

Thermal Reactions and Analysis of Polyacrylonitrile Films

Mohammad A. Semsarzadeh and Azizalah Molaei

Polymer Group, Chemical Engineering Department, Tarbiat Modarres University, Tehran, I.R.Iran

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ABSTRACT

Polyacrylonitrile films are prepared from the polymer and dimethylformamide (DMF). The thermal treatment of the PAN film like the fibre is considered as an important step in the formation of the ladder polymer structure. The kinetics and thermodynamic studies of the PAN films indicated that the peak temperatures and the enthalpies of the reactions are lower than the PAN fibres. The properties of PAN films and fibres are studied on the basis of -CN groups dipole moment and coupling, and their energetics of the reaction with potassium permanganate catalyst and other additives like acetic acid are also determined.

Key Words: polyacrylonitrile film, peak temperature, enthalpy, energetics, potassium permanganate

INTRODUCTION

Carbon science is concerned with solid carbon materials. Solid carbons are generally derived from organic precursors by a pyrolysis process known as carbonization, and that exists in a graphitic and non-graphitic forms. Carbonization is the process of formation of a material with increasing carbon content from organic materials. Graphitization is another solid state transformation by thermal activation. Carbon fibres are filaments consisting of non-graphitic carbon produced by the carbonization of synthetic or natural organic fibres, spun from organic precursors.

Polyacrylonitrile (PAN) is considered as a superior starting material for the carbon fibre. In this process PAN precursor is oxidized while under strain without the need for a hot stretching stages after carbonization. The chemistry of the process of conversion of PAN to carbon fibres is extremely

complex. Two most important processes which occur are: nitrile group reacts to form a closed ring structure; and oxygen aids cross-linking of the chains. Oxidation is the essential PAN stabilization stage, because it allows the subsequent polymer degradation reactions during carbonization to proceed without collapse of the fibre or loss of the orientation.

Carbonization is carried out at temperatures between 1000–1500 °C. Around 50% by weight of the fibre is volatilized. Proceeding from the PAN precursor a complete range of moduli may be obtained (15–400 GPa). Therefore, there has been a consistent research to improve the strength, strain to failure and reliability of the products from various precursors and their treatments. Because the strength of the carbon fibre based on PAN is statistically complex; the decrease in the processing temperature, the prevention of the mechanical damage to surface and the inter-fibre sticking

during oxidation from the precursor have been the focus of critical research and concern, and a large amount of work has been done to understand the underlying mechanism to control and acquire the high quality product.

Although the structure of the carbon fibre from the thermal treatment of the polyacrylonitrile (PAN) fibre has been studied, the kinetics and thermodynamics of polyacrylonitrile films prepared from the solution of the PAN in dimethylformamide has not yet been studied [1–5, 11].

Polyacrylonitrile is known as the precursor of the carbon fibre. The precursor of the carbon fibre undergoes an exothermic reaction which has been used in the thermal reaction of this material in the production of the carbon fibre [1–3]. Since the precursor of PAN for making carbon fibres is spun under certain conditions and has crystalline regions of the order of 30–55 interspersed with the amorphous region, the thermal behaviour of the precursor is largely determined by the chemical and the physical states of this material [3]. It has also been reported that the thermal reaction is mainly the cyclization reaction of the nitrile groups and formation of the ladder structure [1–3].

The stabilization process and the energetic understanding of the PAN-based carbon fibre has been the important subject of research because of its effect on the carbonization of the ladder structure. Thus far, the research has been concentrated on the stabilization consideration of the PAN-based precursors, the mechanism and thermal control of the reaction with the catalysts or other additives and plasticizers [1–11].

In this study, we have undertaken a new approach by considering the kinetics and the energy of activation of the experimentally designed PAN-films casted from a single phase solution of PAN-DMF and investigated the thermal treatment of the PAN films in the presence of the potassium permanganate catalyst and the additional plasticizers like acetic acid.

The properties of PAN films and fibres are studied on the basis of $-CN$ groups dipole moment and coupling, and their energetics with thermodynamics are reported.

