

Effect of Mixed Solvent Consisting of Water and Organic Solvent on Photografting of Glycidyl Methacrylate on Polyethylene Film

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ABSTRACT: The effect of a mixed solvent consisting of water and organic solvents such as acetone and methanol on the photografting ($\lambda > 300$ nm) of glycidyl methacrylate (GMA) on linear low-density polyethylene film (thickness = 30 μm) was investigated at 60°C. Xanthone was used as a photoinitiator by coating the film surfaces with it. The maximum percentage of grafting was observed at a certain concentration of organic solvent in the mixed solvent, which depends on the nature of organic solvents such as methanol (ca. 5 vol %) and acetone (ca. 15 vol %). On the basis of attenuated total reflection infrared spectroscopy of the grafted film, the absorbance ratio of the carbonyl peak of grafted poly(GMA) chains at 1728 cm^{-1} to the methylene peak of polyethylene substrate at 1460 cm^{-1} increased with increasing the concentration (0–15 vol %) of organic solvent, which was commonly observed for methanol and acetone. Distribution of grafted poly(GMA) chains in the cross section of the grafted film was examined using a scanning electron microscope. The results showed that the grafted chains of the GMA-grafted samples prepared in water solvent tended to penetrate into the inside of the film compared

to those of the grafted samples prepared in the mixed solvent due to higher affinity of the GMA monomer to the polyethylene substrate compared to the organic solvents used. Grafted poly(GMA) chains were aminated with ethylenediamine (En) in *N,N'*-dimethylformamide at 70°C for 3 h. It was found that the reactivity toward En was higher for the sample prepared in mixed solvent than for the sample prepared in water solvent. The aminated GMA-grafted sample had the ability to adsorb cupric ions, showing that a higher amount of adsorbed cupric ion is recorded for the sample prepared in mixed solvent than for the sample prepared in water solvent. Complexes of aminated GMA-grafted chains with cupric ion exhibited the catalytic activity of decomposition of hydrogen peroxide at 50°C, and its ability depended on the location of the grafted chains in the film substrate. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 994–1000, 2004

Key words: photografting; polyethylene; mixed-solvent; glycidyl methacrylate; catalytic activity

INTRODUCTION

In a series of our studies,^{1,2} the authors investigated the effect of mixed solvent, which consisted of water and organic solvent such as acetone, methanol (MeOH), dioxane, and tetrahydrofuran on the photografting of hydrophilic monomers such as methacrylic acid (MAA) and *N*-isopropylacrylamide (NIPAAm) on linear low-density polyethylene (LLDPE) film. It was found that the component of the organic solvents in the mixed solvent remarkably influenced both the grafting behaviors and the location of the grafted chains in the LLDPE film substrate. The maximum percentage of grafting was observed at a

certain concentration of organic solvent in the mixed solvent depending on the nature of the organic solvent. Moreover, the grafted chains of the MAA- and NIPAAm-grafted samples prepared in mixed solvent had a tendency to penetrate into the inside of the film texture. This article deals with the effect of mixed solvent on photografting of a hydrophobic monomer, glycidyl methacrylate (GMA), on LLDPE film.

Grafted poly(GMA) has a reactive epoxy group in the side chain which can be utilized for the introduction of various functions due to its high reactivity for numerous functional groups such as hydroxyl, carboxyl, and amine groups.^{3–12} Introduction of the epoxy groups into a polymer by means of a grafting method has been studied on improved adhesion of the polymer with epoxy resin^{13–15} and metals.^{16–20} Moreover, GMA-grafted copolymers can also be utilized as a compatibilizer^{21–26} and a ligand for the formation of a complex^{27–30} and for protein purification.^{27,28} In this

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article we report the effects of the mixed solvent consisting of water and various organic solvents on photografting behavior of GMA onto LLDPE film, including distribution of the grafted chains and characteristics of the resultant GMA-grafted films. The resultant GMA-grafted LLDPE films prepared by photografting in mixed solvent were examined in terms of reactivity toward reaction with ethylenediamine (En), adsorption of cupric ion (Cu^{2+}) with aminated grafted chains, and the catalytic activity of the aminated grafted film/ Cu^{2+} complexes toward decomposition of hydrogen peroxide (H_2O_2) in comparison with the grafted film prepared in water solvent.

