Reactivity of Glycidyl-Methacrylate-Grafted Cellulose Prepared by Means of Photografting

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SYNOPSIS

Photografting was applied to functionalize cellulose, that is, epoxy groups were introduced into the cellulose substrate by photografting of glycidyl methacrylate (GMA) using hydrogen peroxide as a photoinitiator. Dissolving pulp from softwoods was used as the cellulose sample. The GMA-grafted cellulose (G-Cell) was subjected to the following examinations in comparison with epoxy-activated cellulose (E-Cell) prepared by reaction with epichlorohydrin: (1) reactivity of G-Cell toward amines such as ethylenediamine, tetramethylenediamine, hexamethylenediamine, diethylenetriamine, and triethylenetetramine; (2) ability of the aminated celluloses obtained by examination (1) to adsorb cupric ion; and (3) catalytic activity of the aminated cellulose–cupric ion complexes prepared by examination (2) for decomposition of hydrogen peroxide. The amount of amine residue introduced into the substrate was higher for E-Cell than G-Cell, showing the existence of epoxy groups in G-Cell which cannot contribute to the reaction. The ability of the aminated celluloses to adsorb cupric ion was nearly equal for G-Cell and E-Cell though tetramethylenediamine- and hexamethylenediamine-introduced samples did not show the ability. It was found that all complexes prepared by reaction of the aminated cellulose with cupric ion exhibited catalytic activity for decomposition of hydrogen peroxide. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Grafting is known to be a useful means for the functionalization of polymeric substrates. The technique is classified into two: (1) the monomer having a desired function is directly grafted on the substrate and (2) the monomer with a reactive group is first grafted, and the resultant reactive group is used as a reactive site for further functionalization. It is conceivable that the latter method is useful from the viewpoint of introducing wide varieties of function into polymeric materials.

In this study, photografting was applied to the functionalization of cellulose, since the authors have studied photografting of vinyl monomers on cellulose[1-3] and polyolefins,[4-6] which proceeds easily using photoinitiators such as metal ions and aromatic ketones and quinones, respectively. The photografting is thought to have the following characteristics: (1) light is an energy which is easily available in commercial, (2) photo-induced reaction is selective in nature, and (3) photoenergy is very low compared with high-energy radiation such as γ-ray and electron beam, resulting in less deterioration of polymeric materials.

On the other hand, the epoxy group was chosen as the reactive group, since reactivity of epoxy groups[7-11] can be utilized in the introduction of functions into polymeric materials. There are two methods of introducing the epoxy group into cellulose: one is grafting[12-15] of vinyl monomers having epoxy group, and the other is etherification[16-19] of hydroxyl group in cellulose molecule. With the former method, the epoxy groups are introduced into cellulose as grafted chains, while they are directly attached to a main chain of cellulose in the latter method.

In the present study, in order to understand the characteristics of photografting for the functional-

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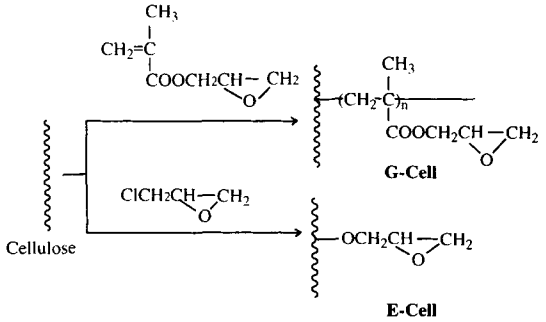
ization of cellulose, glycidyl methacrylate (GMA)-grafted cellulose prepared by photografting was examined in terms of reaction with amines, adsorption of cupric ion (Cu^{2+}) with the aminated cellulose, and decomposition of hydrogen peroxide (H_2O_2) with the aminated cellulose/Cu^{2+} complexes in comparison with epoxy-activated cellulose prepared by reaction with epichlorohydrin.

