Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

IMPROVED DYEABILITY AND MECHANICAL PROPERTIES OF WOOL FIBERS GRAFTED WITH POLY(ACRYLIC ACID) BY GAMMA-RADIATION

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Online publication date: 31 October 2001

To cite this Article El-Mosallamy, El-Said H.(2001) 'IMPROVED DYEABILITY AND MECHANICAL PROPERTIES OF WOOL FIBERS GRAFTED WITH POLY(ACRYLIC ACID) BY GAMMA-RADIATION', Journal of Macromolecular Science, Part A, 38: 11, 1167 — 1174
To link to this Article: DOI: 10.1081/MA-100107136
URL: http://dx.doi.org/10.1081/MA-100107136

J. MACROMOL. SCI.—PURE APPL. CHEM., A38(11), 1167–1174 (2001)

NOTE

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ABSTRACT

Graft copolymerization of acrylic acid onto wool fibers was carried out using a γ-radiation induced technique. The degree of grafting was influenced by the monomer concentration and the radiation dose. The changes in the polymorphism of the grafted wool fibers were investigated and compared with that of the parent fibers. A further increase in the degree of grafting was found to cause a slight reduction in moisture sorption. Affinity towards basic dye and the mechanical properties of wool fibers were improved by the graft process.

Key Words: Wool fibers; Poly(acrylic acid); Grafting; Dyeability; Mechanical properties

INTRODUCTION

Although, natural fibers possess better wearing properties than synthetic fibers, a number of properties such as dyeability, thermal stability, acid and alkali resistance, and mechanical properties have to be attended to. Grafting by either chemical initiation [1-6] or radiation induced reactions [7-10] are considered the most suitable methods to attain such changes in properties. It has been reported in the literature that wool grafted with polymers have better acid and alkali resistance and dyeability, but the tensile strength still did not improve [11-13], however, a few such as grafting poly(acrylic acid) onto wool fibers initiated by quinquevalent Vanadium succeeded in improving their tensile strength [5].

Hence, in the present work, radiation-induced graft copolymerization of acrylic acid onto wool fibers was sought to influence the role of increasing fibers mechanical properties through grafting by induced radiation. The effect of a dose increase to the degree of grafting was carefully followed. The polymorphism of the native and grafted samples was investigated in addition to its effect on the dye-ability, moisture sorption and the mechanical properties of the wool fibers.

EXPERIMENTAL

Materials

Merino wool fibers of 23 μm diameter (supplied by Golden Tex. Company, Cairo, Egypt) was washed before used with a detergent (0.5 g/l Plexophore) in distilled water at 60°C for 30 minutes to remove any undesired materials. Acrylic acid (supplied by Merk, Germany) was purified by distillation under reduced pressure and the middle fraction was collected and used.

Safranine O (C.I. 50240 and λ_{max}= 530 nm) and Oil Red EGN (C.I. 50420 and λ_{max}= 520 nm) dyes are supplied by Aldrich Chemical, Germany. The structure of either are given below.

Grafting Process

One gram of dry wool fibers were immersed in 20 ml of acrylic acid/distilled water mixtures having different ratios in glass ampoules, Mohr·s salt (ammonium ferrous sulfate) was added to the mixture to minimize the homopolymer formation during the radiation process. The reactant mixtures were deaerated by bubbling nitrogen gas for 5 minutes and sealed. The sealed glass ampoules were then subjected to different γ-irradiation doses at room temperature using ^{60}Co gamma source situated at the National Center for Radiation Research and Technology with a dose rate of 1.6 kG_y/h. Grafted wool samples were removed and washed to remove the unreacted monomer and homopolymer, then dried and weighted. The degree of grafting was determined as the percentage increase in weight.

$$\text{Degree of grafting \%} = \frac{W_t - W_o}{W_o} \times 100$$

where W_o and W_t represent the weights of initial and grafted wool samples, respectively.