EXPERIMENTAL

Materials

A commercially available LLDPE film with thickness of 30 μm (density 0.927 g/cm^3 , Idemitsu Petrochemical Co., Ltd., Tokyo, Japan) was used as a film sample. The film sample ($3 \times 10 \text{ cm}$, $\sim 0.08 \text{ g}$) was immersed in an acetone solution containing 0.1 wt % xanthone (XT) and 0.5 wt % poly(vinyl acetate) (weight-average molecular weight = 100,000), removed from the solution, and then dried at room temperature for 2 h under reduced pressure of 5 Torr for the preparation of an XT-coated film. GMA was purified by distillation under reduced pressure (4 Torr at 35°C). XT, En, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Cu^{2+}), H_2O_2 , and hydrophilic organic solvents such as acetone and MeOH were used as received without further purification.

Photografting

Photografting was carried out in a Pyrex glass tube containing the XT-coated film sample and 30 mL of water or the mixed solvent, to which a given amount of GMA (1 mL) was added, under a nitrogen atmosphere. Irradiation of UV rays emitted from a high-pressure mercury lamp (400 W) was performed at 60°C using a Riko Rotary Photochemical Reactor (RH400-10W, Riko Kagaku Sangyo Co., Ltd., Chiba, Japan). The Pyrex glass tubes were rotated around the mercury lamp during the irradiation. After the grafting, grafted films were extracted for 24 h with methyl ethyl ketone for the removal of the homopolymer, poly(GMA), and then dried at room temperature for 24 h under a reduced pressure of 5 Torr. Grafted samples with different percentages of grafting in each system were prepared by varying the irradiation time. The percentage of grafting and the graft efficiency were calculated from the following equations, respectively.

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

Graft efficiency (%)

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

Measurements of attenuated total reflection-infrared (ATR-IR) spectra

The ATR-IR spectra of the surface layers of grafted films were measured with an automatic infrared microscope (AIM-800, FTIR-8700) from Shimadzu Co., Ltd. (Kyoto, Japan). The amount of grafted poly(GMA) chains on the film surface layer was expressed in terms of the absorbance ratio of the carbonyl peak (stretching) band at 1728 cm^{-1} to the methylene peak (scissoring) band at 1460 cm^{-1} .

Scanning electron microscope (SEM)

The distribution profile of Cu^{2+} in the cross section of the aminated GMA-grafted films was measured with an SEM (JSM-5600LV, JED-2200) from JEOL Co., Ltd. (Tokyo, Japan).

Reaction with En

A given weight of GMA-grafted film was added to 30 mL *N,N'*-dimethylformamide, in which known concentrations of En were dissolved, and then the reaction was carried out at 70°C for 3 h. After the reaction, the samples were subjected to measurement of the amount of En residues introduced into the substrate by elemental analysis.

En content (mol %)

$$= \frac{\text{Amount of En residue introduced}}{\text{Initial amount of epoxy group}} \times 100$$

Adsorption of Cu^{2+}

A given weight of aminated GMA-grafted film was added to a 40-mL aqueous $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution with known concentrations, whose pH was adjusted to 5.0 with Clark-Lubs buffer solution, and then the adsorption reaction was carried out at 25°C for 24 h. It was reported that the maximum amount of cupric ions adsorbed on cellulose (dialdehyde cellulose) having hydroxamic acid groups³¹ and GMA-grafted cellulose (dissolving pulp from softwoods)¹⁰ is observed at around pH 5. Accordingly, the system of pH 5.0 was used for the adsorption measurements of cupric ions. After the reaction, the grafted film sample was removed from the solution, and the concentration of Cu^{2+} in the filtrate was determined by chelate titration³² with an EDTA standard solution and (2-pyridyl-

