

Graft Polymerization of Acrylonitrile onto Paper and Characterization of the Grafted Product

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ABSTRACT: The chemical graft copolymerization reaction of acrylonitrile (AN) onto paper sheet was performed. The effect of initiator concentration, monomer concentration, and temperature on the reaction rate was studied. The reaction rate equation of the graft copolymerization reaction is found to be $R_p = K_2 [\text{initiator}]^{0.54} [\text{monomer}]^{1.13}$. The apparent activation energy (E_a) of the copolymerization reaction is found to be 35.99 KJ/mol. The infrared characteristic absorption bands for cellulosic paper structure and the paper gr-AN are studied. Tensile break load, porosity, and burst strength were measured for the grafted and pure paper sheet. It was

found that the mechanical properties are improved by grafting. The chemical resistance of the graft product against strong acid (HCl), strong alkali (NaOH), polar and nonpolar solvents was investigated. It was found that the resistance to these chemicals is enhanced by grafting. From the TGA and DTA data, it is clear that the grafted paper sheet is more thermally stable than pure paper sheet. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1411–1419, 2011

Key words: acrylonitrile; graft copolymerization; paper sheet; characterization

INTRODUCTION

The paper manufacture is an ancient industry in EGYPT, which developed quickly to change the paper properties according to their usages. The graft copolymerization of vinyl monomers onto natural and synthetic polymers by chemical or radiation induced polymerization has been suggested as potentially good means of alternating the properties of the base polymer.^{1–9}

The graft copolymerization of acrylonitrile (AN), methyl methacrylate, and styrene onto paper sheet, cotton and silk was reported.¹⁰ Paper sheets were grafted by copolymerization with styrene-divinylbenzene mixture, methyl acrylate, or other monomers using benzoyl peroxide (BPO) as free radical initiator.^{11,12} Until now, only a small number of studies have been carried out concerning the use of polymeric materials for the consolidation and protection of paper.^{13,14}

The graft copolymerization of AN onto cellulose using the cellulose xanthate-Cr⁶⁺ system proceeds rapidly at normal temperature (0–20°C).^{15–17} No ungrafted homopolymers in solution was formed. The activation energy for this grafting copolymerization was found to be 0.45 KJ/mol, and the reaction order was 1.3.

Graft copolymerization reactions of acrylic acid, acrylates, and AN on cellulosic materials have been investigated^{18–25} by the use of ceric ammonium nitrate in aqueous medium at different temperatures. The variation in the level of incorporation of poly (acrylic acid) grafts on the cellulosic substrate and the dependence of the water and saline retentions of the graft copolymers on the graft level were examined.

Graft copolymerization of vinyl monomers onto cellulose has been previously studied,^{26,27} acrylic monomers appear particularly suitable because they show high filmability, transparency, optical clarity, good adhesive properties, water-repellance and stability to atmospheric oxygen and UV light; thus their use makes possible to achieve the consolidation and protection of the cellulosic materials leading to the improvement of the restoration treatment.^{28,29}

The aim of this work is to study the chemical graft copolymerization reaction of AN onto paper sheet to protect the documents which was written by pencil from long time ago against damage or bacterial action and forgery. Moreover, it is also interesting to increase their preservation time. The effect of initiator concentration, monomer concentration, and temperature on the reaction rate should be investigated. The thermodynamic parameters of activation are given. The obtained grafted paper sheet is characterized by IR spectroscopy, thermogravimetric analysis, electron microscopy, and X-ray diffraction. The chemical and mechanical behavior of the obtained paper sheet grafted with AN will also be given.

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EXPERIMENTAL

Materials

The paper sheets (A4) Japan NPI; grammage 80 g/m² made largely from mechanical pulp which contains bleached cellulose, a noticeable amount of fillers (CaCO₃) (ash 18%). The paper sheet was cut into small pieces of the diameters 3.3 cm length, 2.8 cm width, and 0.1 cm thickness. The paper sheets were treated with different polar and nonpolar solvents to remove any fats from the paper sheet surface or organic additives present in the paper structure or polymeric additives.

AN was a product of Koch Light Company (England) and has specific gravity of 0.806 g/cm³ inhibited with 35–45 ppm hydroquinone monomethyl ether. The monomer was washed with a few drops of 10% sodium hydroxide solution followed by small amount of distilled water, then the monomer was fractionated using a fractionating column of 15 theoretical plates. The fraction which boils at 77°C was collected and used.

The initiator for the free radical graft copolymerization reactions was BPO provided from El-Nasr Pharmaceutical Chemical Company, Abu Zabal, Egypt. It was purified and activated by dissolving in chloroform, then filtered, dried, and kept under vacuum.