Relative Degree of Crystallinity

The relative degree of crystallinity for grafted wool fibers, as well as of the parent fibers, were investigated using a Philips X-ray diffractometer model PW 1140/90 and Fe-filtered CoK_a radiation. the X-ray patterns of the samples were

recorded automatically with a scanning speed of 2° per minute, and the scanning angular range (2θ) from 5 to 30°.

Moisture Sorption

Moisture sorption of pure and grafted wool fibers was determined by the vacuum desiccator method. Whereas, wool samples were placed in a small weighting bottle and dried in vacuum oven over 70°C to constant weight (W_d). The dried samples were then placed in a desiccator containing a saturated solution of potassium bromide (to give a relative humidity of 70% at 20°C ± 1) for 24 hours. The moisturized samples were weighted again (W_m) and the moisture regain is given by:

$$\text{Moisture sorption } \% = \frac{W_m - W_d}{W_d} \times 100$$

Dyeing Procedure

Dyeing of the grafted and controlled wool fibers using Safranine-O and Oil Red EGN were carried out for 60 minutes at 60°C using 1% of the dye, 15% Glauber·s salt and 10% acetic acid, the liquor-to-wool ratio was maintained at 100:1 [14]. After this, the wool sample was filtered and the optical absorbance of the filtrate was measured using a Unicam α-Helios UV vis spectrophotometer. From these results, the dye uptake by the wool fibers was computed.

Mechanical Properties

The mechanical properties in terms of tensile strength and elongation at break were tested for grafted and pure wool fibers at room temperature using a Spinlabe Sletometer Device.

RESULTS AND DISCUSSION

Effect of Monomer Concentration and Radiation Dose on the Degree of Grafting

The effect of monomer concentration on the degree of grafting was studied at various doses (Figure 1). The percentage of grafting was found to increase steadily with the monomer concentration and also by an increase in radiation dose. However, at a dose of 0.8 kG_y, increasing the monomer concentration more than 60% has no influence on the degree of grafting where increasing the percentage of homopolymer is the case instead. While, in the case of higher radiation doses

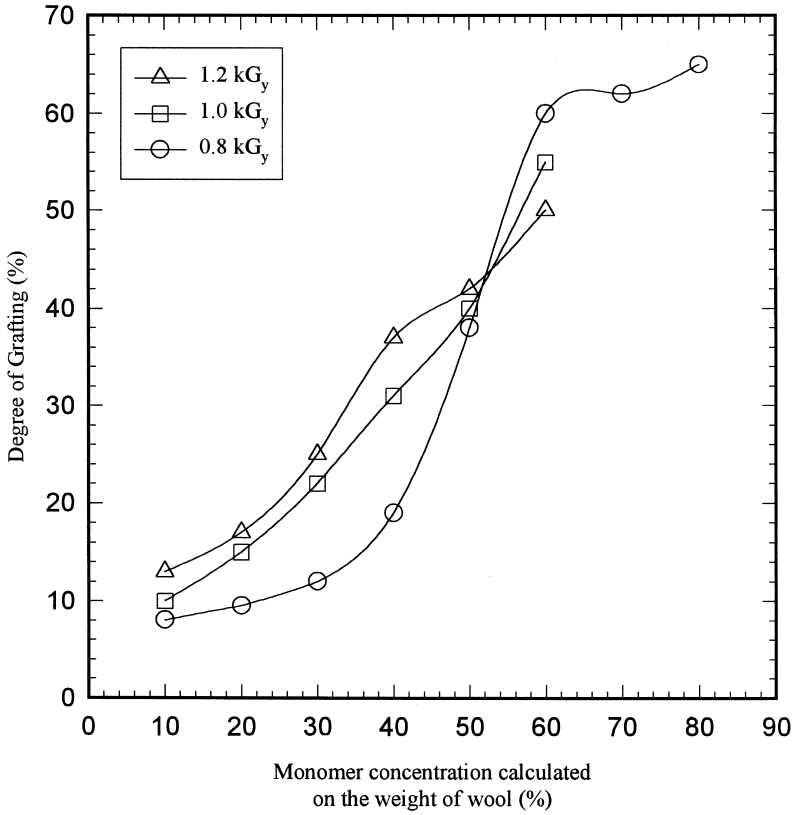

Figure 1. Degree of grafting onto wool fibers as a function of different acrylic acid concentrations at different radiation doses.

