

Reactivity of Glycidyl Methacrylate Grafted Cellulose Film Prepared by Grafting Under Ultrasonic Irradiation

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ABSTRACT: Ultrasonic irradiation largely accelerated ceric salt initiated grafting of glycidyl methacrylate (GMA) on regenerated cellulose film (cellophane thickness = 20 μm) at 60°C in air. The grafting under ultrasonic irradiation was characterized by a higher percent of grafting and graft efficiency and a lower density of GMA-grafted chains in the surface layer of the grafted films compared to the unirradiated system, which was obtained by attenuated total reflectance IR measurements. The grafted films were subjected to amination with ethylenediamine (En) at 70°C for 3 h in *N,N*-dimethylformamide. The amount of epoxy groups in the grafted films, which participated in the reaction with En, reached about 50–60 mol % and was slightly lower for the grafted film prepared in the irradiated system than that prepared in the unirradiated one. Adsorption of cupric ions with the aminated samples was performed at pH 5.0 using Clark–Lubs buffer solution and cupric chloride. The adsorption was extremely retarded for the aminated sample prepared using the unirradiated sample compared to that prepared using the irradiated one. The retarded adsorption phenomenon is discussed in terms of a larger formation of crosslinked structures on the surface layer of the former sample during the amination. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2462–2469, 1999

Key words: ceric salt initiated grafting; ultrasonic irradiation; regenerated cellulose film; glycidyl methacrylate

INTRODUCTION

In our previous study¹ we investigated the effect of ultrasonic irradiation on ceric salt initiated grafting of methyl methacrylate (MMA) on cellulose film (cellophane) under an air atmosphere. We observed that the ultrasonic irradiation accelerates the grafting remarkably, which is characterized by a higher percent of grafting and graft efficiency than those in the system without the irradiation. The accelerating effect of the grafting reaction by ultrasonic irradiation is due to the functions of ultrasound such as mass transfer and

diffusion induced by the cavitation phenomenon. Based on attenuated total reflectance IR (ATR-IR) studies of MMA-grafted films prepared in the systems without and with the irradiation, the density of MMA-grafted chains in the surface layer of the grafted films was lower for the irradiated sample compared to that of the unirradiated one, showing easier penetration of MMA-grafted chains into the film substrate in the irradiated system. It is conceivable that the reactivity of the grafted film may be greatly influenced by the location of the grafted chains in the film substrate. The functions of grafted polyethylene film, such as moisture permeability,^{2,3} catalytic activity,^{4,5} and pH⁶ and temperature⁷ responsive characters, were found to closely relate to the distribution of grafted chains in the cross section of the

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film substrate. Therefore, this article deals with the reactivity of glycidyl methacrylate (GMA)-grafted cellulose film prepared by grafting under ultrasonic irradiation.

GMA was selected as a monomer component to introduce into the film substrate because it has a structure similar to the MMA monomer and an epoxy group with high reactivity to amines. The reactivity⁸⁻¹³ of the epoxy group has been utilized in the introduction of functions into polymeric materials. In the present study, in order to understand the reactivity of GMA-grafted cellulose film prepared by grafting under ultrasonic irradiation, the grafted film was examined in terms of a reaction with ethylenediamine (En) and the adsorption of cupric ions (Cu^{2+}) with the aminated cellulose film in comparison with that prepared in the unirradiated system.

EXPERIMENTAL

Materials

Commercially available regenerated cellulose film (cellophane) with a thickness of 20 μm was used as a film sample (3×10 cm), which was extracted with hot methanol for 24 h to remove additives. Ceric ammonium nitrate (Ce^{4+}), En, triethylenetetramine, β -alanine, *N,N*-dimethylformamide (DMF), and cupric salts such as cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and cupric acetate [$\text{Cu}(\text{CH}_3\text{COO})_2$] were reagent grade. GMA was purified by distillation under reduced pressure.

Grafting

Grafting was carried out at 60°C under an air atmosphere in a Pyrex glass tube containing the film sample, 24 mL of water, 1 mL of GMA (7.6 mmol), and 5 mL of an aqueous solution of nitric acid (5 mmol) in which 30 mmol of Ce^{4+} was dissolved. Ultrasonic irradiation was carried out using an ultrasonic cleaning bath (model NS80-1.5u) from Nihonseiki Seisakusho Ltd. (150 \times 135 \times 100 mm bath size, 28-kHz nominal frequency, 80-W power output). The grafting was carried out under stirring at 600 rpm using the film sample, which was cut in small pieces (about 10 \times 10 mm), under an air atmosphere in the system without ultrasonic irradiation.

