Microwave Irradiation Graft Copolymerization of Hydroxyethyl Methacrylate onto Wool Fabrics

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ABSTRACT: Hydroxyethyl methacrylate was grafted onto woolen fabrics by microwave irradiation in the presence of catalyst $(NH_4)_2S_2O_8$. Various parameters of the graft copolymerization reaction, namely, time, microwave intensity, catalyst, and monomer concentration, were optimized. The graft copolymerization was also compared with conventional heating graft copolymerization at the same condition. Microwave irradiation was shown to improve the reactivity of the monomer. The moisture regain decreased as graft add-on increased. The Max load and the strain at Max load increased as graft add-on increased. The infrared spectra showed an additional peak at 1700 cm^{-1}, confirming ester carbonyl groups of the monomer. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2343–2347, 1998

Key words: woolen fabrics; grafting; microwave irradiation; hydroxyethyl methacrylate

INTRODUCTION

The most important disadvantage of woolen fabrics is the felting shrinkage, due to the presence of overlapping scales on the fiber surface. During washing and friction, scales of adjacent fibers interlock and a "walking" or "ratched" effect occurs, allowing the fibers to migrate until they are completely entangled, thus producing a permanent setting. The elimination of felting shrinkage by coating fiber surfaces with polymers has been studied extensively.[1] The grafting process may lead to the following 2 major effects on wool: opening the surface structure of the wool, thereby causing damage to the defense pattern of the wool molecules; and causing partial degradation of the polypeptide chain, which can cause the wool backbone to be vulnerable to further chemical attack.[2]

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It has been reported that polymer-grafted wool fibers have better acid and alkali resistances and dye uptake. The internal deposition in the wool of variable amounts of polymer may result in changes in tensile properties, felting shrinkage, abrasion and pilling resistance, hygroscopicity, chemical resistance, thermal stability, and dying behavior.[3–5] Lots of different monomers have been grafted onto wool fabrics so as to improve some properties; specifically, many works were focused on the vinyl monomers and methacrylic esters[6,7] and epoxides.[8,9] However, little work has been reported on the modification of wool by grafting hydroxyethyl methacrylate (HEMA) onto wool fabrics. HEMA has been grafted onto cotton and silk extensively.[10,11,12] In this article, the copolymerization of HEMA onto wool fabrics by microwave irradiation is reported. Microwave heating of suitable materials could be used in many cases to activate the reaction of polymerization, especially for the polar materials. HEMA is polar because of its ester function, and the polarity is

Table I The Parameters of the Microwave System in Different Work Mode

Work Mode	The Ratio of Work Time to Static Time in 22 Min	Relative Power to the Full Power (%)	Full Power (W)
1	22 : 0	100.0	900
2	17 : 5	70.7	636
3	13 : 9	44.8	403
4	8 : 14	29.3	264
5	5 : 17	20.0	180

larger than that only with ester group as it bears an alcohol group bound to a flexible segment —CH_2—CH_2—. It has been used to produce a composite material by microwave.[13] Generally, HEMA usually was grafted onto cotton and silk by an ultraviolet method, and it took a long time for copolymerization. From this point, microwave would shorten the reaction time greatly; but if the microwave intensity is too high, homopolymer would occur. The selection of microwave intensity is very important for the reaction.

EXPERIMENTAL

Materials

Undyed woolen fabric was extrated for 24 h with acetone using a Soxhlet apparatus, then washed by water and dried in the oven. Hydroxyethyl methacrylate was a commercial product. It was purified before the experiment. The catalyst $(NH_4)_2S_2O_8$ was also a commercial product.

Graft Copolymerization

The microwave frequency used was 2450 MHz and its power was 900 W, in equipment obtained from National Corporation. A certain weight of woolen fabric was immersed in the aqueous solution, including a certain concentration of HEMA and catalyst. In this copolymerization, the fabric was about 3 g; the aqueous solution was 100 mL and was put the combination into the microwave reactor system for 35 min. After the reaction the fabric was filtered and washed with distilled water, then was extrated with acetone for 12 h and afterwards dried at 110°C and weighed.