EXPERIMENTAL

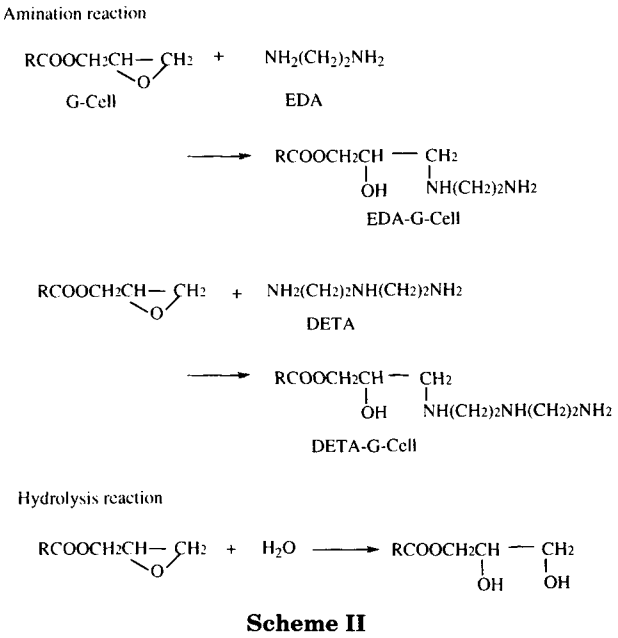
Preparation of Epoxidized Celluloses (Scheme I)

Commercial dissolving pulp from softwoods was used as a cellulose sample. GMA was purified by distillation under reduced pressure. Photografting was carried out in a Pyrex glass tube containing the cellulose sample (0.5 g), 40 mL of 0.01 wt % H_2O_2 aqueous solution, and 2 mL of GMA under nitrogen atmosphere at 60°C for 5–7 min to yield GMA-grafted cellulose (G-Cell) with 30–50% grafting, respectively, which correspond to epoxy contents of 1–2 mmol/g sample. H_2O_2 was used as a photoinitiator in the grafting system. It decomposes by photoirradiation to produce hydroxyl radicals which might extract the hydrogen atom from the substrate to yield cellulose radicals capable of initiating grafting. Irradiation with a high-pressure mercury lamp (400 W) was performed using a Riko rotary photochemical reactor RH-400-10W. Polymerized cellulose sample was extracted for 24 h with methyl ethyl ketone to remove homopolymer. The percent grafting was taken as the percentage of weight increase of the original cellulose.

Preparation of epoxy-activated cellulose (E-Cell)[16] was carried out as follows: The cellulose sample (0.5 g) was treated with 3.2*M* potassium hydroxide aqueous solution at 55°C for 60 min. The pretreated sample was added to 16 mL of dimethyl



Scheme I



Scheme II

sulfoxide and water (1/1 v/v) mixture containing 3.2*M* epichlorohydrin and 0.024*M* tetraethylammonium hydroxide, and the reaction was carried out at 55°C for 60 min to form E-Cell with epoxy contents of 0.4 mmol/g sample (Scheme I).

Reaction with Amines

Ethylenediamine (EDA), tetramethylenediamine (TMDA), hexamethylenediamine (HMDA), diethylenetriamine (DETA), and triethylenetetramine (TETTA) used as amines were of reagent grade and used without further purification.

The epoxidized cellulose (0.4 g) was added to 40 mL of N,N'-dimethylformamide, in which amine with a concentration corresponding to decuple as much as the epoxy content was dissolved, and then a reaction was carried out at 70°C for given times. For example, the reactions of G-Cell ($RCOOCH_2\underset{\diagdown O \diagup}{CH}—CH_2$) with EDA and DETA were as shown schematically in Scheme II.

After the reaction, the samples were subjected to measurements of the amounts of amine residues introduced into the substrate and epoxy groups with elemental analysis and titration method, respectively. The aminated epoxy group was defined as the amount of epoxy groups which participated in the reaction with amines and expressed by the following equation:

Aminated epoxy group (mol %)

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

The amounts of unreacted and decomposed epoxy groups were calculated according to the following equations:

Unreacted epoxy group (mol %)

$$= \frac{\text{amount of epoxy group after reaction}}{\text{initial amount of epoxy group}} \times 100$$

Decomposed epoxy group (mol %) = 100

− (aminated epoxy group

+ unreacted epoxy group)