Ferrous ammonium sulphate hexahydrate, 1,2-dichloroethane, acetone, cyclohexane, petroleum ether, xylene, hydrochloric acid, ethyl alcohol, sodium hydroxide (pellets) were products of B.D.H Chemical Company, England. Benzene (thiophene free), dimethylformamide (DMF), chloroform, and methanol were of chemical pure grade from El-Nasr Pharmaceutical Chemical Company, Laboratory Chemical Division, Abuzabal, Egypt.

Instrumental analysis

Infrared spectroscopy

The infrared measurements on paper sheet, polyacrylonitrile (PAN), and grafted paper sample with AN were carried out by Shimadzu FTIR-430 Jasco spectrophotometer (Japan) using KBr disk technique. In this case, approximately 1 mg of sample was used for pellet preparation with 60 mg KBr then thermal treatment of the pellets in oven at 80°C for 24 h to reduce the humidity content in the cellulose to prevent the overlapping between water and carbonyl bands in the spectra. The paper and polymer samples were analyzed in transmittance with accumulation of 16 scans and the resolution of 4/cm.

Electron microscopy and X-ray diffraction analysis

The electron microscopy analysis was carried out using JSM-T20 Scanning electron microscope (JEOL, Japan) after metallization of the specimen with very

thin layer of gold to obtain a good conductivity and the SEM picture was taken with magnification 1 : 1500. The x-ray diffractometer type Philips 1976 Model 1390 was operated at the following conditions that were kept constant overall the analysis processes: x-ray tube: Cu, Scan speed: 8 (dg/min.), Current: 30 mA, Voltage: 40 kV, Preset time: 10 (s).

Paper testing

Since the physical properties of the paper change with variation of its moisture content, it is necessary to standardize it at a definite temperature and humidity values in order to obtain a standard test results. The process was carried out at 60% relative humidity and at a temperature range from 18 to 20°C.

The tensile break load was measured by a Loyal LR10 universal testing machine. A paper strip of 15 mm width was clamped between two jaws and an increasing load was applied by swinging pendulum from its vertical resting position by a motor. The tensile break load was taken as the force (N/mm²) required to break the strip.

Bursting strength was conducted according to TAPPI standard 403. A Mullen tester (Perkins, Chicopee, MA) was used. The burst strength in N/mm² is given as the pressure at which the paper sheet bursts.

An indication of the porosity can be obtained by measuring the resistance of a paper sample of a given dimensions to the passage of standard volume of air (usually 100 cm³) under standardized conditions of pressure, temperature, and relative humidity using (Gurley Densometer 4110). The porosity value was determined by measuring the time in seconds for the flow of 100 cm³ of air forced through the paper by pressure that results from the weight of the inner cylinder floating freely in an outer cylinder partially filled with light oil.

Chemical resistance determination

Grafted paper sheet with AN and ungrafted one are subjected to the action of the chemical reagents. The loss or increase in weight was determined after different time intervals 24, 48, 72, 98, 120, 144, 168, 192, 218, 240, 264, and 288 h. The used chemical reagents are benzene, acetone, dimethyl formamide, 1N HCl, 5N HCl, NaOH one and 5N at room temperature.

Thermal gravimetric analysis

The thermal gravimetric analysis of the paper sheet and the paper gr-AN samples were performed using thermal analyzer (Shimadzu DT-30 Japan). The weight loss was measured from the ambient temperature up to 600°C, in rate of 10°C per minute to determine the degradation rate of the prepared samples.

Calculations

Statistical analysis

All the recorded data in this study are at least the mean average of three for chemical grafting and five for mechanical tests measurements.

Calculation of graft percent

$$\text{Graft\%} = [(W - W_o)/W_o] \times 100$$

where W = weight of paper after grafting and W_o = weight of paper sheet before grafting.

Calculation of the initial rate of graft copolymerization reaction

$$R_i = [W/(M \times V \times t)]$$

where R_i = initial rate of graft copolymerization reaction, W = weight of polymer (gm), M = molecular weight of monomer, V = volume in liter and t = time in seconds.

Calculation of overall rate of graft copolymerization reaction

$$R_{\text{overall}} = [W/(M \times V \times t)]$$

where R_{overall} = overall rate of graft copolymerization reaction, W = weight of polymer (gm) after 3 h (i.e., at the end of the copolymerization reaction), M = molecular weight of monomer, V = volume in liter, and t = time in seconds.

RESULTS AND DISCUSSIONS

Chemical activation of the paper sheet surface

The chemical activation of the paper surface was carried out by dipping of the paper sheet in ferrous ammonium sulphate (FAS) solution (0.02M) for different time intervals. The investigation of the effect of dipping time on the graft (%) on the paper sheet was carried out. The graft copolymerization reaction of AN as a monomer onto the activated paper sheet for different time intervals and dried, was carried out. The used initiator was BPO as a free radical initiator using DMF as a reaction medium at 60°C under nitrogen atmosphere. The graft (%) is plotted against the dipping time (Min) and the data are graphically represented in Figure 1. From the histogram, it is clear that the optimum time for activation is 20 min. The activation process was kept constant all over the experimental studies.

