

Influence of Metal Ions on Structure and Properties of Acrylic Fibers

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ABSTRACT: The acrylic fibers containing 10.8 wt % of acrylic acid as a comonomer were treated with 5% aqueous solution of sulphates of alkali metals (sodium and potassium) and transition metals (cobalt and nickel) at 90°C for 5 min. The effect of this treatment on the chemical structure, thermal behavior and mechanical properties of this fiber was investigated through FTIR, X-ray, DSC, and TGA techniques. The changes in the chemical structure of the fibers have been noticed as a change in the intensity of characteristic infrared absorption bands. Broadening of the absorption band at 1700 cm⁻¹ due to COO⁻ stretch is also noticed in the case of fibers treated with salts of alkali metals, probably because of formation of a COO⁻M⁺ structure. WAXD studies of the fibers treated with metal salts showed the decrease in the crystallinity of the treated fibers. DSC curves of metalated fibers showed the onset of exothermic cyclization at a higher temperature. The initial modulus of the samples increased after this treatment. The fibers treated with sulphates of alkali metals showed an approximately twofold increase in elongation at break compared to the untreated ones. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1647–1659, 1998

Key words: metal ions; acrylic fibers

INTRODUCTION

Treatment of acrylic fibres with metal salts has generated considerable interest in producing fibers of different structure morphology coupled with specific applications. Ion exchange acrylic fibers^{1,2} have been produced by transforming the nitrile groups to carboxyl groups by alkaline or acid hydrolysis. Mechanism of hydrolysis of acrylic fibers with sodium hydroxide^{3–5} or with sodium metasilicate⁶ has been studied in detail. On the basis of infrared spectra and NMR studies,

one can draw the conclusion that the nitrile group undergoes hydrolysis through amide formation.

Microbicidal acrylic fibers^{7,8} have been produced by using dope additives like 0.1–10.0% Ag_x-H_yA_zM₂(PO₄)₃, where A = alkali metal, M = Zr, Ti, Sn; x, y, z < 1; x + y + z = 1, Ag = 1–7% in acrylonitrile - methylacrylate - Na₂ - acrylamido - 2-methyl propane sulphonate terpolymer in DMF.

The introduction of certain inorganic salts, viz., AgNO₃, HgNO₃, Cr(OCOCH₃)₃, K₂Cr₂O₇, Pb(OCOCH₃)₂, etc., into the fibers, make them suitable as bactericidal and antimicrobial fibers for air sterilization, thermostable fibers for bag filters, catalyst for carbon fiber production, and radiation-protective fibers, respectively.⁹

Electrically conductive polyacrylonitrile fibers¹⁰ have also been produced through a surface modification with nitrogen, copper, or sulphur containing compounds and reductors. Effect of inorganic salts on the thermo-oxidative stabiliza-

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tion and carbonization of acrylic precursor (acrylonitrile–itaconic acid, methyl acrylate) fibers has also been reported.¹¹ It has been demonstrated that NaCl, CuCl₂, CaCl₂, MnCl₂, AlCl₃, and Na₂SiO₄ increase the total gas evolution during oxidative degradation stage. All these salts increase the volume and surface area of the carbonized fibres and decrease the size of micro- and mesopores.

The improvement in the structural perfection and properties of the Special Acrylic Fibres (SAF), which are used as a precursor to carbon fibers, is achieved by modifying them with the salts of transition metals. Such a modification in SAF yield the carbon fibers with improved structure and properties,^{12–17} because the transition metal ion present in the fibers is believed¹⁵ to lower the energy of activation (E_a) for the reactions occurring during the thermo-oxidative stabilization. The acrylic fibers treated with the solutions of copper salt showed a substantial decrease in their E_a for stabilization process,¹⁵ and yielded the stabilized fibers with better properties.^{17,18} Ko et al.^{12,19} studied the effect of potassium permanganate into the SAF on the process of stabilization and ultimate properties of the carbon fibers obtained from these treated fibers. The effect of introduction of cobalt chloride into the SAF on their structure and properties as well as the process of their thermo-oxidative stabilization and characteristics of the resulting carbon fibers has also been investigated.¹⁶

Impregnation of alkaline earth metals into polyacrylonitrile fibers helps in increasing their hygroscopicity. Interaction of CaCl₂ with acrylic fibers and the thermal properties of calcium containing fibers has also been studied.²⁰ Interestingly, salts of alkali metals have been found to give plasticizing effect²¹ as their impregnation into acrylic fibers improves their stretchability. Lasting crimp could also be produced by treating as spun acrylic fibers with K₂SO₄, Na₂SO₄, Li₂SO₄, or LiCl followed by heating.²² The crimp has been attributed to salt induced transverse structural heterogeneity of the fiber. Treatment of PAN gel fibers with CdSO₄ solution along with ethylenediamine solution aids in twisting of the fibers with high twist stability.²³

Effect of LiCl on the dope viscosity²⁴ and AlCl₃ on gelatine²⁵ in acrylonitrile copolymer solutions and Al₂(SO₄)₃ on the rheological behavior of hydrolyzed acrylonitrile terpolymer solutions²⁶ has also been investigated. The gel formation in spinning solution has been explained by ionic cross-

linking. The impregnation of the salts into the fibers could be done at either gel state during the process of spinning or after the spinning by passing the tow of the fibers through the solutions of metal salts at about 90°C, i.e., above T_g .

In the present study, an attempt has been made to investigate the effect of introduction of the sulphates of alkali metals (sodium and potassium) and transition metals (cobalt and nickel) on structure and properties of acrylic fibers.

EXPERIMENTAL

Materials

Acrylic fibers (TF1) spun from acrylonitrile–acrylic acid copolymer containing 10.8 wt % of acrylic acid was used for this study. The fibers were wound around a frame with both of the ends fixed, and then treated with 5% aqueous solutions of sulphates of sodium, potassium, cobalt, and nickel at 90°C for 5 min. The treated samples were washed with distilled water and then dried to a constant weight in a vacuum oven at 50°C.

Measurements

IR spectra of the untreated and treated samples were recorded on a Jasco micro FTIR-100 spectrophotometer, using transmission mode.