The microwave system had 5 work modes, referred to as modes 1 to 5. The parameters of different work mode are listed in Table 1.

Analysis

Moisture regain was determined in the standard condition according to ASTM D629-77.

Mechanical properties were tested on Instron tester, model 3410; the distance between 2 clampers was 50 mm, and the crosshead speed was 100 mm/min. The sample width was 15 mm.

A Nicolet Fourier transform infrared (FTIR) 20SXB was used to analyze the spectrum. Resolution for the infrared spectra was 4 cm^{-1}, and there were 32 scans for each spectrum.

RESULTS AND DISCUSSION

Effect of Catalyst Concentration

The monomer (HEMA) concentration was 4%. The microwave system was set at mode 5. The reaction time was 35 min, and, before this, the microwave system worked at mode 1 for 1 min so as to increase the container temperature and improve the reactivity. The relation between the catalyst concentration and graft add-on is shown in Figure 1. From Figure 1, it can be seen graft add-on attains the highest at 0.05%.

Effect of Monomer Concentration

The catalyst concentration was 0.05%, and the reaction time was 35 min. Microwave reaction system was set at mode 5. The relation between the monomer concentration and graft add-on is shown in Figure 2. At a lower monomer concentration, the graft add-on increased remarkably; but when the monomer concentration was larger than 4%, the graft add-on increased slowly.

Effect of Reaction Time

The monomer and the catalyst concentration were 2 and 0.05%, respectively. Other conditions

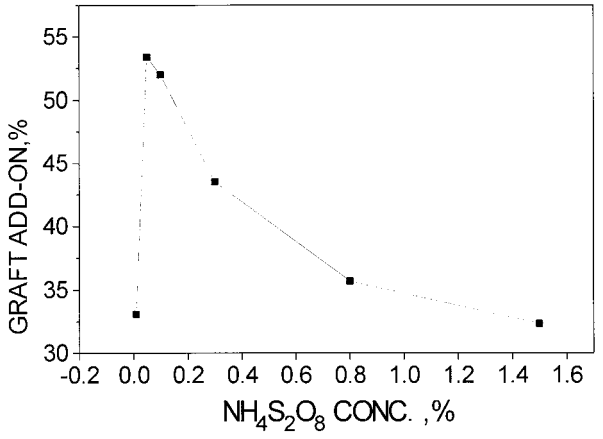

Figure 1 Relation between $NH_4S_2O_8$ concentration and graft add-on.

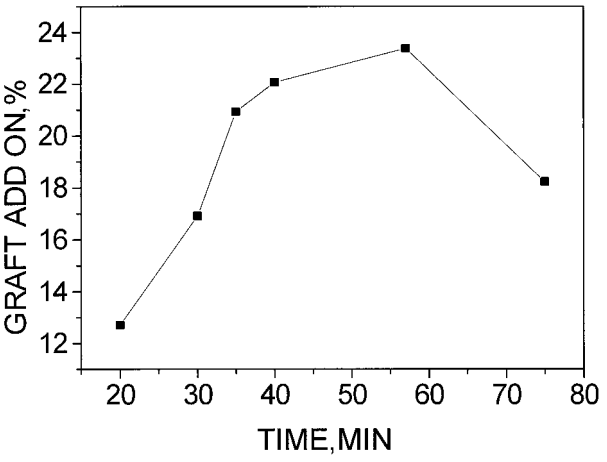

Figure 3 Relation between time of reaction and graft add-on.

were the same as above. The relation between reaction time and the graft add-on is shown in Figure 3. In the figure, it can be observed that the graft add-on attains the utmost value when the reaction time is about 60 min. A longer reaction time would lead to the degradation of the wool keratin or graft polymers. The same activity of chemicals was not obtained with less time.