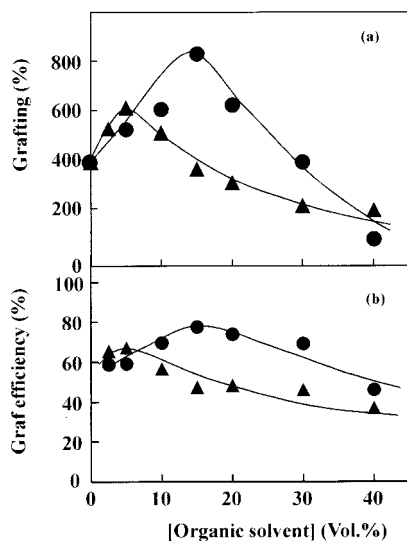


Figure 1 Photografting of GMA on XT-coated LLDPE film in mixed solvent. [GMA] = 0.25 mol/L, [XT] = 0.1 wt %. Irradiation: 60°C, 60 min. (●) acetone, (▲) MeOH. (a) Percentage of grafting; (b) graft efficiency.

lazo)-2-naphthol indicator to determine the amount of adsorbed Cu^{2+} .

Decomposition of H_2O_2

A given amount of aminated GMA-grafted LLDPE film/ Cu^{2+} complex, prepared by the adsorption described above, was allowed to react with 40 mL of aqueous H_2O_2 solution of 3.0×10^{-3} mol/L at 50°C for 5 h. After the reaction, the grafted film sample was removed from the solution, and the concentration of H_2O_2 in the filtrate was determined by titration with aqueous 0.1 M KMnO_4 solution. The amount of decomposed H_2O_2 was calculated according to the equation

$$\text{Amount of decomposed } \text{H}_2\text{O}_2(\%) = \frac{\text{Amount of decomposed } \text{H}_2\text{O}_2}{\text{Initial amount of } \text{H}_2\text{O}_2} \times 100.$$

RESULTS AND DISCUSSION

Grafting behavior

The effect of a mixed solvent consisting of water and organic solvents such as acetone and MeOH on the photografting of GMA on LLDPE film was examined at 60°C, and the results are shown in Figure 1. The abscissa in the figure represent the concentration of organic solvent component in the mixed solvent. The percentage of grafting (Figure 1a) increased with increasing concentration of organic solvent in the mixed solvent, and the maximum percentage of grafting was

observed at a certain concentration of organic solvent in the mixed solvent. The same phenomenon was also observed for the photografting of hydrophilic monomers such MAA¹ and NIPAAm² on XT-coated LLDPE film in a mixed solvent. The appearance of the maximum percentage of grafting at a certain concentration of organic solvent in the mixed solvent was supposed to have originated in the balance between the two effects of organic solvent; one is a positive effect, where the organic solvent promotes monomer solubility in the system. This results in a stimulation of the monomer supply for the radicals on the growing grafted polymer chains, leading to an increase in the percentage of grafting. The other is a negative effect, where the organic solvent participates in the chain transfer from growing polymer radicals to organic solvent and/or termination of the growing polymer radicals by the solvent radicals formed. This may lead to the decreased percentage of grafting at a high concentration of organic solvent. It seems that the explanations for the effect of mixed solvent consisting of water and organic solvent on the photografting of hydrophilic monomers can be applied to hydrophobic monomer, GMA, since both organic solvents, acetone and MeOH, promote the solubility of GMA monomer in the system based on the solubility parameters³³ listed in Table I.

The graft efficiency (Figure 1b), which was taken as the weight percentage of grafted polymer relative to total conversion of monomer in the system, showed the maximum value at the same organic solvent concentration as that of the percentage of grafting (Figure 1a). That is, the use of a proper amount of organic solvent contributed to the improvement of graft efficiency. However, the graft efficiencies were less than 50% at a high concentration of organic solvent, showing the preferential formation of homopolymer compared to grafted polymer. The phenomenon was emphasized for the mixed solvent using MeOH. It was found thus that the formation ratio of grafted polymer to homopolymer in a system is influenced by the composition of mixed solvent.