(1.0 and 1.2 kg_y), increasing the monomer concentration over 50%, hydrogel homopolymer forms rather than grafting [15].

Relative Degree of Crystallinity

The polymorphism of wool fibers was studied before and after grafting using X-ray diffraction. For pure wool fibers, two reflexes were noticed at $2\theta = 9.7$ and 21 which indicate that wool fibers is a semicrystalline material. The same reflexes appeared in the case of grafted samples, but with different intensities (Figure 2). The relative degree of crystallinity of most samples were calculated [16] and are given in Table 1. As shown, an increase in the degree of grafting was accompanied by a decrease in the relative degree of crystallinity. This can be explained on the basis of increasing the amorphous regions due to grafting proceeding the crystalline regions [17]. Thus, as the degree of grafting increases, the amorphous regions become predominant and shadow the crystalline feature of the fiber.

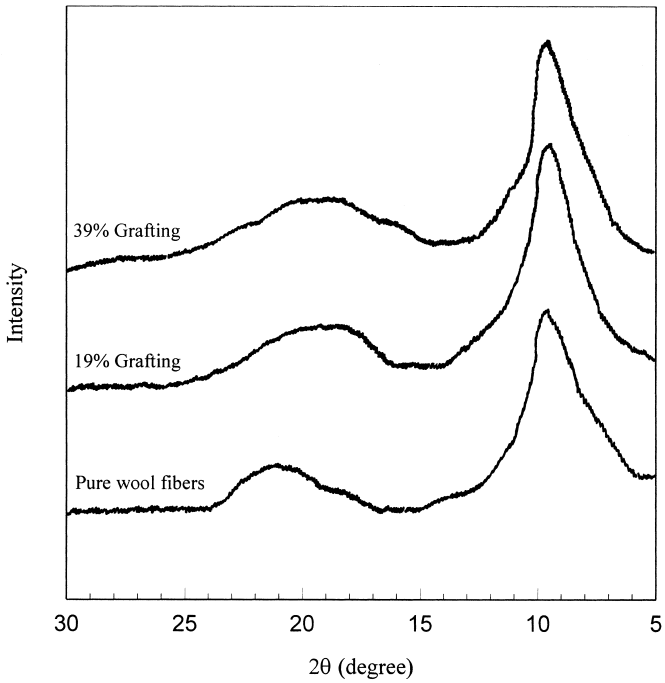

Figure 2. X-ray diffraction patterns for pure and grafted wool fibers.

Moisture Sorption

The hydrophobic properties of grafted wool fibers were tested in terms of moisture sorption, (Table 1). An increase of grafting percent causes a slight decrease in the moisture sorption which is explained on the basis of the molecular

Table 1. Effect of Grafting's Degree on the Relative Degree of Crystallinity, Moisture Sorption and Mechanical Properties of Wool-Graft Poly(Acrylic Acid) Grafted Copolymer Fibers

Grafting (%)	Relative Degree of Crystallinity (%)	Moisture Sorption (%)	Mechanical Properties	
			Tensile Strength (Pascal) $\times 10^{-5}$	Elongation at Break (%)
Ungrafted	79	14	2.45	17.1
8	74	13.3	3.43	21.5
9.5	73.5	12.9	3.53	23.0
12	72.8	12.6	3.92	25.4
19	70.5	12	4.12	28.8
39	66	10.5	5.10	34.0
60	64	8.5	6.37	43.3
62	62.5	8.3	6.47	44.5
65	61	8.2	6.47	45.0

structure of wool and the nature of poly(acrylic acid). Wool contains amide groups in the main chain in addition to water attracting groups such as –OH, $–NH_2$, –SH and –COOH. Thus, blocking of such groups through the grafting process is considered to be principally responsible for the decrease in moisture uptake.

Dye Uptake

Wool as a protein fiber has a direct affinity towards acid dyes due to the salt formation between the negatively charged dye anions and the positively charged basic sites in wool fibers. However, wool fibers have a low affinity for basic dyes due to the small number of available acidic groups present in wool [18].