Effect of Microwave Intensity

The monomer and catalyst concentrations were 2 and 0.05%, respectively. The microwave system was set at different modes with a reaction time of 35 min. The relation between the microwave intensity and the graft add-on is shown in Figure 4. There was a good range of microwave intensity for the copolymerization; it was about from 260–400 W. A higher intensity would lead to greater homopolymerization; on the contrary, a lower intensity could not improve activity. For this reason, in this article, the graft copolymerization were carried out in the microwave intensity of work mode 4. Its microwave intensity was 264 W.

Graft Copolymerization by Conventional Heating

In order to find out the difference between the graft copolymerization by means of microwave heating and that by means of conventional heating, we carried out the graft copolymerization in the same temperature. Monomer and catalyst concentrations were the same in 2 experiments, and the relation between graft add-on and time of reaction of reaction are shown in Figure 5. The

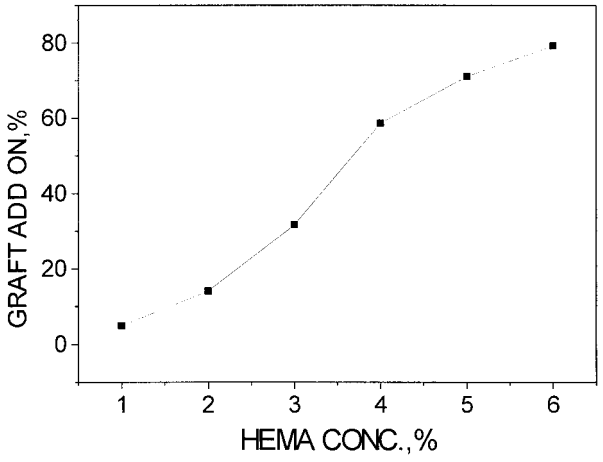

Figure 2 Relation between HEMA concentration and graft add-on.

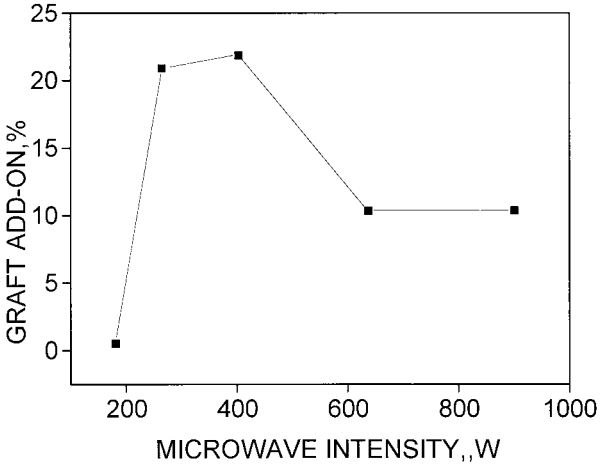

Figure 4 Relation between microwave intensity and graft add-on.

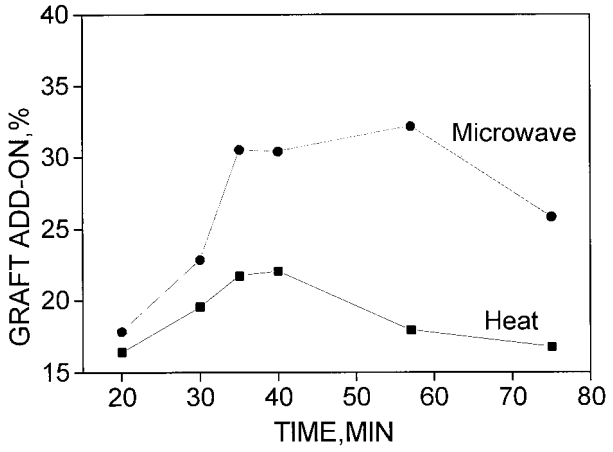

Figure 5 Relation between time of reaction and graft add-on by means of microwave and heat.

