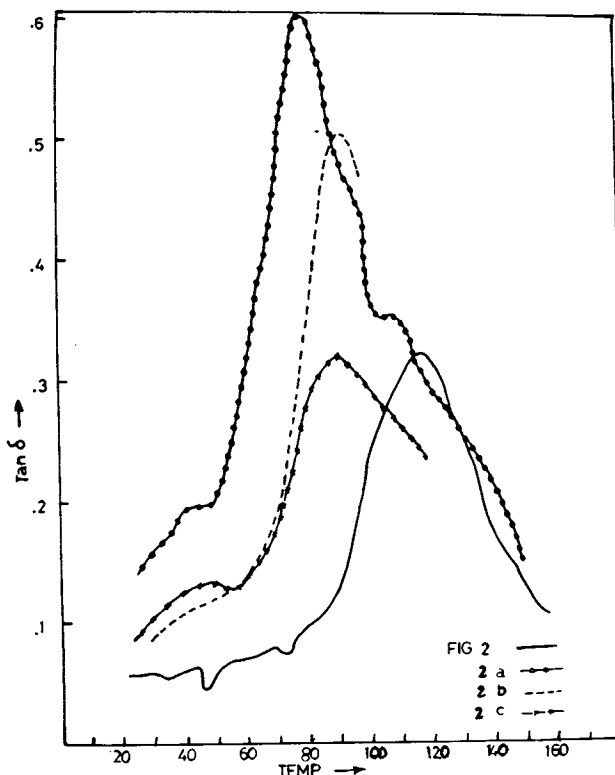


Fig. 2A. Observed $\tan \delta$ with temperature for thermally treated PAN after solvent treatment. Control (thermally treated PAN) treated with (a) phenol; (b) aniline; (c) resorcinol.

RESULTS AND DISCUSSION

Plots of $\tan \delta$ against temperatures for control PAN fiber and solvent-treated fibers are given in Figures 1 and 2. Various curves marked a-h in each figure correspond to treatment with phenol, aniline, resorcinol, methanol, amyl amine, dimethyl amine, ethylene glycol, acetonitrile, respectively. The figures also show the corresponding curves for untreated control and thermally treated control prior to any solvent treatment.

In Figure 1, the control fiber without solvent treatment shows two distinct transition temperatures, at 75° (T_1) and 104° (T_2). Thermally treated fiber shows two transition temperatures at 68° (T_1) and 112° (T_2). The observed transition temperatures for untreated and thermally treated samples are given in Tables I and II, respectively.

Observations regarding the effect of solvent treatment on two glass transition temperatures of control fiber (without thermal treatment) as observed in Figure 1 are:

1. In the aromatic solvents, lower temperature relaxation seems to disappear and higher temperature relaxation shifts to the lower temperature side with the area remaining practically unchanged.

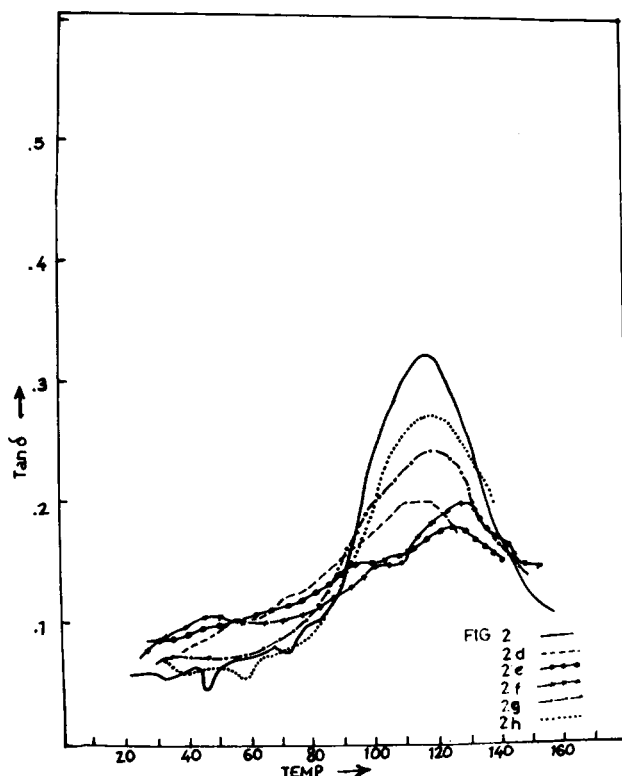


Fig. 2B. Observed $\tan \delta$ with temperature for thermally treated PAN after solvent treatment. Control (thermally treated PAN) treated with (d) methanol; (e) amyl amine; (f) dimethyl amine; (g) ethylene glycol; (h) acetonitrile.

2. In nonaromatic solvents, lower temperature relaxation is shifted to the lower temperature side, but higher temperature relaxation shifts toward the higher temperature side and the area under curve is greatly reduced.
 - A. Aromatic solvents mainly affect the bond for the excitation of relaxation motion corresponding to lower temperature. Whereas aliphatic solvents affect relaxation motion of higher temperature relaxation.