Measurement of Epoxy Content

The epoxidized sample (0.2 g) was immersed in 0.1*M* sodium thiosulfate water–acetone (1/1 v/v) mixture containing a known concentration of acetic acid at 40°C for 20 min. After being cooled to room temperature, the liberated sodium hydroxide was back-titrated by 0.1*M* aqueous sodium hydroxide solution to determine the epoxy content according to the following equation:

$$RCOOCH_2CH\text{—}CH_2 + Na_2S_2O_3 + H_2O \rightarrow RCOOCH_2CH(OH)\text{—}CH_2\text{—}S_2O_3Na + NaOH$$

Adsorption of Cu^{2+}

A given amount of the aminated sample, which was prepared by reaction of epoxidized cellulose with amine, was added to 50 mL of $1.0 \times 10^{-3}M$ aqueous $CuCl_2 \cdot 2H_2O$ solution, whose pH was adjusted by Tris buffer solution, and then adsorption reaction was carried out at 30°C for 24 h. Concentration of ligand was $8.0 \times 10^{-4}M$. After the reaction, the reaction mixture was filtered off, and the concentration of Cu^{2+} in the filtrate was determined by chelate titration[20] using 0.01*M* EDTA standard solution and (2-pyridylazo)-2-naphthol indicator in order to calculate the amount of Cu^{2+} adsorbed.

Decomposition of H_2O_2

A given amount of the aminated cellulose–Cu^{2+} complex, prepared by the adsorption reaction described above, was allowed to react with 40 mL of $2.5 \times 10^{-3}M$ aqueous H_2O_2 solution at 30°C for given times. The complex was then filtered off, and the concentration of H_2O_2 in the filtrate was determined by 0.1*M* aqueous $KMnO_4$ solution. A plot of the logarithm of the concentration of H_2O_2 against time was made to calculate the pseudo-first-order rate constant, k_1.

RESULTS AND DISCUSSION

Reaction with Amines

Reaction of epoxidized celluloses such as E-Cell and G-Cell with amines was examined to compare reactivity of the two epoxidized samples toward amines, and the results are shown in Figures 1 and 2. Two kinds of amine are used; one is an amine which contains amino groups at both ends of the molecule, and the other is a polyamine having secondary amino groups in the molecule. With the former amines, the aminated epoxy group decreased in the order of HMDA > TMDA > EDA, which was commonly observed for G-Cell and E-Cell. The amine with higher basicity is supposed to cause an easier reaction with

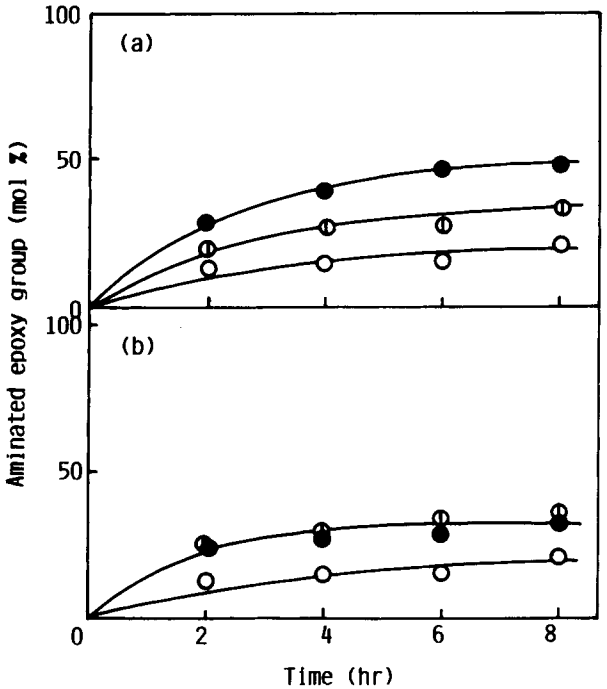


Figure 1 Reaction of G-Cell with amines. (a) (○) EDA, (⊕) TMDA, (●) HMDA; (b) (○) EDA, (⊕) DETA, (●) TETTA. Epoxy content = 1.2 mmol/g sample, concentration of amine = 1.2*M*, temperature = 70°C.