EXPERIMENTAL

The material used was polyacrylonitrile from the Polyacryl Esfahan, Iran. It contains 93% acrylonitrile, 6.1% methyl acrylate and 0.9% methyl allyl sulphonate. The molecular weight of the polymer is 300,000–500,000. Since the polymer is sensitive to humidity and solvents, it was dried at 100 °C for 5 h. The percent humidity of the fibres was about 1–2% by weight. The preparation of the PAN films from DMF was very critical. Fresh dimethylformamide was used with a carefully dried polymer. The films of less than 0.1 mm thickness were prepared by dissolving 1g of the dried fibre in 5 mL of the solvent, and then allowing to reach a constant weight. This process was carried out at temperature less than 70 °C for 17 days or longer. The slow evaporation of the solvent was necessary to reach the equilibrium for the kinetics and thermodynamic studies. The catalyst was 3–10% potassium permanganate solution. The acetic acid plasticizer was a 10% solution and a 50% concentrated solution. PAN-DMF films were placed in the catalyst solution for at least 3 min at 85 °C. Since the acetic acid plasticizer did not affect the PAN fibres at low concentrations and at room temperature, the fibres were refluxed with the concentrated acetic acid for at least 12 h. The percent acid absorbed by the films or fibres was measured by the weight difference of the washed and dried samples. The thermal properties of the PAN films and fibres were studied by TGA and DSC of PL Thermal Science. The structures of the films were studied by a FTIR-IFSS88 infra-red instrument. The mechanical properties of the films were also studied by an Instron 3710-016, and tensile strength and elongation of the samples were reported according to ASTM-D882.

RESULTS AND DISCUSSION

TG and DTG Measurements

The thermogravimetric analysis of the PAN fibres and films were carried out at 150 °C and at higher temperatures required for the thermal treatments

Table 1. Thermogravimetric data of the PAN films and fibres at the start of cyclization reaction $T_c = 250^\circ\text{C}$.

PAN	PAN	PAN-AcOH	PAN-KMnO ₄
	weight loss (%)		
Film	38.55	29.58	39.06
Fibre	39.58	32.00	--

of the films and the fibres (about 250°C). Prior to this temperature the fibres indicated 1.5% weight loss due to the moisture absorption at 150°C . The fibres treated with acetic acid plasticizer also showed the same weight loss. The weight loss of the PAN films catalyzed by KMnO_4 or plasticized with acetic acid is shown in Figure 1. The weight losses of the films at 250°C were 3.6–6%. The values for the same after thermal treatment at 250°C are given in Table 1.

DSC Measurements

The differential scanning calorimetry (DSC) was used to study the reaction peak temperature (T_p), the heat of reaction (ΔH), and the energy of activation (E) of the thermal reaction of PAN films with KMnO_4 or the acetic acid plasticizer. The first order reaction was used to calculate E as described in eqn (2).

$$d\alpha/dt = f(\alpha) \cdot \exp(-E/RT) \quad (1)$$

$$E = (-R/1.052) \cdot (\Delta \ln \phi / (1/T_p)) \quad (2)$$

$$k_0 = \phi E \cdot \exp(E/RT_p) / RT_p^2 \quad (3)$$

where α_p is the extent of reaction at T_p ; $d\alpha/dt$ is the reaction rate at time t ; ϕ is the heating rate, $f(\alpha)$ is the pre-exponential function for the reaction rate. R is the universal gas constant and T the reaction temperature in K. k_0 is the frequency factor. The activation energies of the PAN films and fibres with KMnO_4 are given in Tables 2 and 3. The enthalpies of the thermal reactions of the PAN-films and fibres with KMnO_4 or the plasticizer at different peak temperatures and heating rates are also given in Tables 4 and 5. The

