

GRAFTING ONTO WOOL V. RADIATION-INITIATED GRAFTING OF ACRYLIC ACID ONTO WOOL FIBER*

ZHAO Xin (赵新), LI Cui (李崔), ZHOU Zixiong (周自雄),
WANG Tiandiao (王天雕) and CHEN Shanming (陈善明)

*(Xinjiang Institute of Physics, Chinese Academy
of Sciences, Urumqi, Xinjiang 830011)*

ABSTRACT

This paper deals with graft copolymerization of acrylic acid (AA) onto Xinjiang fine wool fiber in aqueous medium initiated by gamma rays. Graft copolymerization was carried out by the mutual irradiation method in limited air. Percent grafting and percent efficiency have been determined as a function of total dose, dose rate, concentration of monomer, wool weight and reaction temperature. Graft copolymers are characterized with infrared (IR) spectroscopy, scanning electron microscopy (SEM), and X-ray diffractometer. Properties of the grafts were studied, and compared with the virgin fiber.

INTRODUCTION

The oxygen-free atmosphere required for graft copolymerization is not economical in the textile industry. To face the problem, many scientists are engaged in investigating the suitable initiating systems for graft copolymerization and for imparting better properties onto wool by grafting some novel macromolecules^[1-3].

In recent years, chemical modification of wool through grafting of vinyl monomers such as acrylic acid^[4], acrylamide^[5] and methyl acrylate^[6] has received considerable interest. As grafting by radiation is a uniform and clean method and the degree of grafting can be easily controlled, radiation grafting has also been used to initiate grafting of vinyl monomers^[7-8] onto wool. In our project, we have already grafted poly (acrylonitrile) onto wool in the presence of air, with very interesting results^[9]. The present study has been carried out by grafting acrylic acid (AA) onto wool in the presence of air using gamma rays as means of initiation, and the behaviour of the grafts and

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virgin fibers towards alkali and acid have also been investigated.

EXPERIMENTAL

Material

The wool fiber was purified by continuous extraction with petroleum ether. It was then washed with warm acetone, followed by distilled water and air dried. The monomer acrylic acid was purified by distillation at 60°C under a reduced pressure of nitrogen.

Graft copolymerization

Pure Xinjiang fine wool fiber (0.1g) was immersed in 20ml water in a 50ml reaction tube equipped with medical grade rubber stopper. Definite amount of monomer was added to the reaction tube. Gamma irradiation of the reaction mixture was carried out in a 2×10^{15} Bq Cobalt-60 source at room temperature and the graft copolymerization by mutual technique was performed with various doses. After the completion of graft copolymerization, homopolymer was removed from the grafts by solvent extraction in warm distilled water for four hours and the residue obtained was dried until constant weight. Percent grafting and percent efficiency were calculated as follows:

$$\text{percent grafting} = (W_2 - W_1) / W_1 \times 100\%$$

$$\text{percent efficiency} = (W_2 - W_1) / W_3 \times 100\%$$

Where W_1 , W_2 , and W_3 are the weights of wool, grafted wool and monomer used, respectively.

Instruments

(1) The infrared spectra of the samples were taken on IR-27G spectrophotometer using KBr pellet technique. (2) scanning electron photomicrographs was taken on JEM-1200Ex/s with SEM-ASID10, voltage of operation is 40KV. (3) The study of the structure of the PAA-g-Wool graft copolymers was performed by the method of structure analysis at wide angles on Rigaku D/max equipped with a nickel filter, $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

Effect of total dose

The effect of total dose on the grafting of AA onto wool was studied by varying dose in the range of 0.5×10^3 to 3.0×10^3 Gy (Gray < Gy > is the

unit of absorbed dose and $1\text{Gy}=1\text{J/Kg}$). Table 1 shows the changes in percent grafting with increase in total dose at the dose rate of $3.4\times 10^3\text{Gy/h}$. It is observed that percent grafting increases steadily with increasing dose and maximum value occurs at total dose of $2.5\times 10^3\text{Gy}$. Further increase in total dose decreases the percentage of grafting. This indicates that at higher dose, various radical species formed are engaged in mutual termination of growing grafting chains and homopolymerization becomes the preferred process.