TABLE I
Transition Temperature After Solvent Treatment on Control Fiber

Solvent	T_1 (°C)	T_2 (°C)
Control	75	104
Phenol	—	74
Aniline	—	80
Resorcinol	—	82
Methanol	40	106
Amyl amine	58	125
Dimethyl amine	62	122
Ethylene glycol	38	120
Acetonitrile	40	117

TABLE II
Transition Temperature After Solvent Treatment on Thermally Treated Fiber

Solvent	T_1	T_2
Control thermally treated	68	112
Phenol	—	79
Aniline	—	85
Resorcinol	—	88
Methanol	55	115
Amyl amine	47	125
Dimethyl amine	48	128
Ethylene glycol	45	120
Acetonitrile	45	117

- B. Reduction of area of higher temperature relaxation in nonaromatic solutions and shift of the same toward higher temperature side indicates that the mobility after solvent treatment corresponding to this relaxation, as well as energy of activation, increases for the nonaromatic solvent treatment as compared to control PAN.

Aromatic solvents suppressed the lower temperature relaxation. If the lower temperature relaxation is the one related to binding due to dispersion forces, polarizability of the aromatic solvents seems to weaken the interchain dispersion binding. Higher temperature relaxation is often claimed as being due to dipole-dipole forces involving CN groups. The nonaromatic solvents seem to effect this binding in preference to the dispersion binding. The effect of dipole-dipole forces is due to dipole moment of CN bond and binding is due to two antiparallel CN configurations. In the substituted alkyl solvents, groups responsible for interaction with CN dipoles, are OH, NH₂, or CN. These groups are present in both aromatic and nonaromatic solvents. Preferential attack by nonaromatic solvents seems to be a function of accessibility. Nonaromatic alkyl solvents, being smaller in size, approach the bonded CN sites, whereas the aromatic solvents cannot do so. Even the energy of dipole-dipole interaction, which is a function of the separation of dipoles in a complex system of solid polymer, varies over a wide range. The interdipolar distance is controlled by the residual chain configuration. Lower energy dipoles with larger separation are affected by nonaromatic solvents because of both accessibility as well as energy considerations. Thus, part of the relaxation envelop on the lower temperature side is lost and gives impression that T_2 has shifted to the higher temperature side.

The lowering of dipole-dipole relaxation temperature in aromatic solvents is due to increased separation of CN-CN interacting dipoles as aromatic solvents intervene between the chains, which is shown by the loss of dispersion relaxation (T_1). Intervening solvent pushes the chains apart, thus lowering the energy of dipole interaction.

The effect of thermal treatment on the two glass transition temperatures may be understood in the light of conclusions reached above regarding the untreated sample. Thermal treatment raises the higher T_g (T_2) from 104°C to 112°C. It has been established by a number of workers that thermal annealing

of PAN brings about cyclization at the nitrile groups, which affords extended delocalized π electron conjugation resulting in thermal coloration of PAN. As such the interaction of cyclized extended segments is expected to be stronger compared to interchain CN dipole interaction. This is because, apart from the dipole moment, the partial aromatic character of π electrons give higher polarizability and hence higher Van der waal binding. In addition, the ring formation pushes the chains apart and thus the lower T_g due to dispersion forces located in nonpolar part of the chains shows a slight lowering from 75° in untreated to 68° in thermally treated control.

Subsequent solvent treatments of thermally treated samples, however, do not show any marked change in T_1 and T_2 compared to values obtained previously in cases of untreated samples. The difference in the treatment with aromatic and nonaromatic solvents is still observed for thermally treated PAN. Aromatic treated samples show a loss of lower T_g (T_1), whereas the upper T_g (T_2) is lowered and lies within 5°C of the corresponding solvent-treated samples in Table I.

Though the yellowing of the sample shows that interchain cyclization has taken place, but, as proposed in our earlier discussion, pushing apart of the chains by aromatic solvents resulting in loss of T_1 is still observed. Non-aromatic solvents also do not show much change in T_2 . Such behavior is expected, since the number of CN bonds left uncyclized are still considerable as shown by the residual CN band intensity in the infrared spectrum of the samples thermally treated as in present experiment. There are two important deductions arising from the present investigations. The variable effect on two T_g 's (T_1 and T_2) by thermal and solvent treatment has to a certain extent given experimental confirmation as to the origin of the two T_g 's.

The second important contribution of the present work is the fact that, even after thermal treatment, aromatic solvents successfully bring down the higher T_g and thus these could be effective as carriers in dyeing even after thermal-setting treatment to PAN.

Thermomechanical analysis (TMA) of the samples with the same treatments was done and the two transition temperatures observed are given in Table III. It is observed that distinctly different behavior of the polymer with

TABLE III
Transition Temperatures (°C) from Thermomechanical Analysis

Solvents	Control (untreated)		Control (thermally treated)	
	T_1	T_2	T_1	T_2
Control	65	105	60	113
Phenol	46.3	81	45	75
Aniline	43.8	75.5	49	80
Resorcinol	45	81.5	46	85
Methanol	47.5	100	52	110
Amylamine	47.5	126	45	125
Dimethylamine	53.7	119	46	121
Ethylene glycol	43.8	20	52.5	120
Acetonitrile	42.5	117.5	46	118

aromatic and nonaromatic solvents is very well confirmed even in thermo-mechanical analysis. The agreement between the values obtained in the previous method and this method is quite satisfactory. The only difference is that in TMA the lower T_g for aromatic solvents is observed to shift to lower temperature as a minute deviation in the slope, whereas it could not be observed distinctly in the $\tan \delta$ curve.

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