The wide-angle diffraction pattern of the samples, which were placed in the sample holder as finely chopped fibers, was recorded on a Phillips X-ray diffractometer using nickel-filtered Cu_α radiation as the source. The crystallinity index of the samples was determined by the method suggested by Hinrichsen.²⁷ The average crystal size (L_c) and d -spacing were calculated by using eq. (1) (Scherrer equation) and eq. (2) (Bragg's equation), respectively.¹⁶

$$L_c = K\lambda B \cos \theta$$

$$\eta\lambda = 2d \sin \theta$$

where, $\lambda = 0.154$ nm, the wave length of X-ray, K is the apparatus constant (0.98), B is the half-width (in radians) of the X-ray diffraction peak and θ is the angle at which maxima of the diffraction curve appears.

DSC exotherms and TG curves of the samples were recorded under air atmosphere at a scanning rate of 10°C/min on a Perkin–Elmer Delta Series

Thermal Analyser DSC-7 module and TGA-7 module, respectively.

Thermomechanical studies were carried out on a Perkin–Elmer Delta Series, TMA-7 analyzer. A bunch of 100 filaments was suspended vertically in a heating chamber at 25 mN force. The change in the length of the fiber was recorded continuously as the temperature of heating chamber was increased at a rate of 5°C/min.

The samples were tested for their mechanical properties on an Instron 4202 tensile testing machine at a crosshead speed of 0.5 cm/min with a testing length of 5 cm. For each case, at least 15 sample filaments were tested and the average value is reported.

RESULTS AND DISCUSSION

Chemical Transformation

Figure 1 depicts the IR spectra of the fibers treated with the aqueous solutions of sodium sulphate (TF11), potassium sulphate (TF12), cobaltous sulphate (TF13), and nickel sulphate (TF14), overlaid on the IR spectrum of untreated fiber TF1. The major absorptions in the spectra are at 2920, 2240, 1728 (with shoulders at 1620 and 1562 cm^{-1}), 1458, and 1353 cm^{-1} due to the stretching of CH_2 , $\text{C}=\text{N}$, $\text{C}=\text{O}$, bending deformation of CH_2 , and rocking of CH_2 , respectively.^{28–29} Ebdon et al.³⁰ have reported that acrylonitrile units may undergo hydrolysis during polymerization by the aqueous free radical slurry method and the species so formed, i.e., acrylamide and acrylic acid, may also be polymerized with acrylonitrile units. These units show IR absorption due to $\text{C}=\text{O}$ stretching, i.e., 1730 cm^{-1} . Thus, the shoulder appeared in band at 1728 cm^{-1} (Fig. 1) may be attributed to the stretching vibrations due to the CONH_2 group.

A comparison of IR spectra of untreated and treated fibers (Fig. 1) reveals that in case of the fibers treated with alkali metal sulphates (TF11 and TF12), the IR absorption band at 1728 cm^{-1} broadens with the change in the intensity of its shoulders. However, the fibers treated with transition metal ions do not show broadening of this band but exhibited a small change in the intensity of the shoulders of this band (Table I). This indicates that alkali metal ions influence the groups absorbing IR radiation in this range (i.e., COOH , CONH_2 , and COO^-) to a greater extent than the transition metal ions, probably because of a lower

tendency of transition metal ions to replace H^+ of COOH compared to alkali metal ions. Metal ions may replace H^+ of the COOH group (Fig. 2) and, thus, the $\text{COO}^- \text{M}^+$ stretching band⁶ and may contribute to the broadening of band at 1728 cm^{-1} . The band at 1560 cm^{-1} with intensity varying from weak to medium, is assigned to the stretching of carboxyl group in salt form [Fig. 1(b) to (e)].

A change in the intensity of the band at 1120 cm^{-1} (which is attributed to the stretching of the π electron cloud as reported by Muller and Impekov²⁹) may also be seen (Fig. 1). This could be due to the distortion of the πe^- cloud by metal ions. Furthermore, this change is more pronounced in fibers treated with sulphates of transition metal ions, probably because of the smaller size and more positive charge density of these ions. Transition metal ions may attract π electrons from COOH , CONH_2 , and CN groups to establish some linkages with these groups.

IR studies of the treated samples, i.e., TF11, TF12, TF13, and TF14, suggest that the treatment of the acrylic fibers containing an acrylic acid comonomer with the sulphates of alkali metals affects their chemical structure to a greater extent compared to the ones treated with transition metal sulphates.

WAXD Studies

X-ray diffractograms of the untreated and treated fibers are shown in Figure 3. A decrease in the crystallinity of the samples treated with alkali metals is apparent (Table II), which indicates that sulphates of alkali metals disrupt the structure of the fibers. This could be attributed to the two factors viz., (1) the plasticization effect of alkali metal ions,²¹ and (2) the replacement of H^+ of the COOH groups by alkali metal ions during treatment of fibers with sulphates of alkali metals (as discussed above under the heading Chemical Transformations). During the treatment, alkali metal ions may also affect the crystalline phase in addition to amorphous phase of acrylic fibers because of their plasticization effect and also cause replacement of H^+ of COOH groups leading to their conversion into $-\text{COO}^- \text{M}^+$ structure, which may decrease the compactness of the structure, thereby causing a drop in the value of crystallinity index.

Interestingly, an increase in the crystallinity of the fibers treated with sulphates of cobalt and nickel was observed. A similar observation was also made by Ko et al.¹² when they treated the