Table 1 The effect of total dose on percent grafting of PAA onto wool by mutual gamma irradiation method *

Sample No.	Total dose ($\times 10^4\text{ Gy}$)	Percent grafting (%)
1	0.5	3.16
2	1.0	7.49
3	1.5	7.18
4	2.0	7.92
5	2.5	8.20
6	3.0	7.53

* wool=100mg, water=20ml, dose rate= $3.4\times 10^3\text{ Gy/h}$,

[AA]=0.63 mol/L, at 25°C .

Effect of dose rate

Table 2 describes that the percentage of grafting increases with the

Table 2 The effect of dose rate on percent grafting of PAA onto wool by mutual gamma irradiation method *

Sample No.	Dose rate ($\times 10^4\text{ Gy/h}$)	Percent grafting (%)
1	1.38	7.26
2	3.40	8.20
3	5.70	8.90
4	15.12	8.53

* wool=100mg, water=20ml, total dose= $2.5\times 10^3\text{ Gy}$,

[AA]=0.63 mol/L, at 25°C .

increasing dose rate and reaches maximum value at dose rate of $5.7\times 10^3\text{ Gy/h}$. Further increase in dose rate decreases the percent grafting. With the

increase in dose rate from 1.38×10^3 to 5.7×10^3 Gy/h, the active sites on wool increase, and AA may react directly with the active sites on wool to produce graft, besides the growing polymeric chain it may also interest with the active sites to produce graft. Therefore the graft process becomes the preferred process, leading to an increase in percent grafting.

Effect of concentration of monomer

Table 3 represents the effect of concentration of monomer on percentage of grafting. It is observed from Table 3 that percent grafting increases with increasing concentration of monomer. Maximum grafting (8.67%) is obtained at $[AA]=0.94$ mol/L. This may be explained by the fact that with the increase of concentration of monomer, the collision probability between monomer and the active sites on wool backbone increases, leading to an increase in percent grafting. However, further increase in concentration of monomer decreases the percent grafting. This may be due to the fact that at higher monomer concentration, homopolymer formation as well as wastage reactions due to monomer transfer are accelerated.

Table 3 The effect of concentration of monomer on grafting of PAA onto wool by mutual gamma irradiation method *

Sample No.	Monomer concentration (mol/L)	Percent grafting (%)
1	0.13	4.53
2	0.31	5.67
3	0.63	8.20
4	0.94	8.67
5	1.25	7.80

* Wool=100mg, water=20ml, dose rate= 3.4×10^3 Gy/h, total dose= 2.5×10^3 Gy, at 25°C.

Effect of amount of wool

Table 4 clearly shows the effect of wool weight on percent grafting of PAA onto wool by mutual gamma irradiation method. Percent grafting was observed to decrease with the increase in the amount of wool while percent efficiency had an adverse effect on at the identical conditions. The results are in agreement with that of Shukla et al. ^[10,11] This may be explained that with the increasing in the amount of wool the chance of creation of more active sites were increased, leading to increase efficiency, and the percent

grafting decreased due to primary free radicals, which remained almost in constant amount.

Table 4 The effect of wool weight on percent grafting of PAA onto wool by mutual gamma irradiation method *

Sample No.	Wool weight (g)	Percent grafting (%)	Percent efficiency (%)
1	0.1061	8.20	1.92
2	0.5060	5.22	5.81
3	1.0678	3.95	9.30
4	1.7787	1.68	6.89

* Water=20ml, total dose= 2.5×10^3 Gy, [AA]=0.63mol/L, dose rate= 3.4×10^3 Gy/h, at 25°C.

Effect of temperature

The effect of temperature on percent grafting of AA onto wool has been recorded in Table 5. It is observed from the table that percent grafting decreases with the increase of temperature from 25°C to 55°C. With an increase in temperature, the termination of grafting chain free radicals^[12,13] and the formation of large amount of homopolymer may be the main cause of the decrease of grafting yield.

