Some investigations and characterization of radiation-initiated graft polymerization onto fluorinated copolymer

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(Received 21 March 1991; accepted 25 June 1991)

Preparation of a good hydrogel supported on a fluorinated polymer film has been achieved by means of simultaneous radiation-induced grafting of N-vinyl-2-pyrrolidone (NVP) onto (tetrafluoroethylene-perfluorovinyl ether) copolymer (PFA). The conditions at which the graft polymerization proceeded with a suitable yield were determined. Ammonium ferrous sulphate (Mohr's salt), as an inhibitor, failed to inhibit the homopolymerization of NVP during the radiation grafting process. In contrast, the addition of Cu_2Cl_2 (0.5 wt%) effectively inhibited the homopolymerization process and smooth grafted films with suitable grafting yield were obtained. The grafting onto PFA films, which scarcely swell in any solvent or monomer, was critically controlled by the diffusivity of reactants through the grafted layers initially formed near the film surface. The addition of $ZnCl_2$ (3 wt%) to the monomer solution slightly enhanced the grafting and much smoother grafted films were obtained. The dependence of initial rate of grafting on NVP concentration was of the order 0.54. The graft copolymer possessed good mechanical properties and high thermal and chemical stability. Such non-ionic supported hydrogel on fluorinated polymer may be of interest for some practical use in which high electrical conductivity is not required, as in biomaterials.

(Keywords: grafting; fluorinated polymers; vinyl pyrrolidone)

INTRODUCTION

Fluorine-containing polymers have drawn much attention in the past and gained wide practical use because of their thermal and chemical stability and mechanical properties. Recently, much work has been devoted to studying radiation-induced grafting onto fluorinated polymers[1–10]. However, only a few studies have reported on the radiation grafting of vinyl and acrylic monomers onto PFA as a trunk material[7,11,12].

Radiation grafting covers a very broad field of polymer chemistry with numerous potential applications of industrial interest. It is a well known method for modification of the chemical and physical properties of polymers, and is of particular interest for achieving specifically desired properties.

The water-soluble monomers such as acrylic acid, acrylamide and N-vinylpyrrolidone easily homopolymerized during radiation grafting processes and the grafting is heterogeneous. Therefore, the inhibition of such homopolymerization without interfering too much in the grafting process is very important. It can be achieved by using some additives and/or selective inhibitors.

In this study, the preparation of supported hydrogel-(NVP) onto PFA is achieved by using radiation as an initiator. The effect of different inhibitors on the grafting yield and homopolymerization of NVP was investigated. Some selected properties of the prepared graft copolymer were studied.

EXPERIMENTAL

Materials

PFA film of thickness 60 μm (Mitsui Fluoro Chemical Co. Ltd., Japan) was washed with acetone and dried in a vacuum oven at room temperature. N-vinyl-2-pyrrolidone (NVP), Aldrich Chem. Co. Inc., of purity 99% was used. The other chemicals were reagent grade and used as received.

Grafting method

A glass ampoule containing the monomer solution and film sample was deaerated by bubbling nitrogen for 5–7 min, sealed and then subjected to ^{60}Co γ-radiation at a dose rate of 0.2 Gy s^{-1}. The grafted film was washed thoroughly with hot distilled water and soaked overnight in water in order to extract any residual monomer or homopolymer that may have occluded in the film. The grafted film was then dried in a vacuum oven at 60°C for 24 h and weighed. The degree of grafting (G(%)) was determined by the percentage increase in weight:

$$G(\%) = 100(W_g - W_0)/W_0$$

0032-3861/92/204230-06

where W_0 and W_g represent the weights of initial and grafted films, respectively.

Thermal and chemical stability

Thermal stability tests were made in air by keeping the grafted films at a predetermined temperature for 6 h. For chemical stability tests the grafted films were soaked in different mineral and organic acids for 6 h at room temperature (30°C). The percentage weight loss ($\Delta w(\%)$) in the grafted films was then determined.