TABLE I
Solubility Parameter³³ of the Solvents, Monomer, and Polymer Used in This Study

	Solubility parameter (cal/cm ³) ^{0.5}
Water	23.4
MeOH	14.5
Acetone	9.9
MAA	8.5–12.2
NIPAAm ^a	11.18
GMA	7.31
PE	8.1

^a Ahmad, H. *J Macromol Sci Chem* 1982, A17, 585.

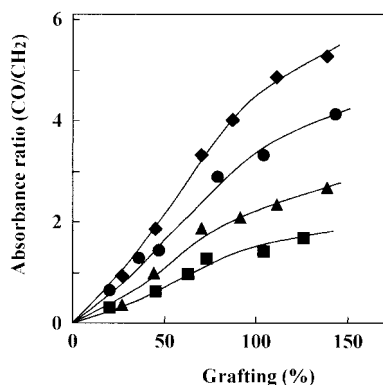


Figure 2 Changes in absorbance ratio of a carbonyl peak at 1728 cm^{-1} to a methylene peak at 1460 cm^{-1} with percentage of grafting in GMA-grafted LLDPE films prepared in water and water/acetone-mixed solvent. (■) Water, (▲) water/acetone (5 vol %)-mixed solvent, (●) water/acetone (10 vol %)-mixed solvent, (◆) water/acetone (15 vol %)-mixed solvent.

Distribution of grafted poly(GMA) chains

The location of grafted chains in PE film substrate may be an important factor for controlling the properties of grafted film when photografting is applied for functionalization of PE materials. In our previous papers,^{1,2} it was observed that pH- and temperature-responsive functions introduced into the LLDPE films by the photografting method were largely influenced by the location of the grafted poly(MAA) and poly(NIPAAm) chains in the grafted films, which was examined by ATR-IR and SEM measurements. Accordingly, it is important to investigate the location of grafted poly(GMA) chains in the grafted film samples prepared in water and mixed solvent. Distribution of grafted poly(GMA) chains was examined on the surface and in the cross section of the grafted film. The grafted poly(GMA) chains of the surface layers of the grafted films prepared in water and water/acetone-mixed solvents 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 grafted poly(GMA) chains at 1728 cm^{-1} to the methylene peak of polyethylene substrate at 1460 cm^{-1} . The absorbance ratio increased with increasing the percentage of grafting, indicating that the surface layer of the grafted film became richer in grafted poly(GMA) chains than LLDPE components. The magnitude of the increase was greater with increasing concentration of acetone in the mixed solvent. Figure 3 shows the absorbance ratio of the GMA-grafted LLDPE films prepared in water and water/MeOH-mixed solvent. The absorbance ratio increased with increasing the concentration of MeOH in the mixed solvent, and the magnitude of the increase was greater with an increase in the concentration of MeOH in the mixed solvent. The results of Figures 2 and 3

indicate that the density of grafted poly(GMA) chains on the surface layer of the grafted film prepared in mixed solvent is higher than that of the sample prepared in water solvent and it increases with increasing concentration of organic solvent in the mixed solvent. This suggests that grafted poly(GMA) chains of the sample prepared in water solvent tended to penetrate more deeply inside the films than those prepared in mixed solvent.

To confirm the results by ATR-IR measurements, distribution of the grafted poly(GMA) chains in the cross section of grafted film was investigated by treating the grafted film with En (see Experimental) and the resultant aminated GMA-grafted films were subjected to formation of a complex with Cu^{2+} . The distribution profile of Cu^{2+} in the cross section of the aminated GMA-grafted film was measured with SEM, and the results are shown in Figure 4. The vertical and horizontal directions in the figure correspond to the relative concentration of Cu^{2+} and the cross section of the films, respectively. The grafted poly(GMA) chains of the sample prepared in water solvent were located inside the film compared to those of the samples prepared in mixed solvent. Thus, the sample prepared in water solvent was characterized by a homogeneous distribution of the grafted chains.