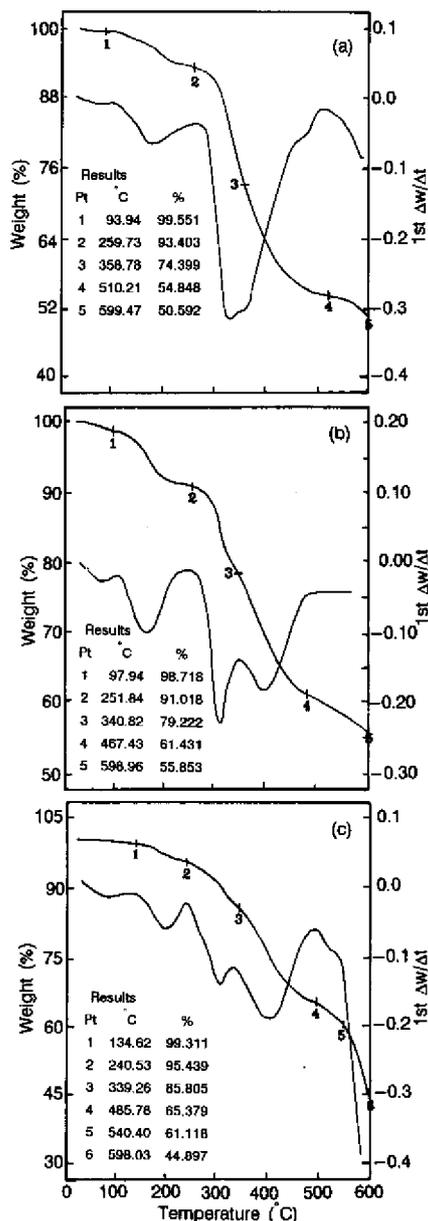


Figure 1. TGA thermograms of PAN films, (a) film, (b) with AcOH, and (c) with KMnO_4 .

Table 2. The activation energy of the PAN films.

PAN	Activation energy (kcal/mol)
PAN film	49.80
Film-DMF-KMnO ₄	43.59
Film-DMF-AcOH	27.35

Table 3. The activation energies of the PAN fibres.

PAN	Activation energy (kcal/mol)
PAN fibre	28.90
Film-KMnO ₄	25.00
Film-AcOH	24.30

activation energies of PAN films and fibres are shown in Figures 2 and 3. The DSC thermograms of the PAN films (PAN-DMF, PAN-DMF-AcOH, PAN-DMF-KMnO₄) with the heating rate of 5 °C/min are shown in Figure 4.

Absorption of Acetic Acid

The absorption of acetic acid in PAN fibres and

Table 4. The heating rate and the exotherm peak temperature and enthalpy of the heat treated PAN films.

PAN	Heating rate ϕ (°C/min)	Peak temp. T _p (°C)	Enthalpy ΔH (kcal/mol)
Film	5	304.88	181.72
	12	313.43	138.30
	15	316.60	118.38
Film-AcOH	5	286.33	137.54
	10	304.72	133.96
	15	309.81	115.94
Film-KMnO ₄	5	264.98	143.63
	15	279.53	130.63

films indicated sensitivity to temperature. Therefore, the samples were allowed to dry at temperature lower than 70 °C for 12 days or longer. The method of drying prevented the discolouration of the samples, bubble formations or other unexpected decomposition reactions. The weight percent of the acetic acid plasticizer absorbed by PAN films are given in Table 6.

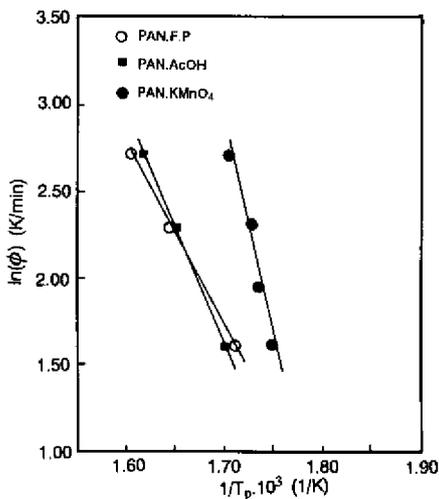
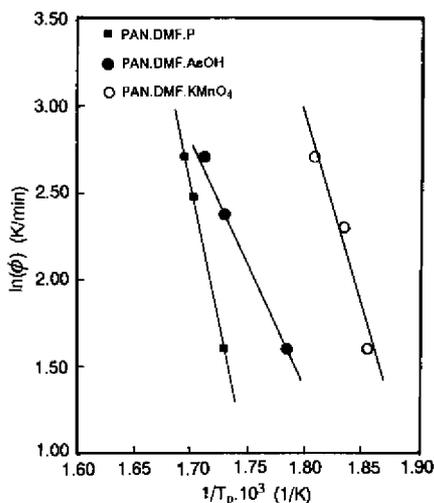
**Figure 2.** Evaluation of the activation energies of PAN precursors from the PAN fibres, and the heating rate dependence of reaction peak temperature.**Figure 3.** Evaluation of the activation energies of PAN precursors from the PAN films and the heating rate dependence of the reaction peak temperature.