Electrical conductivity

Electrical conductivity measurements were made by using a Multi-Mega ohm meter, MOM 11 (Germany).

Mechanical properties

A dumbell-shaped specimen of 80 mm length, with a neck of 25 mm and width of 4 mm was used. The tensile strength and elongation percentage at break were measured by an Instron (Model 1195, UK) at a crosshead speed of 5 cm min^{-1}.

I.r. spectroscopy

I.r. spectroscopy was performed for the grafted and original films by using a Perkin Elmer 398 IR Transmissions Spectrophotometer in the range of wavenumber from 400 to 4000 cm^{-1}.

Swelling measurements have been made by using the same method as described in previous studies[13,14].

RESULTS AND DISCUSSION

Effect of inhibitor

Table 1 shows the influence of ammonium ferrous sulphate (Mohr's salt) on the grafting of aqueous NVP onto PFA films. The degree of grafting increases by the addition of (0.1 wt%) Mohr's salt, but it decreases sharply as the inhibitor concentration increases. Meanwhile, the homopolymerization process of NVP was not inhibited by using Mohr's salt. The grafted films prepared under these conditions were not smooth and the grafting was heterogeneous.

Figure 1 shows the effect of Cu_2Cl_2 concentration on the degree of grafting of NVP onto PFA films. It can be seen that the degree of grafting significantly increases in the presence of Cu_2Cl_2 in low concentration ranging from 0.1 to 0.6 wt%. Thereafter, the degree of grafting tends to decrease as the concentration of Cu_2Cl_2 increases. It was observed that no significant homopolymer was formed in the presence of Cu_2Cl_2, consequently smooth and flat grafted films were obtained.

Since fluorinated polymers hardly swell in any solvent or monomer solutions, the grafting onto PFA film may proceed by the front mechanism in which the monomer solution diffuses through the grafted layer initially formed near the film surface[5,7,9]. Therefore, the grafting process is critically controlled by the diffusivity of monomer solution into the polymer matrix. The diffusion of aqueous NVP into the polymer film was probably restricted by the viscous homopolymer formed in the absence of Cu_2Cl_2 and/or in the presence of Mohr's salt. As a consequence, the graft polymerization is localized on the film surface and terminated at low degrees of grafting. However, in the presence of Cu_2Cl_2 with low concentration, the diffusivity of monomer solution into the polymer may be enhanced due to the inhibition of homopolymerization process. At higher concentrations, some Cu_2Cl_2 may have penetrated inside the polymer film and the grafting process was inhibited to some extent, so the grafting yield was lowered. The addition of 0.5 wt% of Cu_2Cl_2 was enough to effectively inhibit the homopolymerization without interfering too much in the graft polymerization, hence reasonable degrees of grafting were obtained.

Table 1 Effect of Mohr's salt on the grafting of aqueous NVP(50 wt%) onto PFA films at 20 kGy

Mohr's salt concentration (wt%)	Degree of grafting (%)
–	5
0.1	67
0.2	19
0.6	9
1.0	8
1.5	7

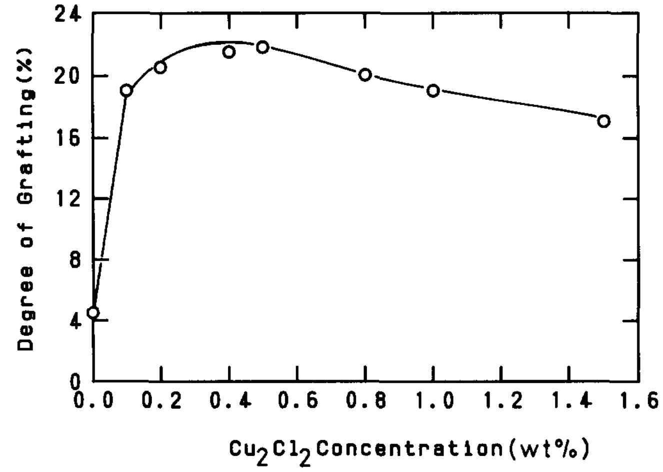

Figure 1 Effect of Cu_2Cl_2 concentration as inhibitor on the grafting of NVP(50 wt%) onto PFA films at 20 kGy