Graft copolymerization of acrylonitrile (AN) onto paper sheet

Effect of initiator concentration

The graft copolymerization reaction of (AN) onto the activated paper sheet strips was carried out in a

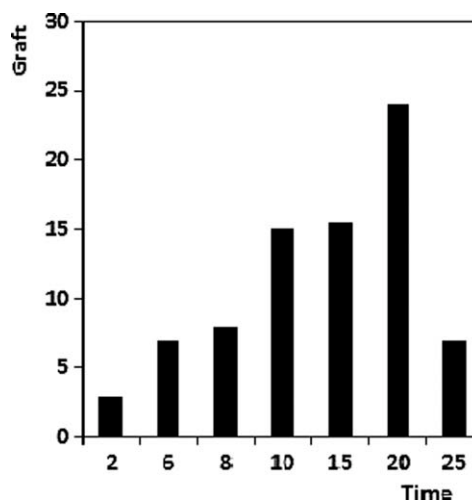


Figure 1 Histogram represents the effect of dipping time in ferrous ammonium sulphate solution (0.02M) on the grafting % of the paper sheet with acrylonitrile.

quickfit pyrex glass tubes of 0.2 L capacity using BPO as a free radical initiator with different concentrations 0.017, 0.025, 0.033, and 0.041M, respectively. The monomer concentration was kept constant at 3.797M in dimethyl formamide (DMF) at 70°C. The graft copolymerization reactions were carried out at different time intervals. The grafted paper strips were subjected to solvent extraction by acetone for 24 h to remove the formed homopolymer, then the conversion (%) was calculated. A graphical relationship between graft yield (%) and duration time (in minutes) for each initiator concentration is represented in Figure 2(A). The initial and overall rate of the graft copolymerization reaction was calculated, and the data are summarized in Table I. From the obtained data, it is clear that both of the initial and overall rates of graft reactions increase as the initiator concentrations increase. The induction period of the graft copolymerization process decrease with the increasing of the initiator concentration. From the obtained initial rate values, the double logarithmic plot between the initial rate of the graft copolymerization reaction and the initiator concentration gave a straight line which is represented in Figure 2(B). The slope of this straight line is found to be 0.54, which is an expression of the reaction order with respect to the initiator concentration.

Effect of monomer concentration

The effect of monomer concentration on the graft copolymerization reaction in the presence of 0.025M BPO as a free radical initiator at 70°C under nitrogen atmosphere was carried out. The investigated monomer concentrations were 2.658, 3.797, 4.557, and 4.936M. The graft yield (%) was measured at

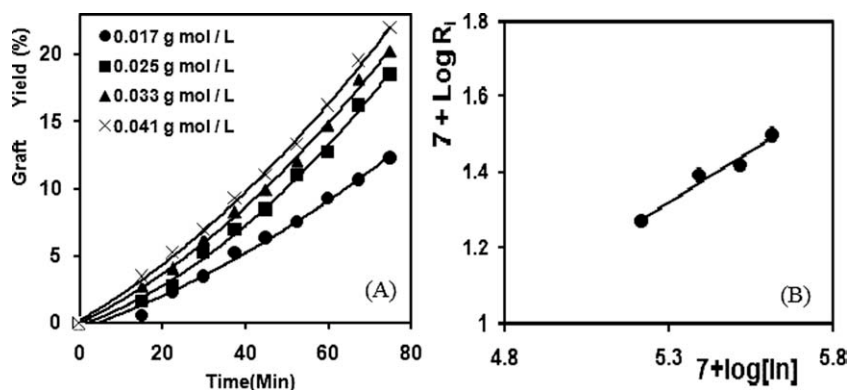


Figure 2 (A) The graft yield% versus Time (Min) curves showing the effect of initiator concentration on the grafting reaction. (B) Double logarithmic plot of initial rate of the grafting reaction versus initiator concentration.

different time intervals for each concentration and the graft yield (%)–time curves are represented in Figure 3(A), from which the initial and overall reaction rates were calculated, and the data are summarized in Table I. It is clear that both the initial and overall reaction rates increase with the increasing of monomer concentration in the range between 2.658 and 4.936M. From the obtained initial rate values, the double logarithmic plot between the initial rate of the graft copolymerization reaction and monomer concentration is represented in Figure 3(B). This relation gave a straight line with slope 1.13 which indicate that the exponent with respect to monomer concentration is a first-order reaction.

Effect of the reaction temperature

The graft copolymerization reactions of (AN) onto activated paper sheet with FAS were carried out at different temperatures (60, 65, and 70°C) using 0.025M BPO as free radical initiator and 3.797M AN (5 mL AN in 15 mL DMF) under nitrogen atmosphere. The graft yield (%) at different time intervals for each investigated temperature was measured, and the relation between the graft yield (%) and time (min) for each temperature is represented in Figure 4(A), from which, it is clear that both of the initial and overall reaction rates increase with raising of the reaction temperature.