Table 5. The heating rate and the exotherm peak temperature and enthalpy of the heat treated PAN fibres.

PAN	Heating rate ϕ ($^{\circ}\text{C}/\text{min}$)	Peak temp. T_p ($^{\circ}\text{C}$)	Enthalpy ΔH (kcal/mol)
Fibre	5	312.23	422.93
	12	332.25	217.24
	15	348.10	181.58
Film-AcOH	5	315.43	437.71
	10	331.79	367.14
	15	345.59	209.19
Film-KMnO ₄	5	274.79	205.15
	15	287.04	181.82

FTIR Measurements

The infra-red absorption of PAN films (Figure 5) indicated the reported absorptions at 1750 cm^{-1} , 1600 cm^{-1} and 2340 cm^{-1} for $-\text{C}=\text{O}$ and $-\text{C}=\text{N}$ groups related to the PAN and the precursor ladder structure [2, 4]. There is no way to verify the ladder structure [3].

Mechanical Measurements

The tensile strength and elongation of PAN films, or the catalyzed PAN films with KMnO_4 and the treated films with acetic acid were tested and the their ultimate stress and elongations at break are given in Table 7.

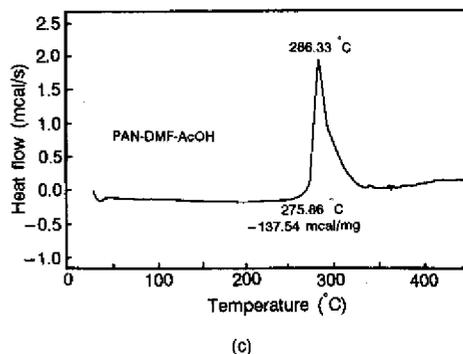
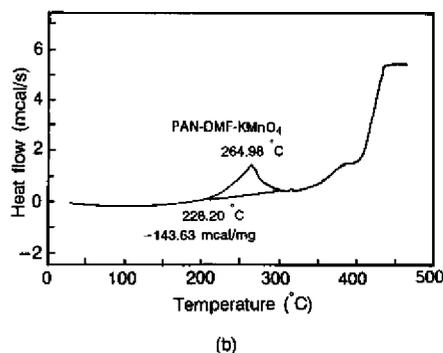
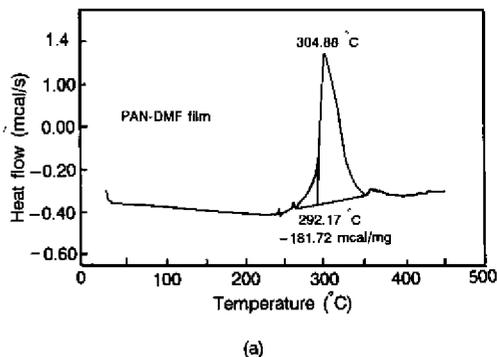
The enthalpies of PAN films from the polymer solution of the PAN-DMF is expected to indicate the solvent interactions. These interactions usually lead to a lower dipole moment of

Table 6. The weight percent of acetic acid plasticizer absorbed in PAN films.

Acetic acid	Temperature ($^{\circ}\text{C}$)	Weight percent absorbed
Concentrated	Room temperature	0.00
Concentrated	85	3.41
Concentrated*	94	4.05
50% Solution	94	1.31

* 2.03% by weight acetic acid was absorbed by the PAN fibres.

$-\text{CN}$ groups in PAN films as compared to the PAN fibres. In the fibre the nitrile groups are

**Figure 4.** DSC thermogram of the PAN films, (a) film, (b) with KMnO_4 , and (c) with AcOH at $5\text{ }^{\circ}\text{C}/\text{min}$.