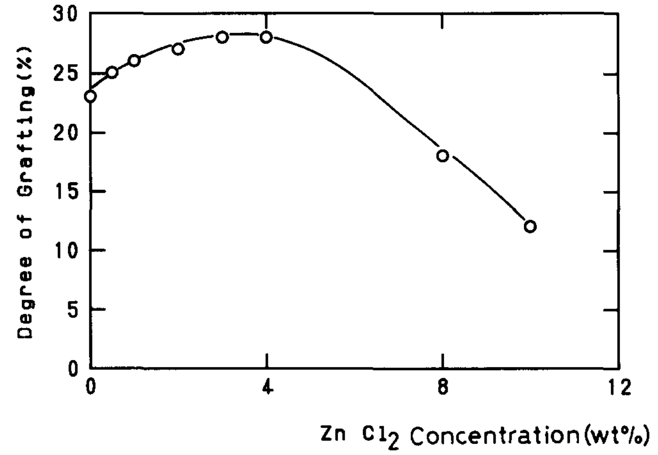

Figure 2 Effect of $ZnCl_2$ concentration on the grafting of NVP(50 wt%) onto PFA films at 20 kGy with 0.5 wt% Cu_2Cl_2 as inhibitor

Effect of $ZnCl_2$

Figure 2 shows the effect of $ZnCl_2$ concentration on the grafting yield of aqueous NVP onto PFA films in the

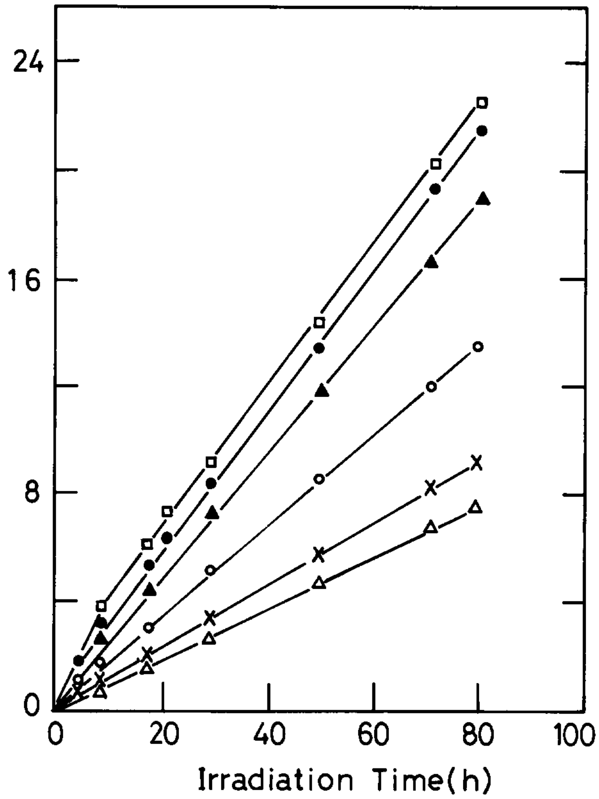

Figure 3 Degree of grafting *versus* irradiation time for the grafting of NVP onto PFA films at various NVP concentrations: (×) 5; (○) 15; (▲) 30; (□) 50; (●) 70; (△) 95 wt%; 0.5 wt% Cu_2Cl_2 as inhibitor

presence of 0.5 wt% Cu_2Cl_2. The grafting yield slightly increases with $ZnCl_2$ concentration and then decreases gradually at higher concentrations. The enhancement effect of $ZnCl_2$ for this grafting system is not remarkable. However, it was observed that the grafting in presence of such inorganic salt seems to be more homogeneous and the grafted films are much smoother and flatter compared with those obtained in the presence of Cu_2Cl_2 alone.