Figure 3 shows the effect of the degree of grafting on the dyeability of wool fibers, where grafted wool fibers performed better dyeability than the ungrafted fibers. This is explained as being due to the minimized resistance of dye diffusion influenced by grafting due to opening the surface structure of the wool fibers. The dye uptake increasing, subsequently, linearly as the degree of grafting increases up to 20%. As the degree of grafting is increased above 20%, a decrease in the dye uptake was observed. This could be due to the increase of population of graft chains which prohibit dye molecules from direct access to respective functioning wool fibers sites.

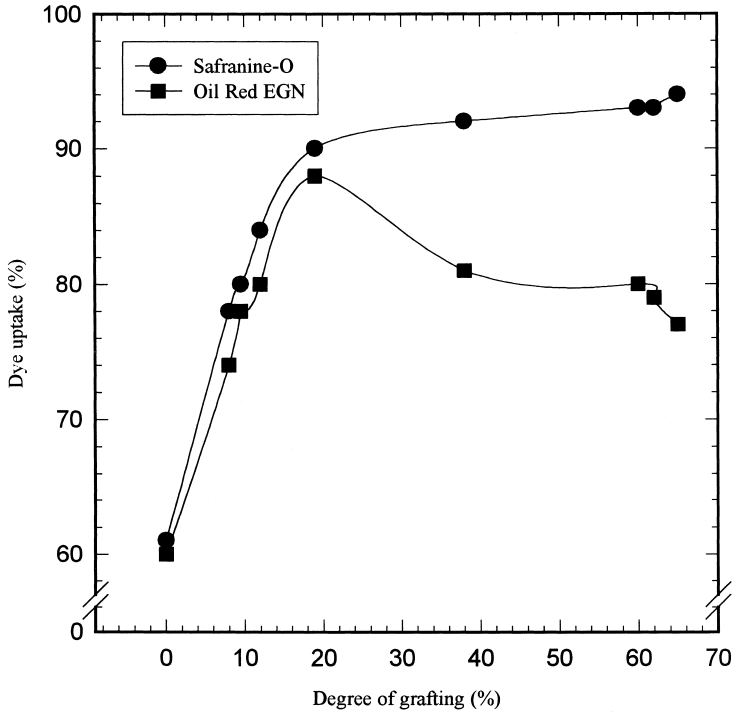

Figure 3. Effect of degree of grafting on the dye uptake for grafted wool fibers dyed with Safranine O and Oil Red.EGN.

A higher uptake of Safranine-O dye was observed for grafted samples compared to Oil Red EGN dye. This can be explained on the basis of the available carboxylic groups responsible for the salt formation with the positively charged dye cation. At a higher degree of grafting, (more than 20 %) the dye uptake becomes nearly constant which could be due to the closure of the open structure of the wool surface leading to a decrease in dye uptake. These two main factors of system closure, due to graft chains, and of available carboxylic groups are considered the most important and controlling factors where dyeing as the subject under study is concerned.

Mechanical Properties

The tensile strength and elongation at break for the grafted and virgin wool fibers were measured and given in Table 1. The results shows that the tensile strength and elongation at break for the samples have increased with the increase of grafting percent. This is attributed to entanglement of the grafted poly(acrylic acid) chains, thus adding to the elastic behavior of the fibers, in addition to the amorphous regions, increase and so improving both mechanical parameters under study. Such an improvement on the mechanical properties of the fibers will definitely throw more weight to the grafted wool fibers by acrylic acid as being more prominent during the spinning and wearing processes.

CONCLUSION

The grafting of merino wool fibers by acrylic acid using γ-radiation at controlled preparation conditions was investigated. Proven improvements towards dyeability using two familiar dyes, moisture uptake properties, fiber increased elasticity were convincingly achieved. Follow up of parameters studied were carefully designed and adopted to illustrate and establish direct relationships to the improved qualities of grafted wool fibers.

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Received April 8, 2001
Revision received July 10, 2001