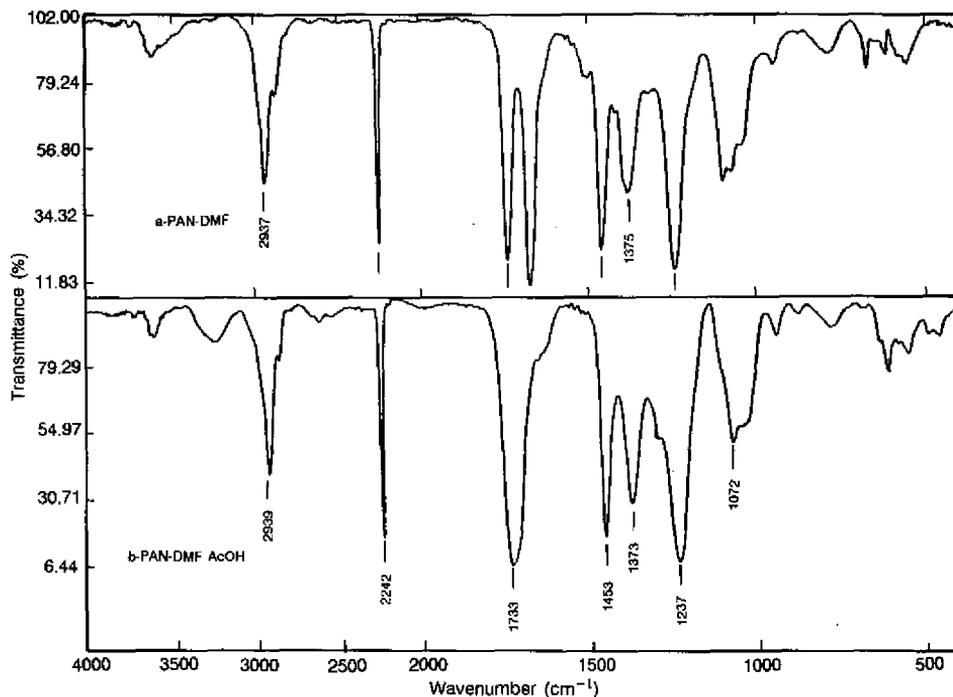


Figure 5. FTIR taken from (a) PAN-DMF film, (b) PAN-DMF AcOH after thermal treatments.

expected to couple strongly and reduce the chain flexibility and the entropy of the annealed fibre [3]. In PAN films, the solvent predetermines the properties of the film. The enthalpy and the entropy of the PAN film depend on the solvent. The PAN-DMF solution is a uniform and stable solution without coagulations, therefore, it is suitable for

the casting of clear films (11). Acetic acid diffuses easily into the PAN-film and reduces the bond strength of the nitrile groups, therefore, T_p of the films are expected to be lower than that of the fibres. Since the enthalpy of films are lower than the fibres, the fibre peak temperatures of the films are smaller. The broader exothermic reaction peak of the PAN films with $KMnO_4$ indicated a higher uptake of oxygen.

Table 7. Mechanical properties of the PAN films.

PAN	Stress (psi)	Elongation (%)	Elongation at break (%)
Film	5264.52	6.63	17.75
Film-AcOH	3435.63	14.17	86.67
Film- $KMnO_4$	3547.30	10.00	64.17

CONCLUSION

As the manufacturing of the carbon fibre involves the ladder polymer and the stabilization process of the precursor is an important stage of the manufacturing prior to the carbonization, we have tried to

study and report the kinetics and the thermodynamics results of the precursor based on the PAN films. The solvent in PAN-DMF system not only facilitates the diffusion of the acetic acid and the KMnO_4 catalyst, it also enhances the diffusion of oxygen into the system.

Furthermore, since the peak temperatures of the PAN films are lower than the fibres, the catalyst KMnO_4 is expected to reduce the peak temperature of the reaction. The enthalpies of the thermally reacted PAN films are also lower. The PAN-films are mechanically more resistant to the breakage due to their larger elongations.

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