In a previous study[13], it was found that $ZnCl_2$ significantly enhanced the graft polymerization of aqueous NVP onto LDPE films. Such enhancement effect was attributed to the formation of a complex between $ZnCl_2$ and the C=O group of NVP, i.e. raising the polarity of monomer. This leads to the increase in the conjugation energy of the π-electron of the C=C of the vinyl group of NVP monomer; hence $ZnCl_2$ affects the rates of elementary polymerization reactions. Therefore, in such a case the formation of longer grafted chains is expected, and higher degrees of grafting were obtained. However, in the present study, the diffusion of $ZnCl_2$ into the polymer matrix is rather difficult because of the poor swelling behaviour of PFA films, so its enhancement effect for this grafting system is limited.

Effect of NVP concentration

Figure 3 shows the effect of irradiation time on the degree of grafting at various aqueous NVP concentrations. The degree of grafting increases linearly with irradiation time for all NVP concentrations. It can be seen that for concentrations ranging from 5 to 50 wt%, the higher the NVP concentration the higher the degree of grafting obtained. However, at concentrations higher than 50 wt%, the initial rate and degree of grafting per dose decrease sharply compared with those obtained at lower concentrations.

Figure 4 shows the logarithmic relationship between the initial rate of grafting and monomer concentration. The effect of NVP concentration on the grafting yield at constant dose (58 kGy) is also shown in *Figure 4*. The initial rate of grafting increases linearly with NVP concentration when ranging from 5 to 50 wt%, but thereafter it drops at higher concentrations. Similar behaviour is observed for the grafting yield obtained at an irradiation dose of 58 kGy.

The behaviour observed for this graft polymerization is typical of a reaction in which the kinetics are critically controlled by the rate of diffusion of monomer into the film[8,15]. It was reported by Chapiro[15] that the maximum rate of grafting appears at *ca.* 60% NVP solution in benzene during the direct radiation grafting onto PTFE films at 50°C. In the same study, the rate of grafting dropped sharply at higher monomer concentrations. The same behaviour was also observed in our previous study on the post-radiation grafting of aqueous NVP onto PTFE and FEP films[8].

The dependence of initial rate of grafting on monomer concentration is calculated from the linear part to be of the order 0.54. This result may indicate that this grafting system proceeds by a radical mechanism with bimolecular termination of growing chain radicals[6]. The decrease in grafting rate and yield at high NVP concentrations is probably due to the enhancement of some homopolymer formation at such concentrations and the viscosity of the reaction medium increased. This resulted in decreasing the rate of monomer diffusion and the grafting was lowered.

Swelling behaviour

Figure 5 shows the percentage water uptake for the grafted films as a function of degree of grafting. The percentage water uptake initially increases proportionally with degree of grafting and it tends to level off above 40% grafting. The extent of water uptake for the PFA-g-PNVP films is much lower than that observed for LDPE-g-PNVP in the previous study[13]. This is due to the difference in rate of water diffusion through the