Photografting was carried out in a Pyrex glass tube containing xanthone-coated film (which was prepared by immersing the film sample in an

acetone solution containing 0.3 wt % xanthone at room temperature, removing it from the solution, and then drying under reduced pressure at room temperature), 29 mL of water, and 1 mL of GMA under a nitrogen atmosphere without ultrasonic irradiation. Irradiation with a high-pressure mercury lamp (400 W) was performed at 60°C for 30 min using a Riko rotary photochemical reactor (RH400-10W).

Polymerized film was extracted with methyl ethyl ketone for 24 h to remove homopolymers of poly(GMA). The percent of grafting and graft efficiency were calculated by the following equations:

$$\text{grafting (\%)} = \frac{\text{weight of grafts}}{\text{weight of original film}} \times 100$$

graft efficiency (%)

$$= \frac{\text{weight of grafts}}{\text{weights of grafts and homopolymer}} \times 100$$

Measurement of ATR-IR Spectra of Grafted Film

ATR-IR spectra of the surface layer of the grafted film were measured with an IR Nicolet spectrometer (model Magna-IR 750). The absorbance ratio of the carbonyl peak (1728 cm^{-1} stretching) of the GMA-grafted chains to the ether peak (1050 cm^{-1} stretching) of the cellulose was obtained.

Reaction with En

A given amount of GMA-grafted film was added to 30 mL of DMF in which known concentrations of En were dissolved, and then a reaction was carried out at 70°C for 3 h. After the reaction the amount of En residue introduced into the substrate was subjected to a measurement with an elemental analyzer (model PE2400 Series II, Perkin Elmer). The aminated epoxy group was defined as the amount of the epoxy group that participated in the reaction with En and is expressed by the following equation:

aminated epoxy group (mol %)

$$= \frac{\text{amount of En residue}}{\text{initial amount of epoxy group}} \times 100$$

Adsorption of Cu^{2+}

A given amount of the aminated sample, which was prepared by the reaction of the GMA-grafted

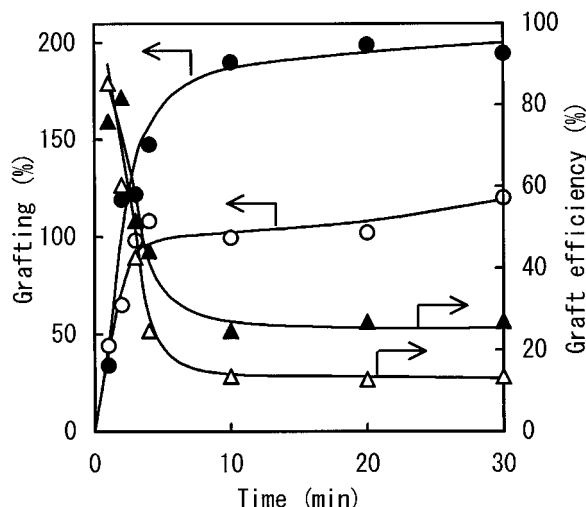


Figure 1 Ce^{4+} -initiated grafting of glycidyl methacrylate onto cellulose film under ultrasonic irradiation: $[\text{GMA}] = 0.33 \text{ mol/L}$, $[\text{Ce}^{4+}] = 5.0 \text{ mmol/L}$, (O, Δ) without irradiation; (●, \blacktriangle) with irradiation.

sample with En, was added to 50 mL of aqueous $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution with known concentrations whose pH was adjusted to 5.0 by Clark-Lubs buffer solution; the adsorption was carried out at 30°C for 24 h. The adsorbed amount of Cu^{2+} was determined by measuring the concentration of Cu^{2+} in the solutions before and after the adsorption using an inductively coupled argon plasma atomic emission spectrophotometer (model ICAP-575, Nippon Jarrell-Ash).

Electron Probe Microanalysis (EPMA)

The distribution profile of Cu^{2+} in the cross section of the aminated film was measured with electron probe microanalyzer (model EPM-810 of Shimadzu).