The explanations for the effect of the mixed solvent consisting of water and organic solvent on the distribution of grafted poly(MAA) and poly(NIPAAm) chains were given in detail previously.^{1,2} It has been proposed based on the solubility parameters (Table I) of acetone, MeOH, and water that the affinity of the organic solvents to polyethylene substrate is higher than that of water, indicating that the organic solvents also assist the penetration of hydrophilic monomers into the inside of the film, resulting in the penetration

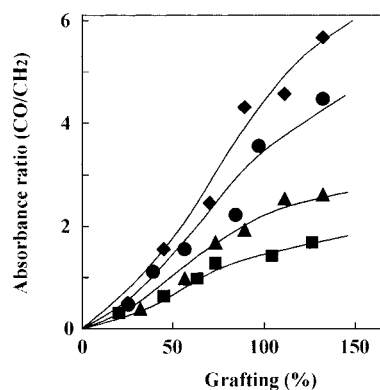


Figure 3 Changes in absorbance ratio of a carbonyl peak at 1728 cm^{-1} to a methylene peak at 1460 cm^{-1} with percentage of grafting in GMA-grafted LLDPE films prepared in water and water/MeOH-mixed solvent. (■) Water, (▲) water/MeOH (5 vol %)-mixed solvent, (●) water/MeOH (10 vol %)-mixed solvent, (◆) water/MeOH (15 vol %)-mixed solvent.

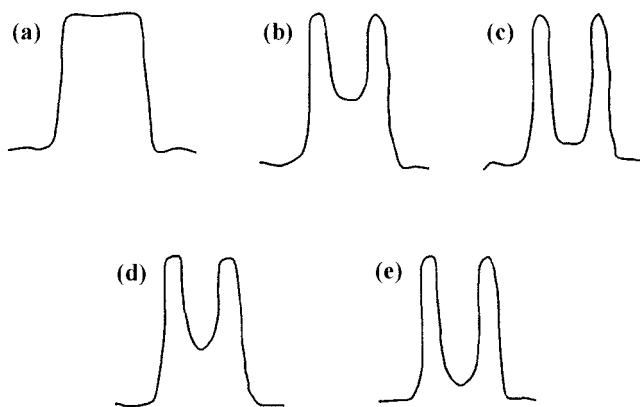


Figure 4 Distribution profiles of Cu^{2+} in the cross section of aminated film measured by SEM. (a) Water (grafting = 65%), (b) water/acetone (5 vol %)-mixed solvent (grafting = 67%), (c) water/acetone (15 vol %)-mixed solvent (grafting = 62%), (d) water/MeOH (5 vol %)-mixed solvent (grafting = 68%), (e) water/MeOH (15 vol %)-mixed solvent (grafting = 67%).

of grafted poly(MAA) and poly(NIPAAm) chains into the inside of the polyethylene substrate. As clearly seen from Figure 4, unexpected results were observed for the distribution of the grafted poly(GMA) chains. That is, the grafted chains of the sample prepared in water solvent have a tendency to penetrate into the inside of the film compared to those prepared in mixed solvent. It is not clear why the grafted chains located in the inside of the sample were prepared in water solvent. However, it is plausible based on the solubility parameter in Table I, where the solubility parameter of GMA monomer to that of PE substrate is very close compared to that of acetone and MeOH, indicating that the GMA monomer has a higher affinity to the PE substrate compared to acetone and MeOH. The GMA monomer itself more efficiently competes with acetone and MeOH for diffusion into the LLDPE substrate, resulting in penetration of grafted chains into a deeper layer of the film surface. This supports the belief that the grafted poly(GMA) chains of the sample prepared in water solvent tend to distribute homogeneously into the inside of the film. This results in the lower density of grafted poly(GMA) chains on the surface layer of the grafted film prepared in water solvent compared to those prepared in mixed solvent, which is shown in Figures 2 and 3. On the other hand, with the grafting system using mixed solvent, a part of the GMA monomer in the system dissolves in the organic solvent component to reduce the concentration of GMA in the vicinity of the PE substrate, depending on the concentration of organic solvent in the mixed solvent. This may weaken the diffusion of GMA into the PE substrate, leading to the grafted chains located on the film surface at higher concentration of organic solvent. It was found from

the above results that organic solvents in the mixed solvent have an influence on both the grafting behaviors and the location of grafted chains on the photografting of hydrophobic monomer, GMA, on the LLDPE film.