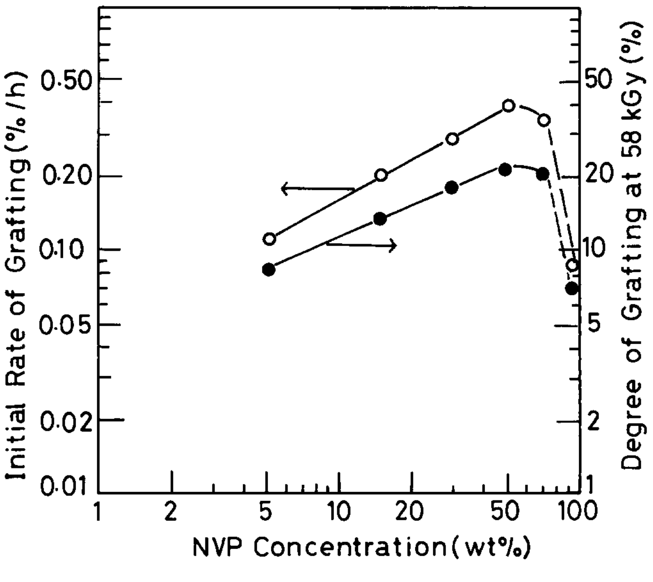

Figure 4 Logarithmic plots of initial grafting rate and grafting yield obtained at 58 kGy *versus* NVP concentration

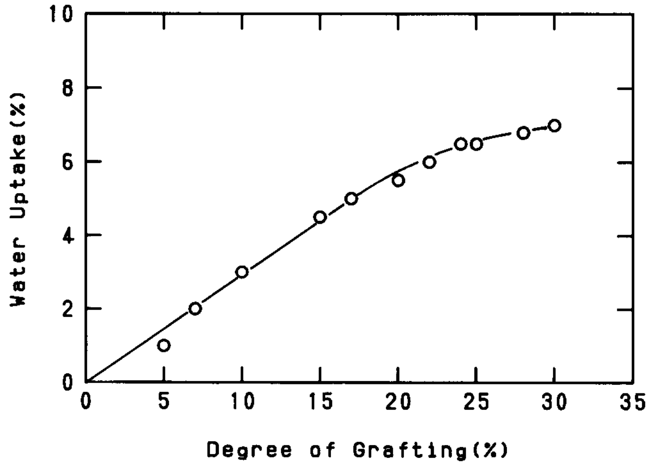

Figure 5 Percentage water uptake *versus* degree of grafting for the grafted films

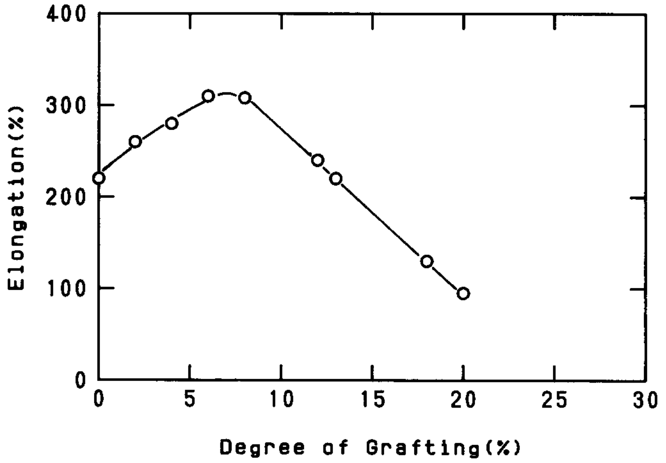

Figure 6 Percentage elongation for the grafted films *versus* degree of grafting

grafted chains in both systems, since the diffusion through PFA-g-PNVP graft copolymer is more difficult.

It can be assumed that a crosslinking network structure is formed in the grafted film and its content in the bulk of polymer substrate increased as the degree of grafting increased. Consequently, the swelling of the grafted films tended to level off at higher percentage of grafting because of the restriction on water diffusivity through such network structure.

Mechanical property

Figures 6 and *7* show the change in percentage elongation and tensile strength respectively, for the PFA-g-PNVP copolymer. The percentage elongation gradually increases with degree of grafting to reach a maximum around 8% grafting. Thereafter, it gradually decreases with further increase in degree of grafting. Tensile strength gradually increases with degree of grafting and tends to level off at higher degrees of grafting.

Results suggest that at lower degrees of grafting, the grafting process occurred near the surface of the film and the crosslinking network structure was not formed throughout the whole bulk of the polymer. Therefore, the percentage elongation increases because of some steric effect of such randomness in the grafting process.