RESULTS AND DISCUSSION

Grafting Behavior

Figure 1 shows the effect of ultrasonic irradiation on Ce^{4+} -initiated grafting of GMA on cellulose film. The grafting proceeded easily even under an air atmosphere and the percent of grafting in the unirradiated system reached about 100% within the reaction time of 5 min. The percent of grafting in the irradiated system was much higher than that of the unirradiated system, showing that the ultrasonic irradiation markedly accelerates Ce^{4+} -initiated grafting of GMA on cellulose film. The

graft efficiency was also higher for the irradiated system than for the unirradiated one, although the value considerably decreased at the earlier stage of polymerization. Thus, the grafting of GMA on cellulose film under ultrasonic irradiation was characterized by a higher percent of grafting and graft efficiency than those of the unirradiated system. In our previous article¹ on Ce^{4+} -initiated grafting of MMA on cellulose film, we considered that the accelerating effect of the diffusion of Ce^{4+} and MMA monomer into a film substrate by ultrasound results in a higher percent of grafting and graft efficiency in the irradiated system compared to the unirradiated one. The promoted grafting reaction due to ultrasonic irradiation observed in the present system also seems to be based on the functions of ultrasound such as mass transfer and diffusion.

GMA-grafted chains of the surface layer of the resulting grafted films were examined by ATR-IR measurements, and the results are shown in Figure 2. The vertical axis of the figure is the absorbance ratio of the carbonyl peak of GMA-grafted chains at 1728 cm^{-1} to the ether peak of the cellulose substrate at 1050 cm^{-1} . The absorbance ratio increased with an increase in the percent of grafting, indicating that the surface layer of the grafted film becomes rich in the GMA-grafted chains compared to the cellulose components. The magnitude of the increase was lower for the irradiated sample than for the unirradiated one, suggesting easier penetration of GMA-grafted chains

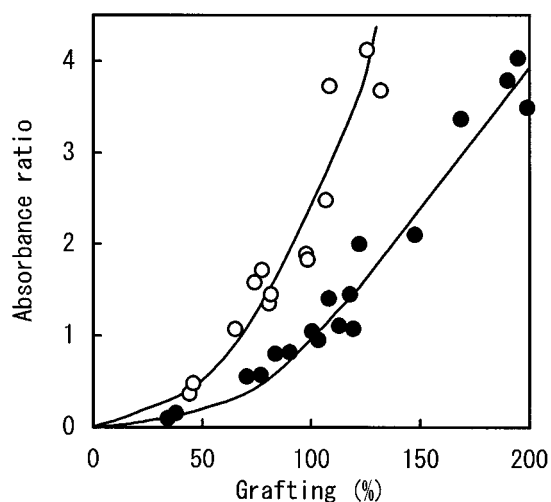


Figure 2 Changes in the absorbance ratio of the carbonyl peak at 1728 cm^{-1} to the ether peak at 1050 cm^{-1} with the percent of grafting in GMA-grafted cellulose film: (O) without irradiation, (●) with irradiation.

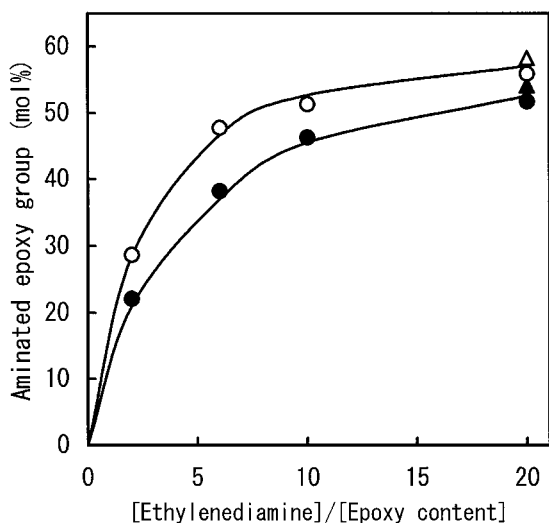


Figure 3 Reaction of GMA-grafted film with ethylenediamine: (O) without irradiation, 75.7% grafting, amination at 70°C for 3 h; (Δ) without irradiation, 75.7% grafting, amination at 70°C for 24 h; (●) with irradiation, 77.1% grafting, amination at 70°C for 3 h; (▲) with irradiation, 77.1% grafting, amination at 70°C for 24 h.

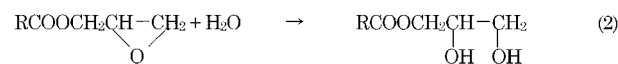
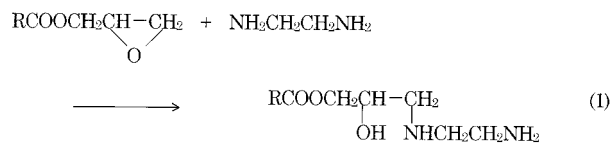
into the film substrate in the irradiated system. Thus, we found that the distribution of GMA-grafted chains in the cross section of the grafted film may differ between the two grafted films, the unirradiated and irradiated samples.