Thermodynamic activation parameters for the graft copolymerization reaction of acrylonitrile onto paper sheet

The apparent activation energy (E_a) for the graft copolymerization reaction of AN onto paper sheet was calculated between three different temperatures for the paper sheet strips activated with FAS by plotting $\log R_i$ versus $(1/T) K^{-1}$ [c.f., Fig. 4(B)]. This relation gives straight line. The slope of this line is introduced in Arrhenius equation to give the apparent activation energy. The enthalpy and entropy of activation for the graft copolymerization reactions of the investigated monomer system onto paper sheet strips can be calculated by determination of k_2 -values at different temperatures from the following equation:

$$R_i = k_2[\text{monomer}]^x[\text{initiator}]^y$$

where x and y are exponents with respect to monomer and initiator respectively. The enthalpy (ΔH^*) and entropy (ΔS^*) of activation associated with k_2 were calculated using Eyring equation;

$$K_2 = KT/h e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT}$$

where K is Boltzmann constant and h is Planks constant.

TABLE I
Effect of Initiator and Monomer Concentration on the Grafting Copolymerization of Acrylonitrile onto Paper Sheet

Sample no.	Effect of initiator				Effect of initiator monomer	
	Concentration (mol/L)	Rate of grafting (mol/(L s) $\times 10^6$)		Concentration (mol/L)	Rate of grafting (mol/(L s) $\times 10^6$)	
		Initial	Over all		Initial	Over all
1	0.017	1.862	2.222	2.658	1.738	1.803
2	0.025	2.455	3.354	3.797	2.455	3.354
3	0.033	2.618	3.669	4.556	3.141	7.966
4	0.041	3.141	3.983	4.936	3.548	9.497

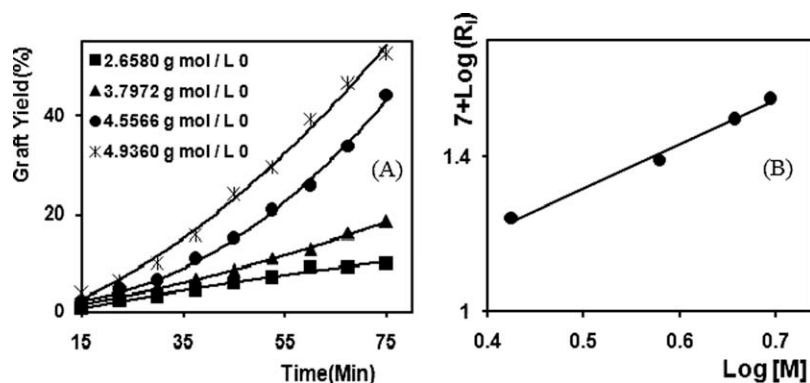


Figure 3 (A) The graft yield% versus Time (Min) curves showing the effect of monomer concentration on the grafting reaction. (B) Double logarithmic plot of initial rate of the grafting reaction versus monomer concentration.

By dividing the above equation by T and taking its natural logarithm, one obtains the following equation:

$$\text{Log}(k_2/T) = \text{Log}(K/h) + (\Delta S^*/2.303R) - (\Delta H^*/2.303RT)$$

By plotting of $\text{Log}(k_2/T)$ versus $(1/T)$ we obtained a linear relationship with slope $(\Delta H^*/2.303R)$ and intercept $[\text{Log}(K/h) + (\Delta S^*/2.303R)]$ [c.f., Fig. 4(C)]. From the slope and intercept, the values of ΔH^* and ΔS^* are found to be 32.61×10^3 J/mol and -63.4×10^3 J/(mol K), respectively.

The characterization of the grafted paper sheets

Infrared spectroscopic analysis (IR)

The IR absorption bands and their assignments of the investigated paper sheet, PAN homopolymer and grafted paper sheet with AN are summarized in Table II. The weak absorption band appearing at 705/cm in case of the paper sheet appears at 706/cm with slight shift in case of grafted paper sheet. The medium band appearing at 879/cm in case of

the paper sheet appears also in case of grafted copolymer, which may be attributed to out of plane C—C—O stretching vibration. The sharp band appearing at 1093/cm in case of PAN appears also in case of grafted paper sheet as a medium band at 1088/cm which may be attributed to C—O—C stretching vibration or out of plane stretching for C—N group. The broad band appearing at 1431/cm in case of paper sheet appears also in case of PAN as a sharp band at 1452/cm and as a broad band in case of the grafted paper sheet at 1448/cm, which could be attributed to the scissoring of CH_2 group. The medium band appearing at 2245/cm in both cases of PAN and grafted paper sheet could be attributed to the stretching vibration of CN group. The medium band appearing at 2915/cm in case of paper sheet appears also as strong absorption band at 2934/cm in case of PAN and at 2924/cm as a medium absorption band in case of grafted paper sheet which is attributed to CH stretching vibration in aliphatic groups. The broad band appearing at 3379/cm in case of paper sheet appears also at 3420/cm in case of the grafted paper sheet which could be attributed to the stretching vibration for H-bonded OH group indicating an interaction between the