However, at higher degrees of grafting, the grafting may have reached into the centre of the film and the crosslinking network structure formed in the bulk of the polymer. Therefore, a decrease in percentage elongation and an increase in tensile strength were observed.

Thermal and chemical stability

Figure 8 shows the percentage remaining weight for the grafted films as a function of annealing temperature. There is no significant weight loss of the grafted films at temperatures below 200°C. Thereafter, the weight decreased gradually as the temperature was elevated. Such weight loss increases above the softening point of the polymer substrate (over 250°C).

Table 2 shows the chemical stability of the graft copolymer, which was soaked in different acidic solutions for 6 h. No significant weight loss in the grafted films was observed, especially at lower degrees of grafting. At higher degrees, the percentage weight loss in the grafted films is about 1%.

Results showed that such hydrogel supported on fluorinated polymer possesses good thermal and chemical stability, which may make it acceptable for some practical uses.

Electrical conductivity

Figure 9 shows the semi-logarithmic relationship between the specific electrical conductivity and degree of

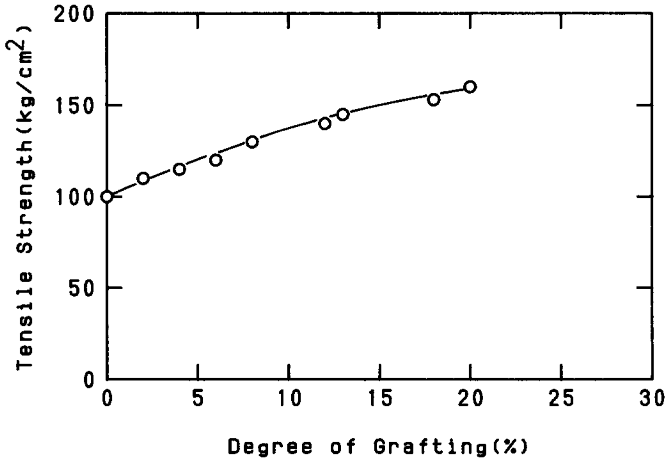

Figure 7 Tensile strength for the grafted films *versus* degree of grafting

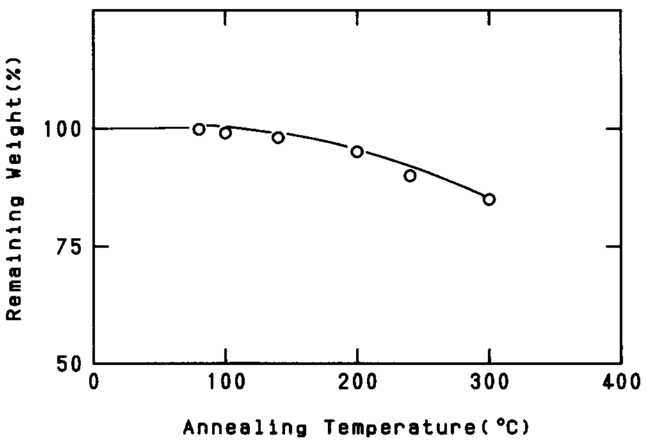

Figure 8 Thermal stability of the grafted films having 19.5% grafting at different annealing temperatures for 6 h annealing time

Table 2 Chemical stability of the grafted films soaked for 6h in different acidic solutions at room temperature (30°C) expressed as weight loss (%)

	Weight loss (%)		
Degree of grafting (%):	4	10	19.5
Acetic acid (5N)	0.1	0.3	1.0
H_2SO_4 (5N)	0.1	0.2	0.6
Oxalic acid (2.5N)	0.15	0.2	0.7