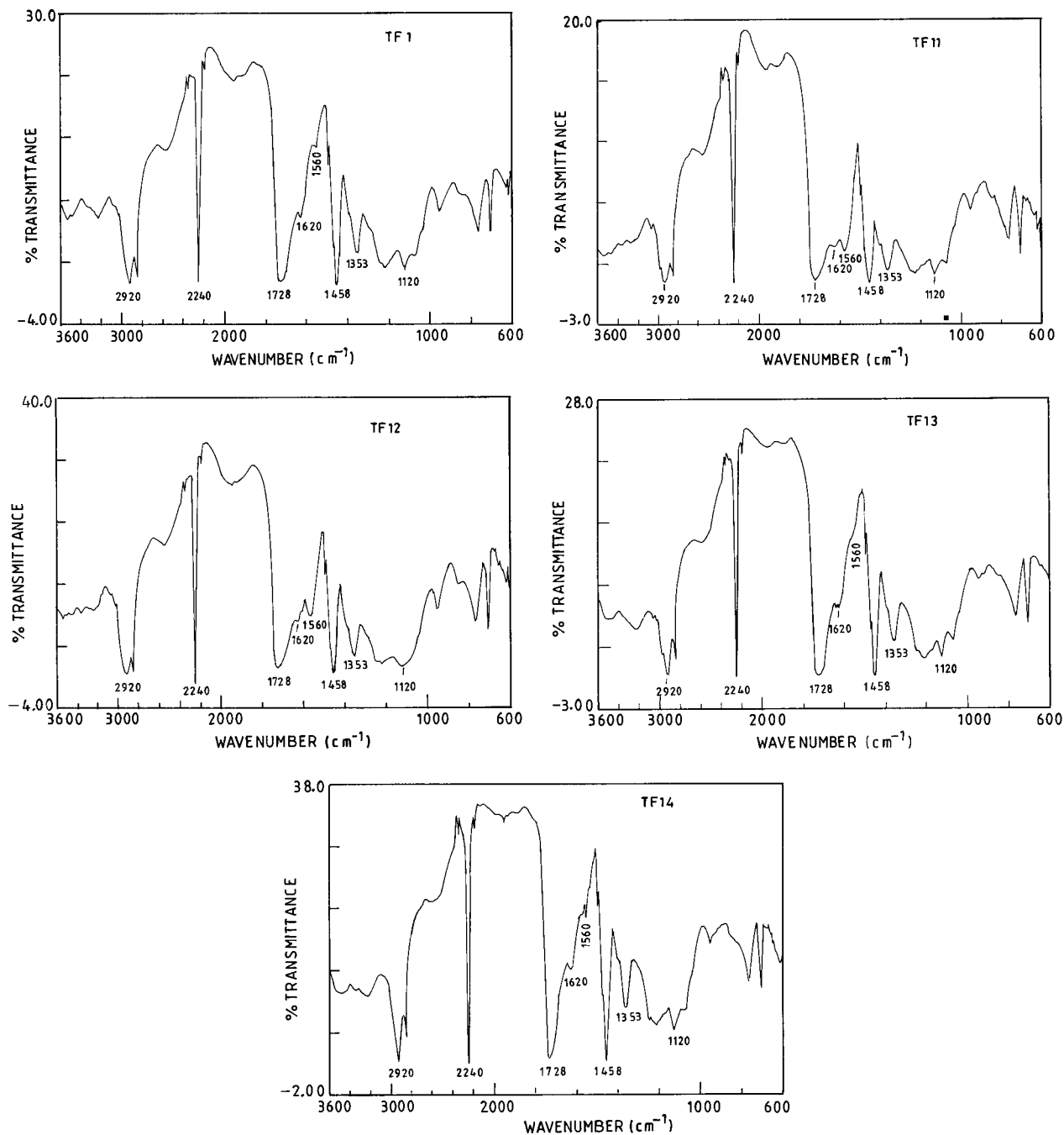


Figure 1 FTIR spectra of untreated fibers (TF1) and fibers treated with sodium sulphate (TF11), potassium sulphate (TF12), cobaltous sulphate (TF13), and nickel sulphate (TF14).

acrylic fibers with aqueous solution of potassium permanganate. An increase in the crystallinity of the fibers could be attributed to the creation of small crystallites in the amorphous phase due to the introduction of segmental mobility ($T_g = 75^\circ\text{C}$ in the presence of water²⁰), or through intermolecular crosslinks through metal ions, which may

cause orderly arrangement of some of the acrylonitrile (AN) units of the polymer chains.

Bragg spacing (d), has also shown a marginal variation for the treated samples. The change in the chemical structure of the samples as a result of the treatment, which may cause imperfection at the boundary of the crystallites and,

Table I Relative Intensities of Various IR Absorption Bands Present in Treated and Untreated Fibers

Fiber	I_{1720}/I_{2240}	I_{1620}/I_{2240}	I_{1590}/I_{2240}
TF1	0.90	0.56	0.21
TF11	0.82	0.56	0.51
TF12	0.75	0.50	0.43
TF13	0.94	0.57	0.22
TF14	0.96	0.54	0.28

thus, could result into the redistribution of the Bragg spacing.³¹

Thermal Behavior

DSC Studies

DSC curves of P(AN-AA) fibers, TF1, and the fibers treated with sulphates of alkali metals, i.e., sodium (TF11), potassium (TF12), and transition metals, i.e., cobalt (TF13) and nickel (TF14), recorded under air atmosphere at a heating rate of 10°C/min are illustrated in Figures 4 and 5, respectively. The parameters such as temperature of initiation T_i , finish T_f , peak T_{pk} , and heat

change ΔH , obtained from these exotherms are shown in Table III. DSC exotherms of fibers treated with the sulphates of sodium and potassium are narrow and initiate the cyclization reaction at higher temperature, i.e., 257 and 249°C, respectively, compared to the untreated fibers ($T_i = 211^\circ\text{C}$). Moreover, the treated fibers have exhibited lower values for ΔH (520 and 420 J/g for fibers TF11 and TF12, respectively) than untreated fibers (722 Jg^{-1}). In the case of untreated fibers, free $-\text{COOH}$ groups (of acrylic acid) are available and, thus, the exothermic reaction might have started through ionic mechanism, which starts at a lower temperature and proceeds with a slower rate,³² thereby resulting into a broader exotherm with lower value of T_i . Whereas, in the case of fibers treated with sulphates of alkali metals, H^+ of the COOH group has been replaced by Na^+ or K^+ (as the case may be), which perhaps form comparatively stronger bond with COO^- and might have hindered the initiation of exothermic reaction. Thus, it starts at a higher temperature but propagates at a higher rate like in the homopolymer as reported by Grassie and McGuchan,³² consequently showing a narrower exotherm with higher temperatures of initiation and a lower value of ΔH .