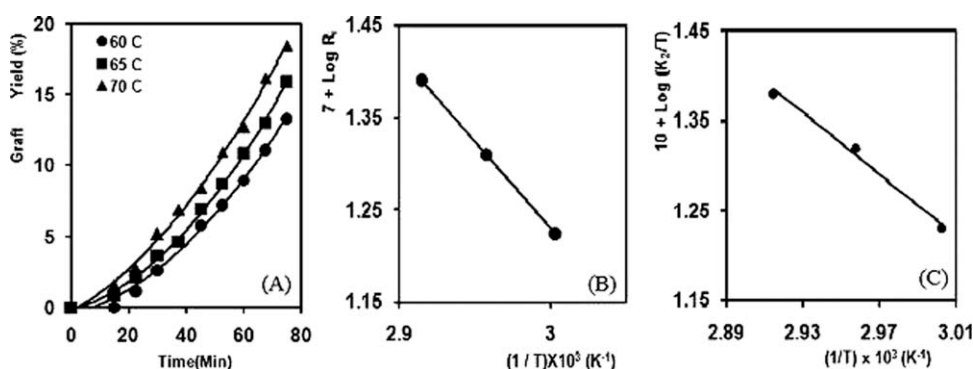


Figure 4 (A) The graft yield% versus Time (Min) curves showing the effect of temperature on the grafting reaction. (B) Relation between logarithm of initial rate of the graft copolymerization reaction versus $(1/T)$. (C) Relation between K_2/T and $(1/T)$.

TABLE II
Infrared Absorption Bands and Their Assignments in Case of Paper Sheet, PAN, and Grafted Paper Sheet

Wave number (cm ⁻¹)			
Investigated samples			Assignments
Paper sheet	PAN	Grafted paper	
567 ^w	541 ^m	565 ^w	Deformation C—C skeletal
610 ^w	—	607 ^w	
662 ^w	661 ^m	661 ^w	
705 ^w	—	706 ^w	In plane rocking for CH ₂ group
—	719 ^m	719 ^w	
—	781 ^m	781 ^w	
879 ^m	—	879 ^m	In plane C—C—O stretching vibr.
1050 ^b	—	1057 ^b	Stretching vibration of C—O—C or out of plane stretching for C—C—O or C—N
1107 ^w	1093 ^s	1088 ^m	
1159 ^m	—	1160 ^m	
1250 ^w	1254 ^m	1253 ^w	Stretching vibr. of C—O group
1431 ^b	1452 ^s	1448 ^b	Scissoring of CH ₂ group
—	2245 ^s	2254 ^m	Stretching vibr. of CN group
2915 ^m	—	2924 ^m	Asymmetric stretching for CH in aliphatic chain groups
—	2934 ^s	—	
3379 ^b	—	3420 ^b	Stretching vibr. for H-bonded OH group.

w = weak, m = medium, b = broad, s = sharp.

cellulosic OH group and CN group of the grafted monomer. Other interest absorption bands and their assignments are summarized in Table II.

Electron microscopy and X-ray diffraction analysis

X-ray diffraction patterns for paper sheet and grafted paper sheet with AN are represented in Figure 5(A,B). From the figure, it is clear that the paper sheet is crystalline and the grafted paper sheet with AN is amorphous with small portion of crystallinity.

The electron microscopy pictures for the pure paper sheet and the grafted paper sheet with AN are represented in Figure 5(C,D). The scanning electron microscopy is generally used to detect the topography of the grafted surface, which usually changes due to the graft copolymerization reaction with AN monomer onto the paper surface. From the figures, it is clear that the graft process with AN monomer gives a polymeric chains which completely cover the cellulosic fibers.

Mechanical properties of the grafted and ungrafted paper sheet

The tensile strength, porosity, and burst strength are important properties for paper manufacturing. These properties are measured as described in the experimental part, the breaking load is reported in N/mm².

The tensile strength values for the investigated ungrafted paper sheet and grafted paper sheet with AN are summarized in Table III. From the table, it is clear that, the graft copolymerization reaction enhances the tensile strength of the paper sheet.

The porosity of the ungrafted and the grafted paper sheet samples was measured as described in the experimental part, and the data are given in Table III. From the porosity data, it is clear that the porosity of the paper gr-AN sample is higher than the ungrafted paper sheet indicating that the absence of polymer on the fibre surface or in the intra- and inter-fiber space leads to more opened structure which gives higher porosity value.

The burst strength values (N/mm²) show that the graft copolymerization reaction with AN slightly improve the mechanical properties of the paper sheet.