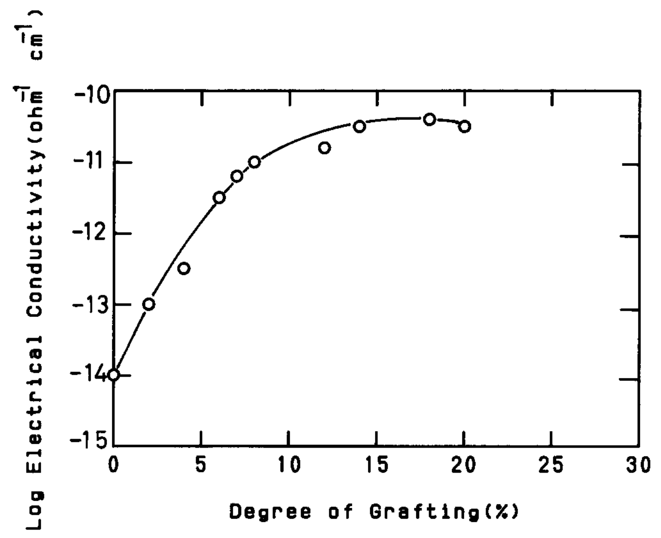

Figure 9 Semi-logarithmic relationship between the specific electrical conductivity of the grafted films and degree of grafting

grafting. The specific electrical conductivity initially increases proportionally with the degree of grafting and it levels off above 8% grafting. This result is coincident with that obtained for the mechanical properties and swelling behaviour of the graft copolymer.

This result can be reasonably explained by assuming that the mobility of grafted chains is probably higher at low degrees of grafting due to the smaller amount of crosslinking compared with that at higher degrees of grafting. This resulted in increasing the specific electrical conductivity of the graft copolymer. However, at higher degrees of grafting, the crosslinked network structure restricted the mobility of graft chains and no further increase in specific electrical conductivity was observed. It can be expected from the behaviour of specific electrical conductivity that the grafting may reach the centre of film at degrees of grafting higher than 8% grafting[11]. The effect of ionizing radiation on the polymer substrate during the radiation grafting process must also be taken into consideration and its influence on the electrical properties included[16].

I.r. spectroscopy

I.r. spectra of the grafted and original films are shown in *Figure 10*. On the grafting of NVP onto PFA, certain changes are encountered in the i.r. spectra of the grafted films. The main characteristic features of the i.r. spectra of the graft copolymer are the appearance of new bands around 3400, 1650, 1450 and 850 cm^{-1}. These bands are characteristic for the structure of NVP. The strong broad band that appears at 3400 cm^{-1} is assigned to the hydroxyl groups and/or hydrogen bonding, which may indicate the existence of crosslinking network structure