Reaction with En

The reaction of GMA-grafted films such as the unirradiated and irradiated samples with En was examined to compare the reactivity of the two samples toward En, and the results are shown in Figure 3. The concentration of En in the system ranges from 2 to 20 times as much as the epoxy group content, which is calculated from the percent of grafting of the GMA-grafted film. The aminated epoxy group increased with increasing concentration of En in the system, and the value was slightly lower for the irradiated sample compared to the unirradiated one. Similar values were recorded for the system with the reaction time of 24 h. These results may closely relate to the difference in the location of GMA-grafted chains in both samples: that is, the grafted chains of the irradiated sample may distribute the film inside compared to those of the unirradiated one, resulting in a lower aminated epoxy group.

In the present system the amination is conceivably a main reaction, which is schematically

shown in eq. (1), where R denotes GMA-grafted chains.



About 40–50 mol % of the initial amount of epoxy groups may remain unreacted after the amination reaction, although some parts of the epoxy groups are decomposed by the hydrolysis reaction according to eq. (2). The existence of the epoxy groups, which do not participate in the amination, was examined by FTIR measurement using ATR and transmittance methods (Fig. 4). There was no absorption peak due to the epoxy group at 850 cm^{-1} in the IR spectra measured with the ATR method, which was commonly observed for the unirradiated and irradiated samples. This sug-

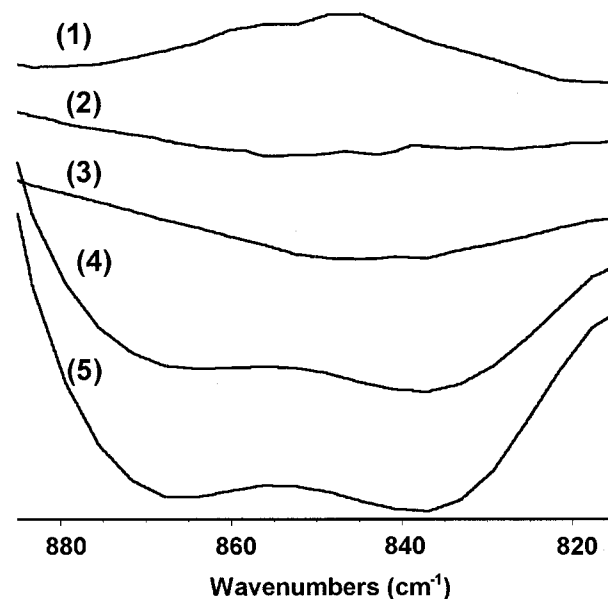


Figure 4 Absorption spectra of aminated GMA-grafted cellulose film measured by FTIR. ATR method: (1) without irradiation, GMA-grafted film (74.5% grafting); (2) without irradiation, aminated film (aminated epoxy content = 55.9 mol %); (3) with irradiation, aminated film (aminated epoxy content = 51.7 mol %). Transmittance method: (4) without irradiation, aminated film (aminated epoxy content = 55.9 mol %); (5) with irradiation, aminated film (aminated epoxy content = 51.7 mol %).

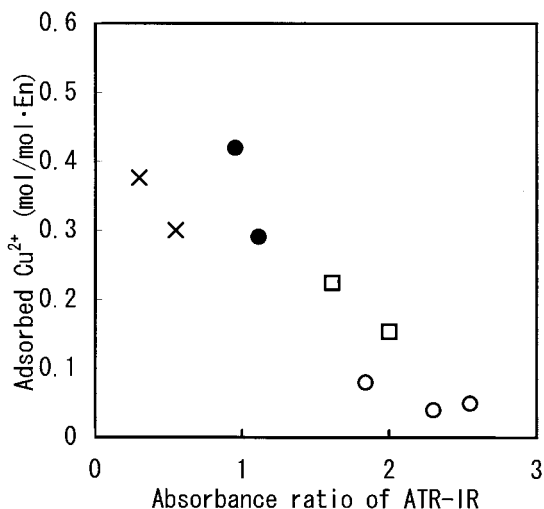


Figure 7 Relationship between the amount of adsorbed Cu^{2+} and the absorbance ratio of the carbonyl peak at 1728 cm^{-1} to the ether peak at 1050 cm^{-1} in the GMA-grafted films: (O) without irradiation, (●) with irradiation, (□) grafting under stirring (600 rpm), (×) photografting. Adsorption was carried out at 30°C for 24 h in the system using Clark-Lubs buffer solution (pH 5.0). [En residue] = 2.0 mmol/L, $[\text{Cu}^{2+}] = 10.0\text{ mmol/L}$, grafting = 100–120%.