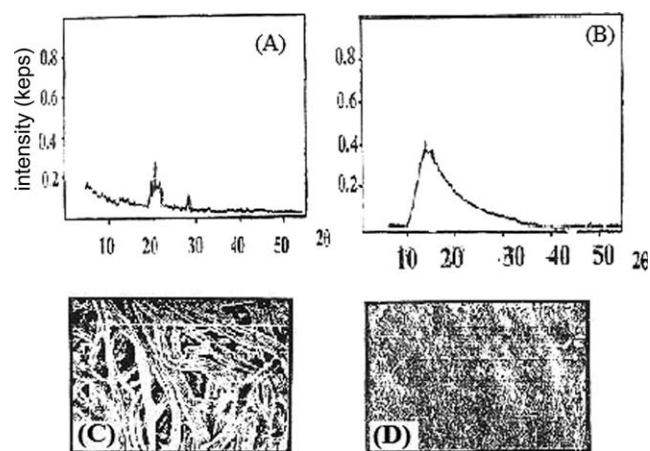


Figure 5 (A) X-ray for the ungrafted paper sheet. (B) X-ray for the grafted paper sheet by AN monomer. (C) SEM for the ungrafted paper sheet. (D) SEM for the grafted paper sheet by AN monomer.

TABLE III
Mechanical Properties of Grafted Paper Sheet
with Acrylonitrile

Samples names	Tensile strength (N/mm ²)	Porosity (s dL ⁻¹)	Burst strength (N/mm ²)
Paper sheet	8.53 (SD = 02)	40.300 ± 0.2	0.2303 ± 0.02
Paper gr AN	11.35 (SD = 03)	31.800 ± 0.3	0.2573 ± 0.01

Chemical resistance of the grafted paper sheet

In case of HCl, two concentrations are investigated (1N and 5N). An increase in the weight of ungrafted and grafted paper sheet is found after 24 h but with higher value in case of the ungrafted one [c.f., Fig. 6(A,B)].

In case of 1N HCl, the weight of the grafted paper sheet increases after 24 h up to 53.4% then decreases to give 43.5% increase after 288 h, but in case of the ungrafted paper sheet, the weight increases after 24 h to 85% value then decreases to 59.5% at the end of the test time (288 h). But in case of 5N HCl, a

destruction of both samples occurs after 72 h with lower value of increase in weight % in case of the grafted paper sheet.

In case of NaOH solution (1N and 5N), the ungrafted paper sheet is destroyed after 96 h, but the grafted paper sheet with AN increases in weight after 24 h to 99% then decreases to 11.6% after 288 h [c.f., Fig. 6(C)]. In case of 5N NaOH, the grafted paper sheet increases after 24 h to 99% then decreases to 15% at the end of the experiment [c.f., Fig. 6(D)].

The effect of acetone on the grafted and ungrafted paper sheet shows lower swelling effect in case of grafted paper sheet and also in case of DMF [c.f., Fig. 7(A,B)].

In case of benzene, the ungrafted paper sheet [c.f., Fig. 7(C)] shows a slight decrease in weight percentage from -1.7 to -1.5% which means the solubility of organic dye or polymer present in the paper structure, but in case of grafted paper sheet a slight increase is observed.

In general, the grafted paper sheet has a good resistance to the investigated chemicals which means