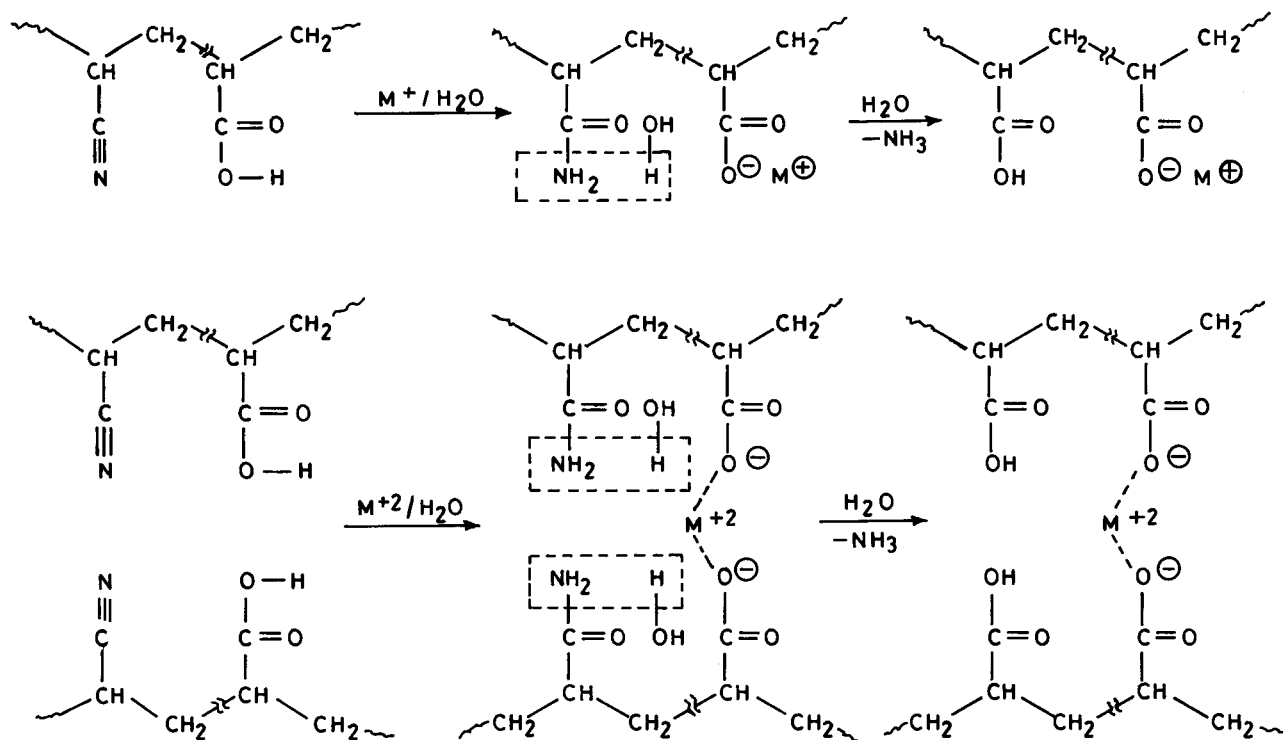


Figure 2 Reaction scheme showing chemical transformations in polyacrylonitrile fibers on treating them with aqueous solutions of the metal ions.

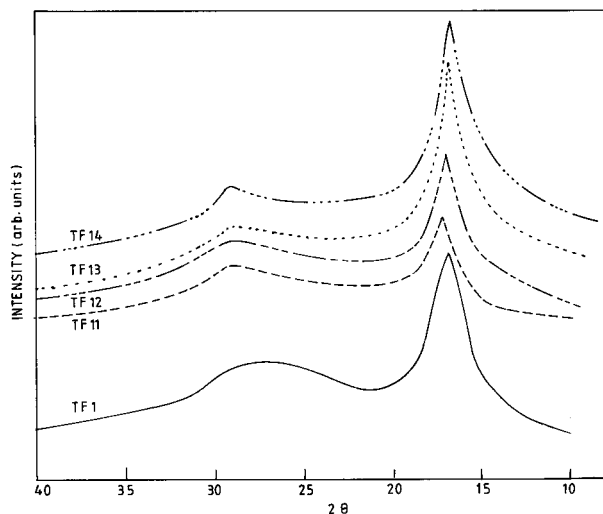


Figure 3 X-ray diffractograms of untreated fibers (TF1) and fibers treated with sodium sulphate (TF11), potassium sulphate (TF12), cobaltous sulphate (TF13), and nickel sulphate (TF14).

Interestingly, the DSC exotherms of the fibers treated with sulphates of transition metal ions showed broad peaks. It is proposed that this peak could be attributed to the interactions among CN, CONH₂, and COOH groups of polymers with metal ions as a result of the introduction of segmental mobility around this temperature range. A second peak of the exotherm may be due to the exothermic cyclization reaction. Here, also, the T_i values are higher (241 and 248°C for TF13 and TF14, respectively) than T_i value (211°C) for the DSC exotherm of untreated fibers, perhaps due to the same reason as given in the case of fibers treated with sulphates of alkali metals, i.e., replacement of H⁺ of COOH by metal ions. The values of ΔH for fibers treated with sulphates of transition metals are even lower than those of fibers treated with sulphates of alkali metals. This may be due to the ease of complex formation by transition metals with the COOH and CN groups, which participate in the exothermic cyclization reaction.

Thermogravimetric Studies

The thermogravimetric and their derivative curves of the untreated P(AN-AA) fiber TF1 and the fibers treated with sulphates of sodium (TF11), potassium (TF12), cobalt (TF13), and nickel (TF14) recorded in air atmosphere at a heating rate of 10°C/min are shown in Figures 6 and 7, respectively. The weight loss data obtained

from these curves are illustrated in Table IV. Thermal degradation of the fibers seems to be a multistep process that slowly begin at 258°C in untreated fiber TF1, with a weight loss of about 40% up to 520°C, and thereafter a rapid step of weight loss starts. The treatment of the fiber with the sulphates of alkali metals (Na⁺ and K⁺) causes differential behavior of weight loss of the fibers, as may be seen from Figure 6(b) and (c). In these cases, the weight loss starts at about same temperature as in untreated fibers [Fig. 6(a)], but appears to be slow up to 460°C with a weight loss of about 16%, followed by a rapid weight loss of approx. 23%. Within a temperature range of 40°C, i.e., between 460 to 500°C. This is followed by a comparatively slower degradation step up to 580°C, and thereafter weight loss occur rapidly.