Table 5 The effect of temperature on percent grafting of PAA onto wool by mutual gamma irradiation method *

Sample No.	Temperature (°C)	Percent grafting (%)
1	25	8.20
2	35	7.62
3	45	7.12
4	55	5.94

* Wool=100mg, water=20ml, dose rate= 3.4×10^3 Gy/h, total dose= 2.5×10^3 Gy, [AA]=0.63 mol/L.

Characterization of graft copolymer

1. On comparison of IR spectra of wool and PAA-g-wool, it is observed from Fig. 1 that a strong peak at 1390 cm^{-1} in the grafted sample assigned to $>\text{C}=\text{O}$ group of PAA, and a weak peak at the same band is in the IR spectrum of wool. This indicates that PAA covalently bonded to wool backbone^[9], that is the formation of graft copolymers.

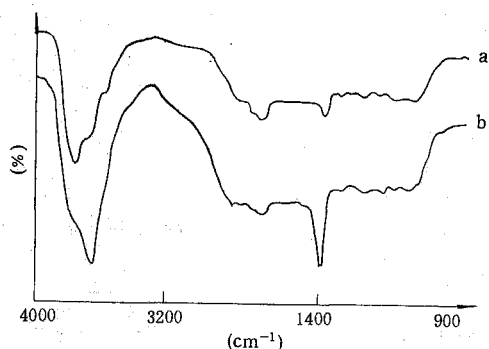


Fig. 1 The IR spectra of wool and PAA-g-wool
(a) Wool; (b) PAA-g-wool

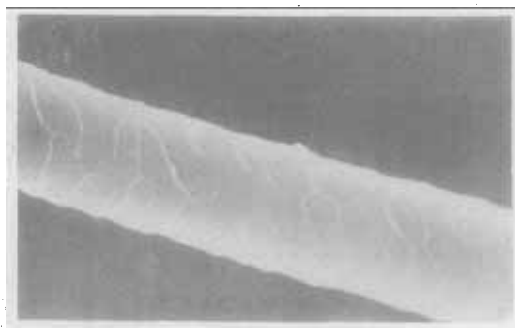


Fig. 2 The scanning electron micrographs of grafted wool

2. The comparative study of scanning electron micrographs of wool and grafted wool gave another strong evidence for true grafting of PAA onto wool as seen in Fig. 2.

Table 6 The X-ray diffraction data of wool and its copolymer *

Sample No.	d_1	d_2	r_{1s}	r_{2s}
Wool	5.65	12.50	6.84	41.70
PAA-g-wool	5.59	11.81	6.10	24.20

* d_1 stands for the average distance between adjacent molecules, and r_{1s} for short-range order of non-crystalline substance.

3. Table 6 describes the X-ray diffraction data of wool and its grafted copolymer. Wool can be considered as non-crystalline substance as its crystallinity is low. It is observed from Table 6 that the scope for short-range order of grafted wool is lower than that of virgin fiber, so is the average distance between adjacent molecules.

Physical properties of graft copolymer

1. Solubility in alkali solution

The behavior of the graft copolymer and the virgin wool fiber towards alkali was tested by determining the percentage of solubility in alkali with time. For this, the samples were immersed separately in aqueous solution of 0.1 mol/L NaOH solution for 1h at 45°C using wool—liquor ratio of 1 : 100. The method used was similar to that of Giri et al. [14] The treatment showed that the grafted samples are easily soluble in alkali than the virgin wool fiber. This is probably due to the formation of the corresponding sodium salts, and to some extent due to the solubility of polyacrylic

acid chain.

2. Solubility in acid solution

A similar procedure was adopted with 0.1 mol/L HCl using a wool—liquor ratio of 1 : 100 at room temperature. The result of acid treatment showed that the grafted samples have better resistance towards acid than the virgin wool fiber.

Keywords:

Graft copolymerization; Gamma radiation; Properties of wool fiber; Alkali and acid solubility

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