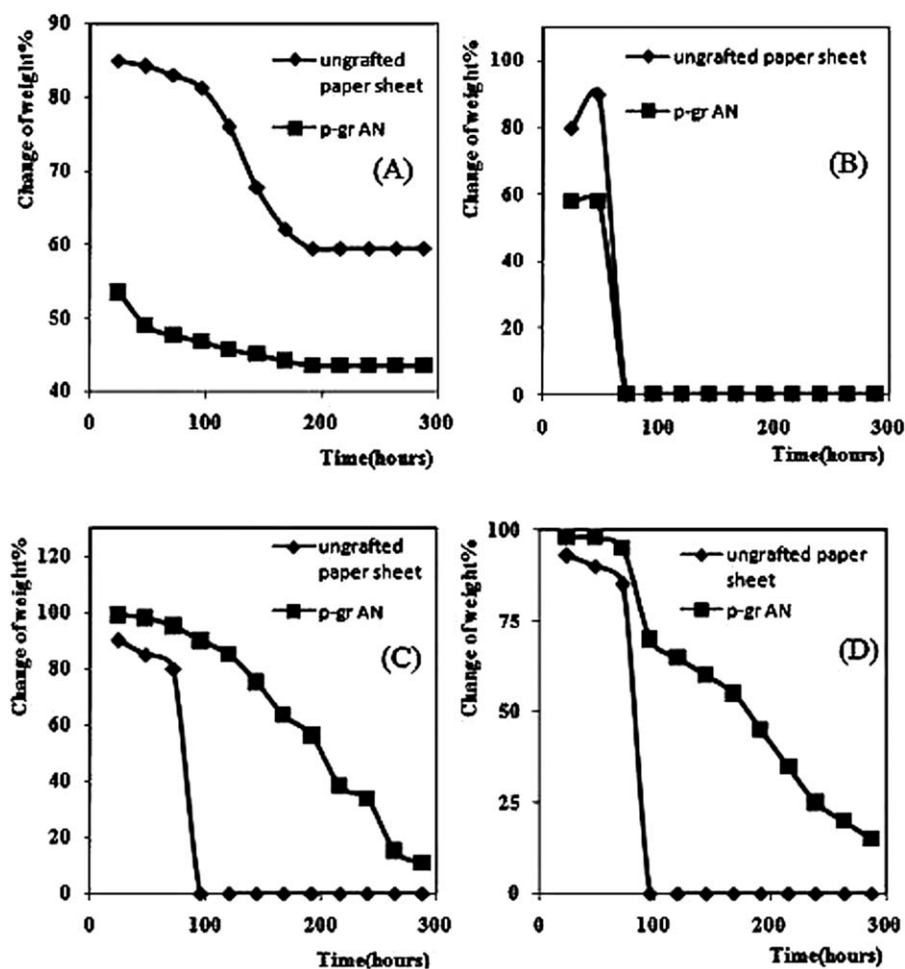


Figure 6 Relation between the change in paper weight percentage and time in hours showing the effect of (A) 1N HCl, (B) 5N HCl, (C) 1N NaOH, and (D) 5N NaOH.

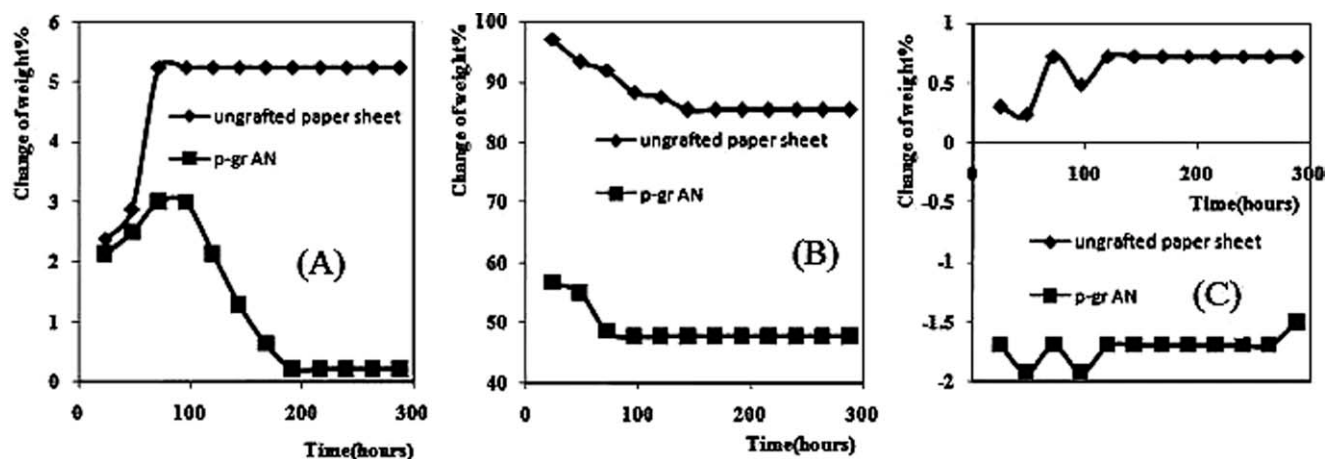


Figure 7 Relation between the change in paper weight percentage and time in hours showing the effect of (A) Acetone, (B) DMF, and (C) Benzene.

that the graft with AN enhances the chemical resistance of the paper sheet. All experiments indicate a high resistance of grafted paper sheet against the investigated chemicals than that in case of ungrafted one (c.f., Figs. 6 and 7).

TGA and DTA

Thermal analysis was carried out under nitrogen atmosphere at heating rate $10^{\circ}\text{C}/\text{min}$. The TGA data are summarized in Table IV, from which it is clear that the first stage on TGA curve for ungrafted paper sheet and paper gr-co-AN samples is attributed to the loss of water molecules (humidity) in the range between 35 and 120°C . The weight loss is 1.88% in case of pure paper and 5.4% in case of the grafted paper with AN.

The endothermic peak for this process appears in case of paper sheet at 44°C and at 46°C in case of paper gr-co-AN. It is also noticed from the TGA curves that, there is no weight loss for both investigated samples in the temperature range between 120 and 210°C and there is no peaks on the DTA curves which confirm our observation from TGA. This

means that there is no chemical or physical change in this stage. The third stage in the range between 210 and 400°C , thermal degradation of the two samples begin with a drastic change in the weight loss ranged from 60.28 for pure paper in the range between 230 and 400 and 44.6 for the grafted paper sheet in the range between 210 and 384 .