Transition metals sulphates, i.e., Ni and Co, also appear to influence the thermal degradation of the fibers. This treatment apparently retards the rate of the first step of degradation, however, the rate of second step of degradation increases appreciably, which results into a weight loss of approx. 60% from 500 to 560°C.

The low molecular weight gaseous products such as ammonia (NH₃) and hydrogen cyanide (HCN) are supposed to be produced during the first step of thermal degradation of PAN polymers up to about 350°C.³³ NH₃ is probably produced from the terminal imine, and HCN is eliminated from the units that have not undergone cyclization, and at a temperature above 350°C, the low molecular weight species containing conjugated carbon–nitrogen sequences evolve.³³ The retardation of the first step of thermal degradation of the fibers treated with sulphates of alkali metals as well as of transition metals is probably due to the involvement of the CN groups in the complex formation with the metal ions. The rapid weight

Table II Structural Parameters of Treated and Untreated Fibers

Fiber	Crystallinity		Average Crystal ^a Size Lc (nm)
	Index	<i>d</i> -Spacing	
TF1	0.33	0.52	6.34
TF11	0.30	0.515	6.85
TF12	0.31	0.52	7.96
TF13	0.38	0.53	8.34
TF14	0.36	0.53	7.96

^a These values were calculated without using correction factor for X-ray machine.

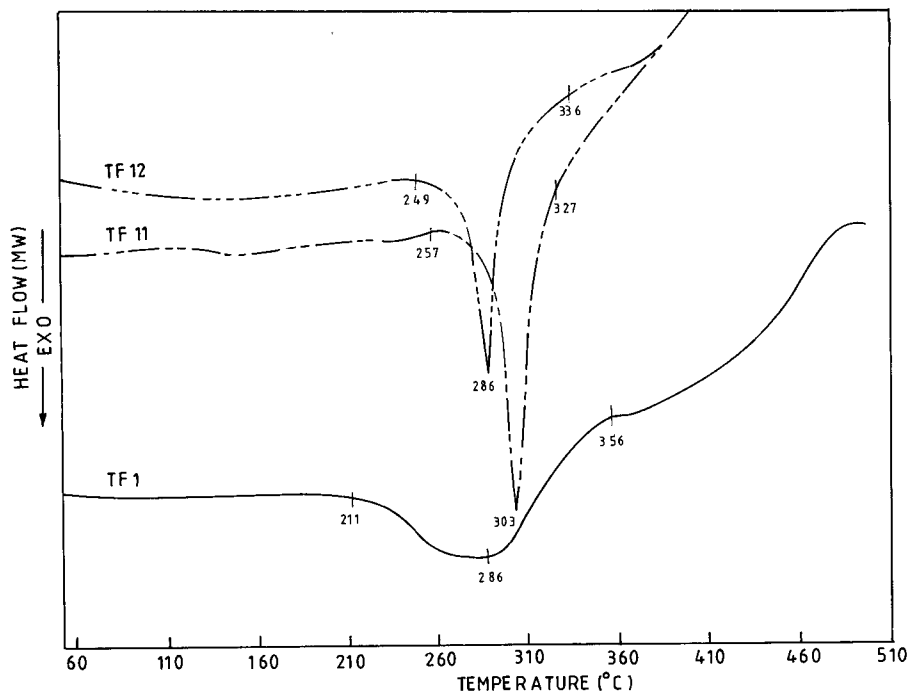


Figure 4 DSC exotherms of untreated fibers (TF1) and fibers treated with sulphates of sodium (TF11) and potassium (TF12) recorded under air atmosphere at a heating rate of 10°C/min.

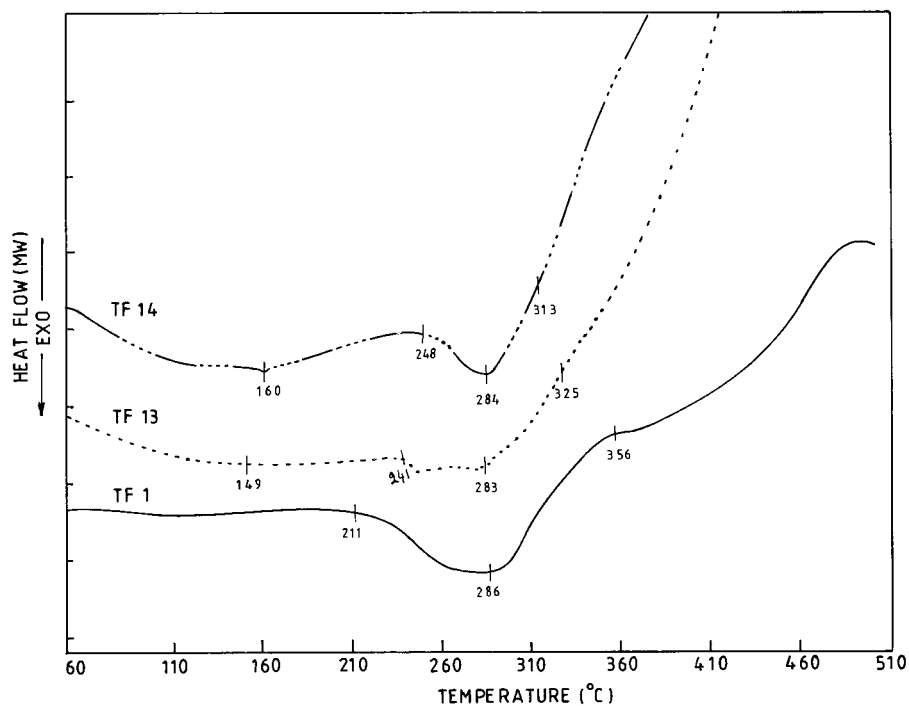


Figure 5 DSC exotherms of untreated fibers (TF1) and fibers treated with sulphates of cobalt (TF13) and nickel (TF14) recorded under air atmosphere at a heating rate of 10°C/min.