Reaction with En

Figure 5 shows the reaction of grafted poly(GMA) chains with En, which was carried out in *N,N'*-dimethylformamide at 70°C for 3 h. The abscissa in the figure represent the concentration of En in the system, which ranges from 5 to 20 times as much as the epoxy group content of GMA-grafted film. The En content, the amount of En residues introduced into the grafted poly(GMA) chains, increased with an increase in the concentration of En used in the system. The magnitude of the increase was higher for the sample prepared in water/acetone-mixed solvent than that of the sample prepared in water solvent. Similar results were recorded for the system with a reaction time of 24 h. It is conceivable that the different reactivities between both GMA-grafted films are ascribed to the difference in the location of grafted poly(GMA) chains in both samples. That is, the grafted chains of the sample prepared in mixed solvent were located on the film surface compared to those of the sample prepared in water solvent, as shown in Figure 4, resulting in higher En content. It was confirmed that epoxy groups of grafted poly(GMA) chains have the ability to react with En, and the ability was largely influenced by the location of the grafted poly(GMA) chains in the grafted film.

Adsorption of Cu^{2+}

The primary amino groups in the En residue introduced to the GMA-grafted films may be expected to form a complex with metal ions such as Cu^{2+} . The

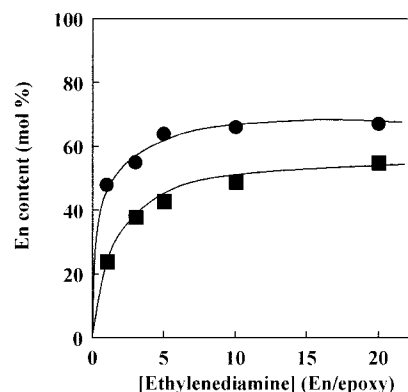


Figure 5 Reaction of GMA-grafted film with ethylenediamine at 70°C for 3 h. (■) Water (grafting = 102%), (●) water/acetone (10 vol %)-mixed solvent (grafting = 97%).

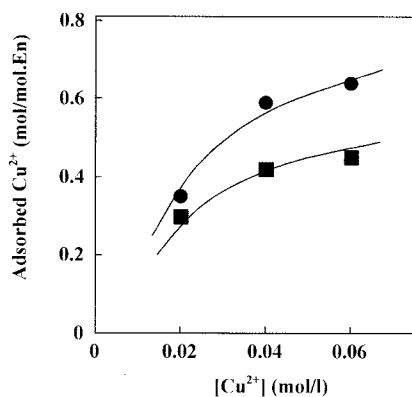


Figure 6 Adsorption of Cu^{2+} with aminated samples in the system using Clark–Lubs buffer solution. pH 5.0, 30°C, 24 h. (■) Water (grafting = 102%, En content = 58 mol %), (●) water/acetone (10 vol %)-mixed solvent (grafting = 97%, En content = 57 mol %).

adsorption reaction of Cu^{2+} to aminated GMA-grafted film was examined to understand their reactivity to form a complex with Cu^{2+} , and the results are shown in Figure 6. The amount of adsorbed Cu^{2+} was expressed by mole number of adsorbed Cu^{2+} per 1 mol En residue in the sample. The mole number of 0.5 in the vertical axis of Figure 6 implies that the number of En necessary for the complexation with 1 Cu^{2+} is estimated at 2. The amount of adsorbed Cu^{2+} increased with increasing the concentration of Cu^{2+} and reached about 0.6 when used the Cu^{2+} concentration of 60 mM. The amount of adsorbed Cu^{2+} of the sample prepared in water/acetone-mixed solvent was higher than that of the sample prepared in water solvent. It is supposed that the higher reactivity of the sample prepared in water/acetone-mixed solvent might be ascribed to the grafted chains of the sample prepared in mixed solvent located at the film surface compared to those prepared in water solvent.