It has been reported that thermal decomposition of cellulose includes two processes.^{30–32} One is a

TABLE IV
The Data of Thermogravimetric Analysis TGA and DTA of the Ungrafted Paper Sheet and Paper gr-co-AN and the Decomposition Rate

Temperature range ($^{\circ}\text{C}$)	Paper weight loss%		Maximum degradation rate ($^{\circ}\text{C}$)
	Pure	Grafted	
35–120	1.88	5.4	Pure paper 351, Grafted paper 411
230–400	60.28	–	
210–384	–	44.6	
400–500	8.36	–	
384–500	–	20.72	
Above 500	29.3	29.30	

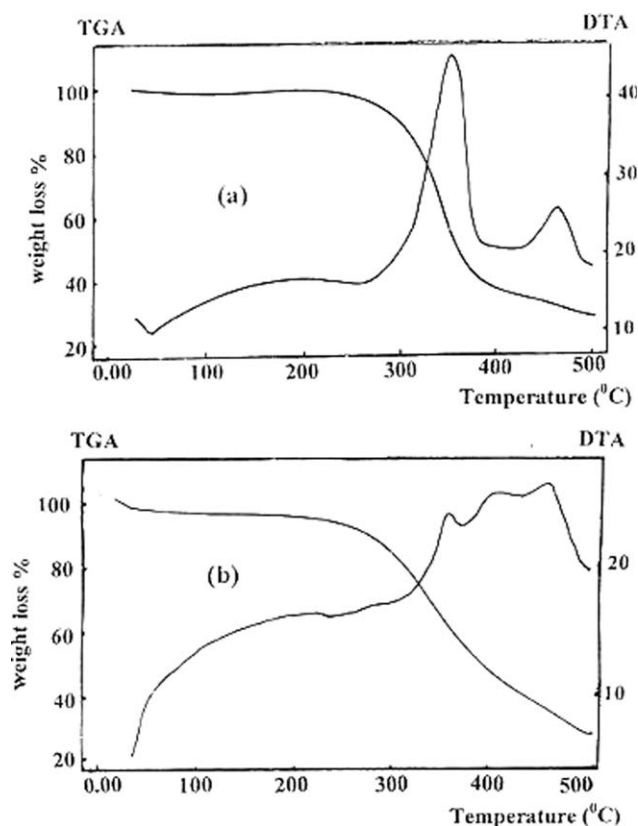


Figure 8 TGA and DTA for (a) Ungrafted paper sheet. (b) Paper gr-co-AN.

reduction in chain length because of bond scission with the generation of free radicals, dehydration, formation of carboxylic and carbonyl groups, CO₂ and CO emission, and carbon formation. The other process includes the depolymerization of cellulose by scission of the glucosidic units and formation of levo glucosan. The latter reactions occur simultaneously with the decomposition of the cellulose molecules.

From the DTA data, it is clear that there are different endo- and exothermic peaks in the above two stages confirm the degradation and recombination of the degradable fragments discussed above. In case of the ungrafted paper sheet, there are two exothermic peaks centered at 351.4 and 462.6°C. In case of paper sheet grafted with AN, there are three exothermic peaks at 335, 411, and 440°C. From the above observations, one can conclude that the maximum in decomposition rate in case of the grafted paper sheet is higher than the ungrafted paper sheet by about 60°C which means that the graft paper sheet is more heat resistance than ungrafted one (c.f., Table IV and Fig. 8).

CONCLUSION

The above results reveal the following conclusions:

1. The increase of both initiator and AN concentrations enhance the graft copolymerization reaction. Also the raising of the reaction temperature enhances the graft process.
2. From the kinetic data, we can calculate the order of the reaction with respect to the initiator and monomer concentrations, the rate law in our case is as follows: Rate = $K_2[\text{initiator}]^{0.54}[\text{monomer}]^{1.13}$. The apparent activation energy (E_a), the thermodynamic parameters (ΔH^* and ΔS^*) are calculated and the data are 32.61×10^3 J/mol and -63.4×10^3 J/(mol K), respectively.
3. The graft copolymerization reaction of AN onto paper sheet is established through the infrared spectroscopic analysis on the ungrafted paper sheet and the grafted product.
4. The X-ray diffraction pattern of paper sheet and the grafted product with AN shows a small portion of crystallinity in case of the grafted product. The scanning electron microscopy pictures of the ungrafted and grafted paper sheet shows that the pores present in the paper sheet are filled by the grafting process and the cellulosic fibers were coated with polymeric chains leading to higher porosity values.
5. The mechanical properties of the grafted paper sheet are higher than the ungrafted one, also the porosity of the grafted product is higher than the ungrafted one.
6. The chemical resistance of the grafted product is higher than the ungrafted paper sheet.
7. From the TGA data, it is clear that the grafting process on the paper sheet enhances its heat resistance.

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