Table III DSC Parameters Obtained from DSC Exotherms of P(AN-AA) Fiber and the Fiber Treated with Sulphate of Sodium, Potassium, Cobalt, and Nickel

Sample	Ti °C	Tf °C	ΔT (Tf-Ti) °C	Tpk °C	ΔH Jg ⁻¹
TF1	211	356	145	286	722
TF11	257	327	70	303	520
TF12	249	336	87	286	420
TF13	241	325	84	282	343
TF14	248	314	66	284	241

loss in these samples at higher temperatures is apparently due to the cleavage of bonds between the —CN group and metal ions, and thus, now these so liberated —CN groups may involve in chain scission reactions leading to the formation of low molecular weight volatile species.

Thermomechanical Studies

Thermomechanical curves (Fig. 8) of the fiber TF1 and the fibers treated with sodium sulphate

(TF11) and cobalt sulphate (TF13) have shown distinct changes in the shrinkage behavior of fiber TF1 on its treatment with metal salts. The physical and chemical shrinkage (occurring due to the relaxation of stresses in the amorphous phase and cyclization of nitrile groups, respectively), which were quite distinguishable in the TMA curve of fiber TF1 but are nearly overlapping each other in the treated samples. The two types of shrinkage have overlapped to such an extent in sample TF11 that it is difficult to identify them in the TMA

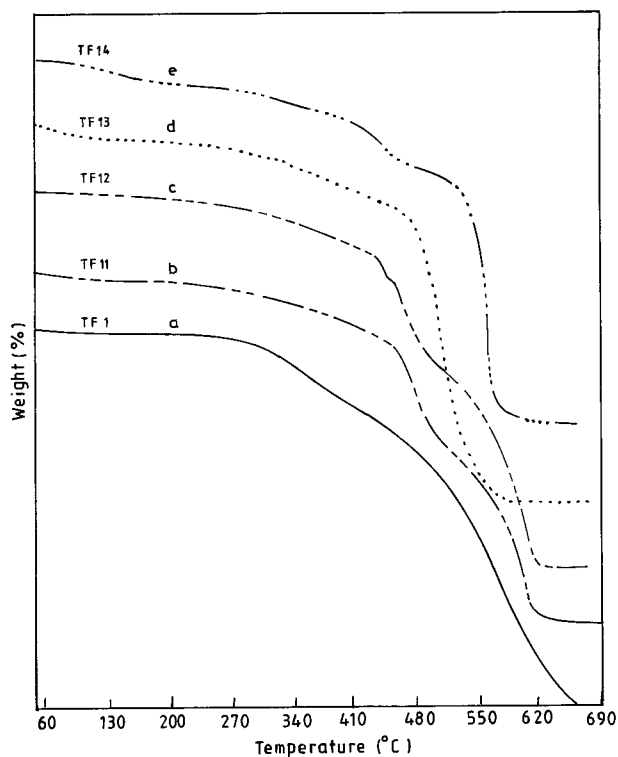


Figure 6 TG curves of untreated fibers (TF1) and fibers treated with sulphates of sodium (TF11), potassium (TF12), cobalt (TF13), and nickel (TF14), recorded under air atmosphere at a heating rate of 10°C/min.

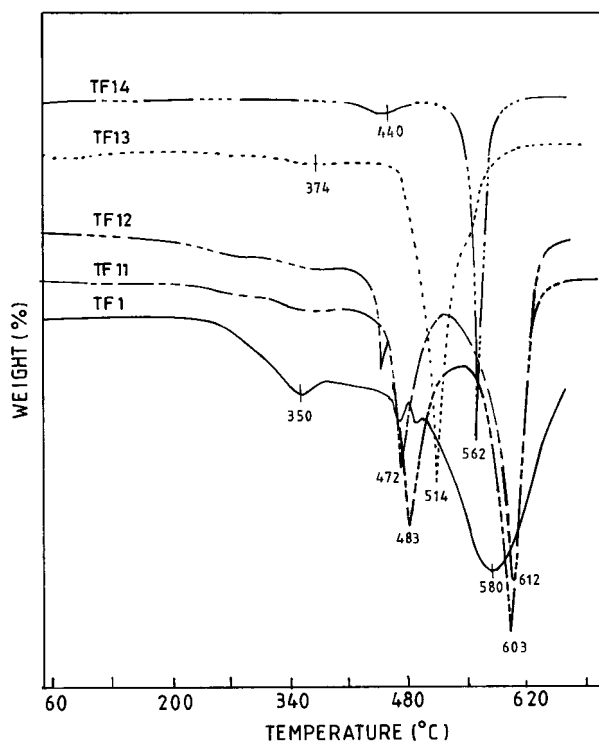


Figure 7 DTG curves of untreated fibers (TF1) and fibers treated with sulphates of sodium (TF11), potassium (TF12), cobalt (TF13), and nickel (TF14) recorded under air atmosphere at a heating rate of 10°C/min.

Table IV Weight Loss at 410°C in Air at a Heating Rate of 10°C/min

Sample	DTG Curves Maxima (°C)		Weight Loss (%) at				
	$D_{\max 1}$	$D_{\max 2}$	400°C	450°C	500°C	550°C	600°C
TF1	350	580	26.2	36.2	51.4	79.4	94.9
TF11	483	603	11.7	16.9	37.3	52.0	90.4
TF12	472	612	10.4	38.6	55.2	75.1	98.3
TF13	374	514	15.2	21.7	38.0	92.8	98.3
TF14	440	562	18.0	32.4	42.1	95.9	97.3

curve. Moreover, the physical shrinkage has decreased from 52.0% (TF1) to 46.3% (TF13) by treating the fibers with cobalt sulphate, probably because of relaxations of some stresses in the amorphous phase during the treatment itself (at 90°C in water) or formation of intermolecular crosslinks through metal ions.

Interestingly, the DMax.I (first maxima of derivative curve) has also shifted towards the higher temperature side in the treated samples (Table V). This indicates the increase in the cohesive energy density among the polymeric chains in the amorphous phase, as a result of impregna-

tion of metal ions. This could happen due to complex formation by metal ions with the polymeric substrate.