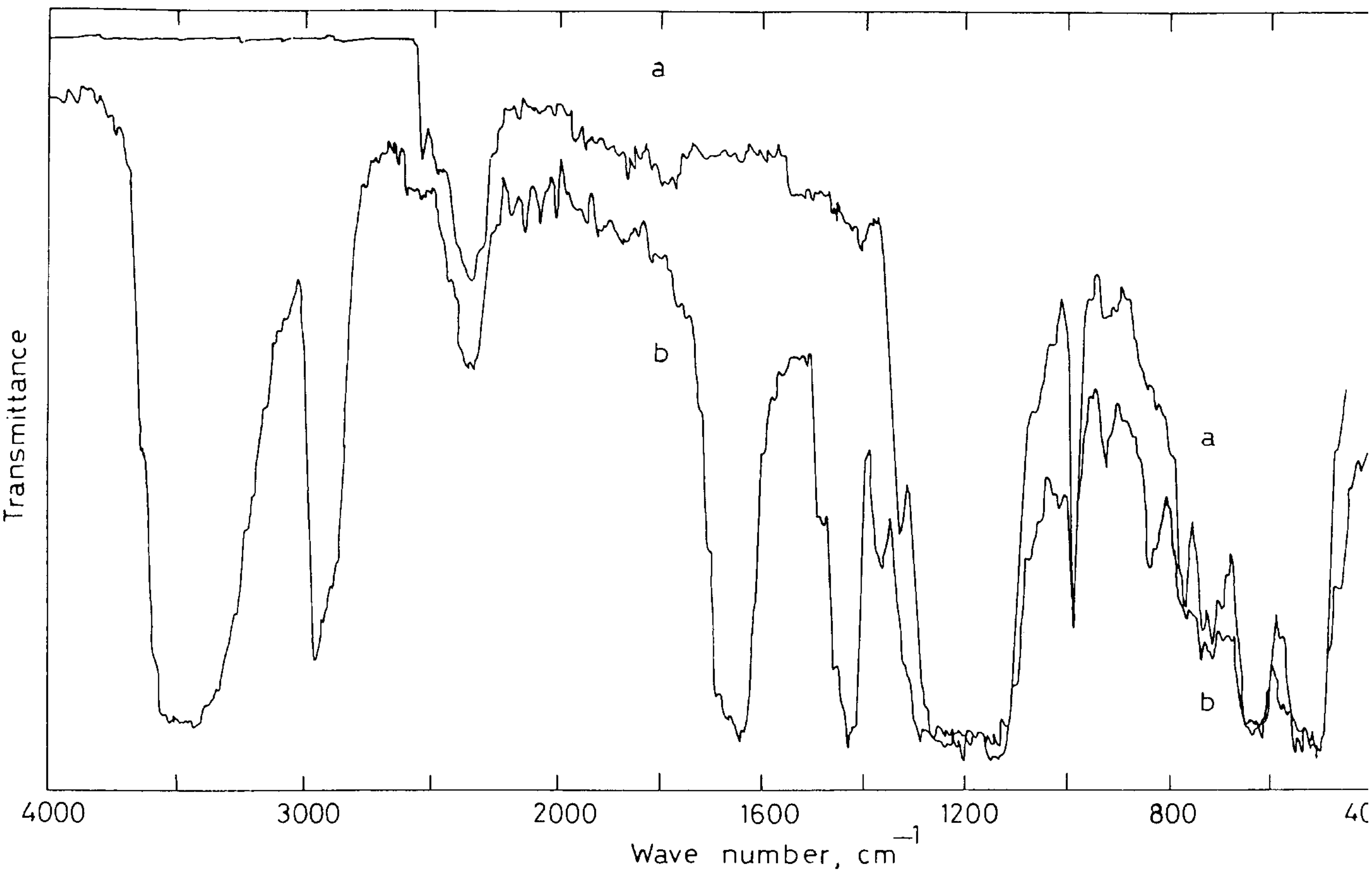

Figure 10 I.r. spectra of the original and grafted films: (a) original PFA film; and (b) grafted film having 19.8% grafting

in the graft copolymer[6,17]. The band appearing at 850 cm^{-1} is probably due to the change in crystallinity and morphology of the polymer caused by grafting and crosslinking[17]. The degree of grafting can be followed from the intensity of the band appearing at 1650 cm^{-1}, which is assigned to the C=O groups of the NVP structure.

CONCLUSIONS

The radiation-induced graft polymerization of aqueous NVP onto PFA films was achieved by the addition of Cu_2Cl_2 as an inhibitor. Smooth and flat grafted films were obtained. The addition of Mohr's salt to the reaction medium, however, failed to inhibit the homopolymerization process and the grafting was not homogeneous. The enhancement effect of $ZnCl_2$ on the grafting process by forming a complex with the C=O group of the NVP structure is limited due to the restriction in its diffusion into the PFA matrix. The grafted films possessed good thermal and chemical stability, suitable mechanical properties for handling, reasonable swelling and electrical properties. Therefore, such grafted copolymer may be of interest in some practical applications in which the high electrical conductivity is not required, such as biomaterials. Poly(vinylpyrrolidone) has been applied for more than 30 years in plasma expander without toxic effects[18] and can be used in contact with blood for long periods.

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