Figure 7 presents the relationship between the amount of adsorbed Cu^{2+} and the absorbance ratio of the carbonyl peak at 1728 cm^{-1} to the ether peak at 1050 cm^{-1} obtained by ATR-IR measurement of GMA-grafted samples, which were prepared in various grafting systems. The grafted samples were subjected to the amination with En followed by the adsorption of Cu^{2+} with the resulting aminated samples. The amount of adsorbed Cu^{2+} decreased with an increasing absorbance ratio. It was confirmed thusly that the adsorption tends to be retarded for the aminated sample where GMA-grafted chains locate densely at the film surface.

Figure 8 shows the adsorption of Cu^{2+} with the aminated samples in the system of pH 4.8 without Clark-Lubs buffer solution. We observed that the amount of adsorbed Cu^{2+} increases with the concentration of Cu^{2+} and reaches about 0.5 even in the unirradiated sample. With the adsorption system with Clark-Lubs buffer the Cu^{2+} forms a complex with the phthalate component in the buffer and the resulting complex may be too bulky to diffuse into the film inside through the crosslinked structure on the film surface, leading to a lower amount of adsorbed Cu^{2+} in the unirradiated sample where grafted chains locate

densely at the film surface. The formation of a Cu^{2+} -phthalate complex was confirmed by a spectroscopic study on the aqueous solution consisting of cupric chloride and potassium hydrogen phthalate with various concentrations of both the components where two phthalate molecules are coordinated with one Cu^{2+} . With the adsorption system without the buffer, on the other hand, Cu^{2+} may easily diffuse into the film inside because of no complex formation with a bulky structure and it can coordinate with the En residue, resulting in a higher amount of adsorbed Cu^{2+} even in the unirradiated sample.

The retarded adsorption was also recorded for the aminated samples prepared using triethylenetetramine in place of En, which is shown in Table I. The table also includes the results of the adsorption with the aminated sample prepared using β -alanine. The amount of adsorbed Cu^{2+} was nearly equal between the aminated samples prepared using the unirradiated and irradiated samples. This may have originated in the formation of aminated samples without the crosslinked structure due to the amination. The reaction of GMA-grafted film with β -alanine conceivably proceeds according to eqs. (4) and (5).

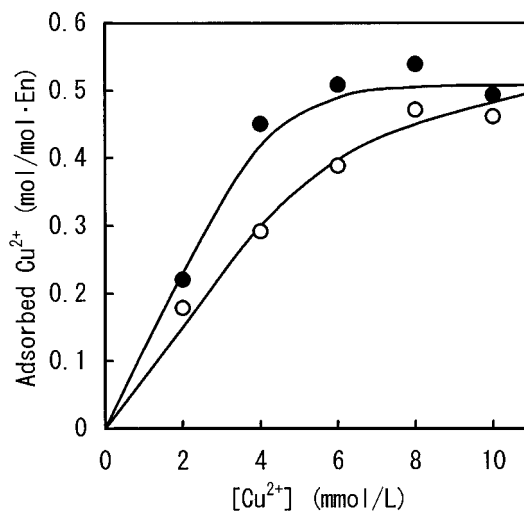
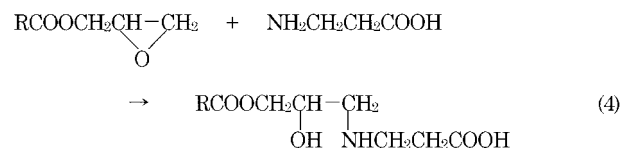


Figure 8 Adsorption of Cu^{2+} with aminated samples in the system without Clark-Lubs buffer solution (pH 4.8). [En residue] = 2.0 mmol/L, grafting = 115–125%.

Ce⁴⁺-initiated grafting of GMA on cellulose film is a useful means for preparation of grafted cellulose samples with a homogeneous distribution of grafted chains. The resulting GMA-grafted sample smoothly reacts with En in less formation of crosslinked structures in the surface layer of grafted chains compared to that prepared in the unirradiated system.

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