Mechanical Properties

The stress-strain behavior of fibers TF1 treated with the sulphates of alkali metals (sodium and potassium) and transition metals (cobalt and nickel) is depicted in Figures 9 and 10, respectively. There is a slight drop in the tenacity of treated fibers, but initial modulus increases, irrespective of the nature of the treatment. Treated

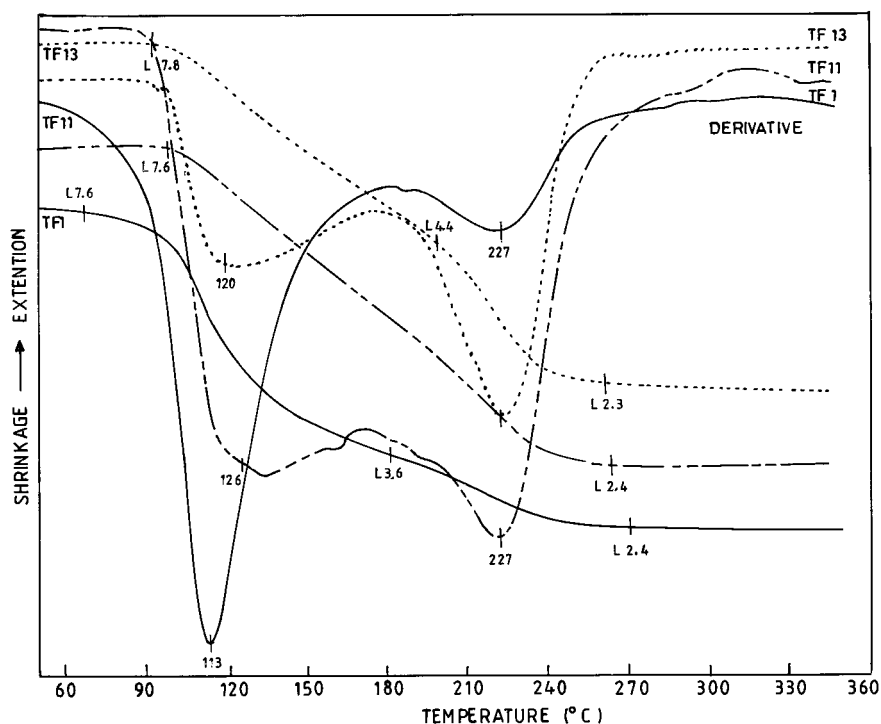


Figure 8 Thermomechanical curves of untreated fiber (TF1) and the fiber treated with sodium sulphate (TF11) and cobalt sulphate (TF13) recorded at a heating rate of 20°C/min.

Table V Parameters Obtained from Thermomechanical Curves of Untreated P(AN-AA) Fiber (TF1) and the Fibers TF1 Treated with Sodium Sulphate (TF11) and Cobalt Sulphate (TF13)

Fiber Code	Shrinkage %		Derivative Maxima	
	Physical	Chemical	Physical	Chemical
TF1	52		113	227
TF11		68.4 ^a	126	227
TF13	46.3		120	227

^a Total shrinkage, i.e., physical + chemical shrinkage.

samples also show interesting change in their deformation properties under stress. The stress-strain behavior of these samples could be explained on the basis of Rosenbaum's model,³⁴ which suggests that the initial high modulus portion of the Hookean's region could be attributed to the glassy deformation, i.e., the deformation of intermolecular bonds. Thus, the fibers with stronger intermolecular bonds may have a higher initial modulus. The second portion of recoverable strain may be due to the stretching of the helices of PAN molecules and could depend upon the nitrile group interactions.

The change in the initial modulus and elongation at break (Table VI) due to the treatment of

the fibers with the sulphates of alkali and transition metals, could be attributed to the variation in the intermolecular forces among the polymer chains as a result of the formation of new bonds. The metal ions may replace H⁺ of the COOH groups and could also undergo complex formation with nitrile groups of the polymer chains.⁹ The complex formation would lead to the creation of some additional bonds, thus causing networking of the polymer chains, which might be responsible for the increase in the initial modulus. The metal ion having a higher coordination number would

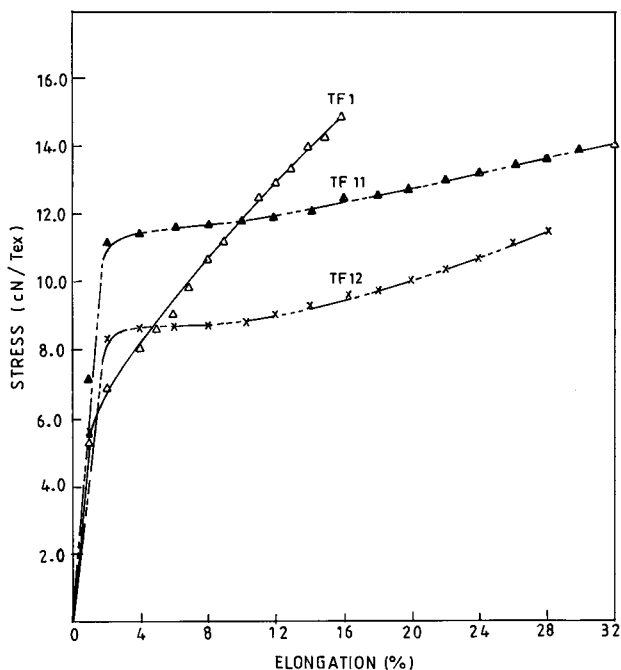


Figure 9 Stress-strain curves of the untreated fiber (TF1) and the fiber treated with sodium sulphate (TF11) and potassium sulphate (TF12).

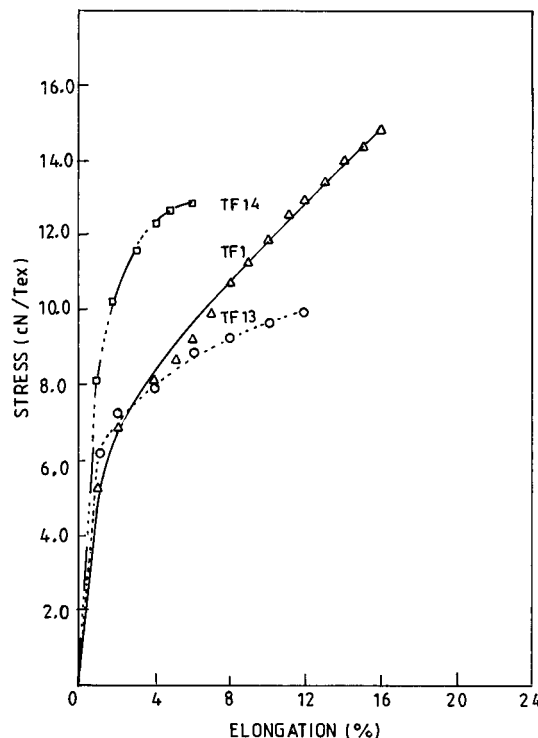


Figure 10 Stress-strain curves of the untreated fibers (TF1) and the fibers treated with cobaltous sulphate (TF11) and nickel sulphate (TF12).