regulation of the 2 methods was very similar, but the graft add-on by microwave irradiation was higher than that of conventional heating. In the microwave heating, the monomer and the catalyst were heated at the same time as that at which the solution was heated, and the temperature distribution was more uniform than that in the conventional heating. The monomer and the catalyst can absorb the microwave energy positively in the former condition; but in the conventional heating, the chemicals was only heated negatively, and the temperature distribution was not uniform from the outer to the inner in the reaction bottle. Another most important reason is that the solution temperature increased more rapidly in the microwave heating than that in the conventional heating. Except for the heating effect, the microwave would have some nonheating effect on the graft copolymerization.

Moisture Regain

The moisture regain for the control wool fabrics and those for the grafted are shown in Table II. From Table II, it can be observed that the moisture regain decreases remarkably at low graft add-on; but when the graft add-on is larger than 10%, the moisture regain decreases very slowly. This agrees that the function group become less when the graft add-on increases.

Mechanical Property

The mechanical properties of grafted woolen fabrics with HEMA are shown in Table III. From the test results, it can be seen, evidently, that the Max load increases as the graft add-on increases; the same can be said about the as the strain at Max load.

Table II Effect of Graft Add-On of HEMA on Moisture Regain of Woolen Fabric

Graft Add-On (%)	Moisture Regain (%)
0	7.98
4.86	6.51
14.14	6.22
31.74	6.17
58.68	6.04
71.07	5.20

FTIR Analysis

The spectra for the grafted woolen fabric are given in Figure 6, which shows an additional peak at 1700 cm^{-1}, confirming the introduction of ester carbonyl groups belonging to the graft.

CONCLUSION

The results reported in the present study show that HEMA can be grafted onto woolen fabrics successfully by microwave irradiation. The polymer deposition within the fabric resulted in the changing of some properties. The moisture regain would decrease as the graft add-on increased. The mechanical properties would be improved. All the parameters, including monomer and catalyst concentrations, time of reaction, and microwave intensity, have a strong influence on the graft add-on. Compared to graft copolymerization by means of conventional heating, graft copolymerization

Table III The Mechanical Properties of Grafted Woolen Fabrics with HEMA

Graft Add-On (%)	Max load (kN)	Strain at Max Load (%)
0	0.1655	24.64
4.86	0.1694	29.00
14.14	0.1654	27.40
31.74	0.1940	33.15
58.68	0.2089	35.71
71.07	0.2030	30.28

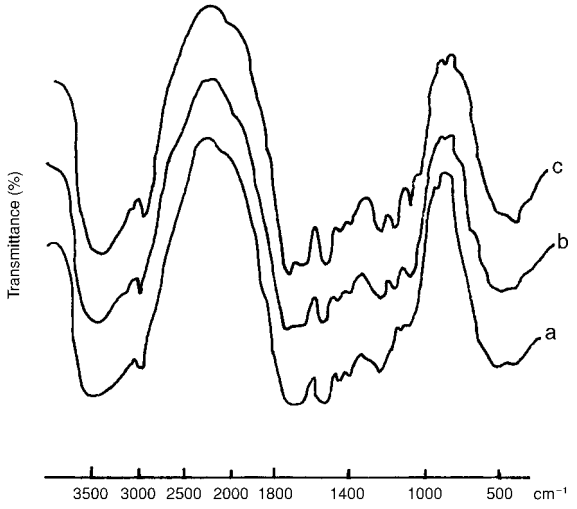

Figure 6 Infrared spectra: (a) control woolen fabric; (b) grafted wool fabric with graft add-on of 14.14%; (c) grafted wool fabric with graft add-on of 31.74%.

by microwave irradiation yields much higher graft add-on. The results showed that microwave energy not only has a heating function but also has a certain nonheating function for some polar materials.

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