Decomposition of H_2O_2

It is well known that free-metal ion and complexes of polymeric ligand with metal ions^{34–39} (polymer-metal complexes) exhibit catalytic activity toward decomposition of H_2O_2 . Therefore, the complexes prepared by reaction of the aminated GMA-grafted film with Cu^{2+} are expected to exhibit catalytic activity for decomposition of H_2O_2 . Figure 7 shows the amount of H_2O_2 decomposed with complexes of GMA-grafted LLDPE film/ Cu^{2+} . The horizontal axis represents the ratio of the amount (mol) of adsorbed Cu^{2+} to the amount (mol) of En residues introduced into grafted poly(GMA) chains. The amount of decomposed H_2O_2 of the complexes was higher than that of the free Cu^{2+} (Figure 7, dotted line), showing that the complexes prepared by reaction of the aminated GMA-grafted

film with Cu^{2+} have catalytic activity for the decomposition of H_2O_2 . It has been reported that complexes⁴⁰ prepared by polymer ligands and Cu^{2+} exhibit higher catalytic activity for decomposition of H_2O_2 than free Cu^{2+} . As clearly shown in Figure 7, the amount of decomposed H_2O_2 of the complexes was higher for the sample prepared in water/acetone-mixed solvent than for the sample prepared in water solvent. This difference might be ascribed to the location of grafted poly(GMA) chains at the film surface in the sample prepared in water/acetone-mixed solvent, resulting in an increase in the catalytic function of the aminated samples. Thus, it was confirmed that complexes prepared by reaction of aminated GMA-grafted film with Cu^{2+} exhibit catalytic activity for the decomposition of H_2O_2 , and its ability is influenced by the location of grafted chains in the polymer substrate.

CONCLUSION

It has been concluded that epoxy groups can be introduced into LLDPE films by photografting of GMA using XT-coated film, which is largely influenced by the use of a mixed solvent consisting of water and organic solvent such as acetone and MeOH. The maximum percentage of grafting was observed at a certain concentration of organic solvent in the mixed solvent. The grafted chains of the sample prepared in water solvent tended to penetrate into the center of the film compared to those of the sample prepared in mixed solvent due to higher affinity of the GMA monomer to the PE substrate compared to the organic solvents used. The reactivity of the introduced epoxy groups toward En was higher for the sample prepared in mixed solvent compared to the sample prepared in

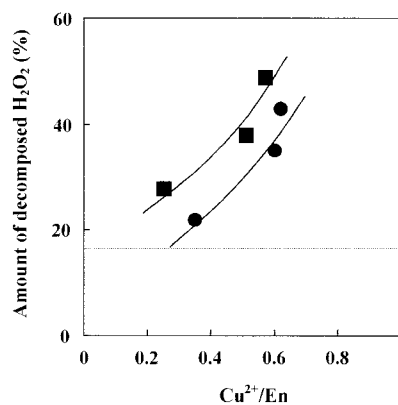


Figure 7 Decomposition reaction of H_2O_2 with complexes of GMA-grafted LLDPE film/ Cu^{2+} . Decomposition of H_2O_2 was carried out at 50°C for 5 h. $[\text{H}_2\text{O}_2] = 3.0 \times 10^{-3}$ mol/L, $[\text{CuCl}_2] = 3.0 \times 10^{-4}$ mol/L, (■) water (grafting = 97%), (●) water/acetone (10 vol %)-mixed solvent (grafting = 102%). The dotted line represents the amount of decomposed H_2O_2 in the system with free Cu^{2+} .

water solvent. Aminated GMA-grafted film can be utilized to attach the ability to form a complex with Cu^{2+} and catalytic activity for the decomposition of H_2O_2 to the substrate.

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