Table VI Mechanical Properties of the Untreated and Treated Fibers

Fiber Code	Tenacity (MPa)	Elongation at Break (%)	Initial Modulus (MPa)
TF1	15.0	16	524.2
TF11	14.1	32	716.7
TF12	11.5	28.5	533.1
TF13	10.6	12	654.9
TF14	13.2	16	780.2

lead to a higher degree of crosslinking and could be accountable for a higher initial modulus.

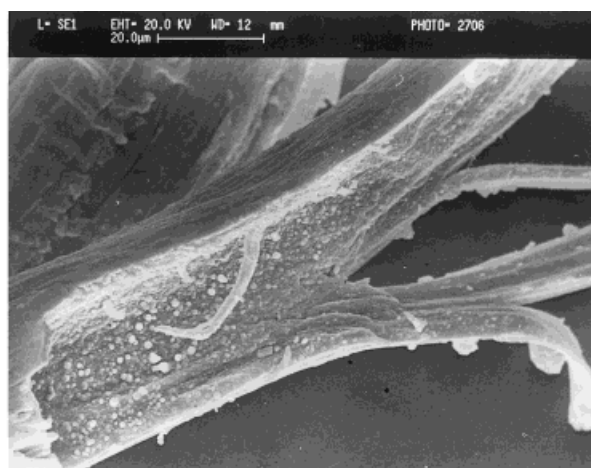
The observed decrease in the tenacity of the

samples could be due to the increase in the surface defects and flaws in the sample (during the treatment), which might facilitate the fracture of the sample.

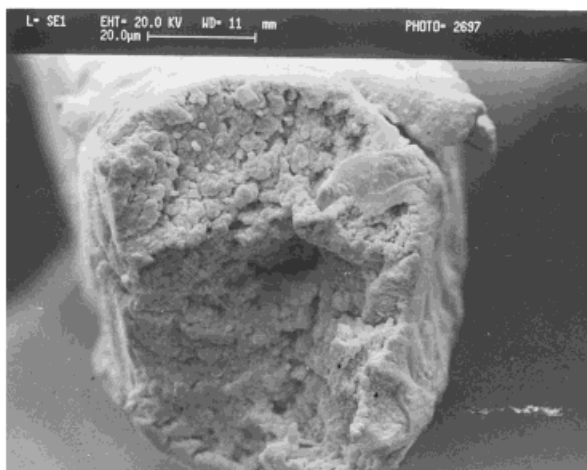
Interestingly, a considerably high increase in the elongation at break (i.e., from 16% for the samples TF1 to 32 and 28.5% for samples TF11 and TF12, respectively) has been observed in the case of samples treated with the sulphates of sodium and potassium, whereas it (elongation at break) decreases significantly (up to 6%) on treating the sample with nickel sulphate. The significant improvement in the stretchability of the acrylic fibers is also noticed by Abdurakhomanova et al.,²¹ in the presence of alkali metal salts. It seems that alkali metal ions, i.e., Na⁺ and K⁺,



(a)



(b)



(c)

Figure 11 SEM fractographs of (a) untreated fibers (TF1), (b) fibers treated with sodium sulphate (TF11) and (c) fibres treated with nickel sulphate (TF14).

are found to decrease nitrile–nitrile dipolar interactions, thereby exhibiting plasticizing action, which might be responsible for the exceptionally higher increase in the elongation at break. Furthermore, the drop in the crystallinity of the samples treated with alkali metal sulphates (as discussed under the heading WAXD Studies) could also be attributed to higher deformation of these samples. In case of sample TF14, the very low value for elongation at break may be due to greater capacity of Ni⁺² to form a coordination complex with the CN and COOH groups of the polymeric chains, thereby leading to higher degree of networking of polymer chains.

Fracture Morphology

Fractured surfaces of the untreated fiber (TF1) and fibers treated with sodium sulphate (TF11) and nickel sulphate (TF14) are shown in Figure 11. In TF1 and TF14 samples [Fig. 11(a) and (c)], the fracture occurred along the plane transverse to the draw direction and showed granular cross-section, as occurs in the case of the fibers of low crystallinity and distribution of internal defects.³⁵ It seems that the fracture was initiated from a defect or flaw at the surface and propagated through the internal defects, thus causing the failure. Interestingly, the fractograph [Fig. 11(b)] of the fiber treated with sodium sulphate shows the sign of fibrillation, which might have taken place during the fracture, which does not seem to occur along the plane transverse to the draw direction. The occurrence of fibrillation may be due to the plasticization effect of the alkali metal salts.

CONCLUSIONS

The treatment of the acrylic fibers (having acrylic acid as a comonomer) with the aqueous solutions of sulphates of alkali metals (sodium, potassium) and transition metals (cobalt, nickel) at 90°C, causes some changes in their chemical as well as physical structure. The changes in the chemical structure appear to be more in the case of samples treated with the sulphates of alkali metals compared to the samples treated with the sulphates of transition metals. The initiation of the DSC exotherm shifts towards a higher temperature as a result of the treatment of acrylic fibers with metal sulphates due to the replacement of H⁺ of the COOH group by metal ion and thereby hinder-

ing the initiation of cyclization through ionic mechanism. The initial stage of thermal degradation of the acrylic is retarded by incorporation of metal ions.

The treatment also affects the tensile properties of the fibers as tenacity of the fibers decreases. The initial modulus, elongation at break has also shown an approximately twofold increase for the samples treated with the sulphates of alkali metals due to the plasticizing effect of alkali metal ions.

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