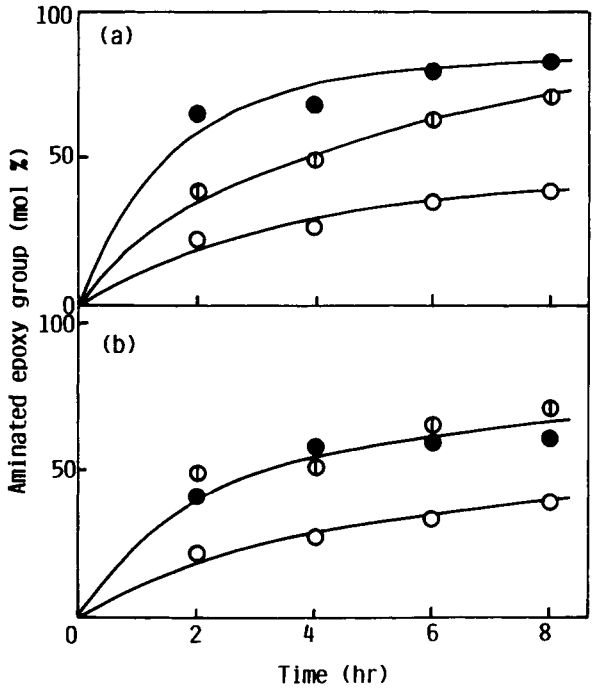


Figure 2 Reaction of E-Cell with amines. (a) (○) EDA, (⊖) TMDA, (●) HMDA; (b) (○) EDA, (⊖) DETA, (●) TETTA. Epoxy content = 0.4 mmol/g sample, concentration of amine = 0.36*M*, temperature = 70°C.

epoxy group. Khalil et al.[15] examined reaction of GMA-grafted cellulose with amines in water medium and reported that the aminated epoxy group increases with increasing the basicity of amines, diethylamine > ethylamine > ammonia. On the other hand, the aminated epoxy group in the latter amines decreased in the order of TETTA ≈ DETA > EDA.

Table I shows the comparative results of G-Cell and E-Cell in the reaction with amines. As shown in Scheme II, amination is conceivable to be a main reaction in the present system. The aminated epoxy group in each amine was higher for E-Cell than G-Cell. On the other hand, hydrolysis of the epoxy groups also proceeds as a side reaction. There was no large difference in the decomposed epoxy group due to the hydrolysis reaction between G-Cell and E-Cell. It is supposed, moreover, that primary and/or secondary amino groups in the amine residue introduced into the substrate may participate in further reaction with epoxy groups to result in cross-linking reaction. However, the possibility of the reaction could not be proved in this study. The proportion of unreacted epoxy groups was higher for G-Cell than E-Cell, showing that about 50% of the epoxy groups in G-Cell is retained after the reaction at 70°C for 8 h. This tendency was common for both amines. The result of G-Cell suggests the existence of epoxy groups on the grafted chains which cannot contribute to the amination. It is not clear why G-Cell exhibits lower reactivity toward amines compared to E-Cell. It is conceivable, however, that the difference in the structure between the two samples may affect the reactivity. Epoxy groups in G-Cell exist on grafted chains, while those in E-Cell are attached to a main chain of cellulose, which is shown in Scheme I. Okamoto et al.[21] examined adsorption reaction of cupric ions with grafted fiber having amidoxime groups, which was prepared by radiation-induced grafting, and observed the existence of amidoxime groups which cannot participate in the adsorption. They explained

Table I. Reaction[a] of Epoxidized Celluloses with Amines

Epoxidized Cellulose	Amine	Aminated Epoxy Group (mol %)	Decomposed Epoxy Group (mol %)	Unreacted Epoxy Group (mol %)
G-Cell	Ethylenediamine	22	21	57
G-Cell	Tetramethylenediamine	35	13	52
G-Cell	Hexamethylenediamine	49	14	37
E-Cell	Ethylenediamine	40	33	27
E-Cell	Tetramethylenediamine	77	19	4
E-Cell	Hexamethylenediamine	84	16	0
G-Cell	Diethylenetriamine	38	11	51
G-Cell	Triethylenetetramine	32	13	55
E-Cell	Diethylenetriamine	72	12	10
E-Cell	Triethylenetetramine	60	17	23

[a] G-Cell: Epoxy content = 1.1 mmol/g sample, concentration of amine = 1.1*M*. E-Cell: Epoxy content = 0.4 mmol/g sample, concentration of amine = 0.4*M*; temperature = 70°C, time = 8 h.

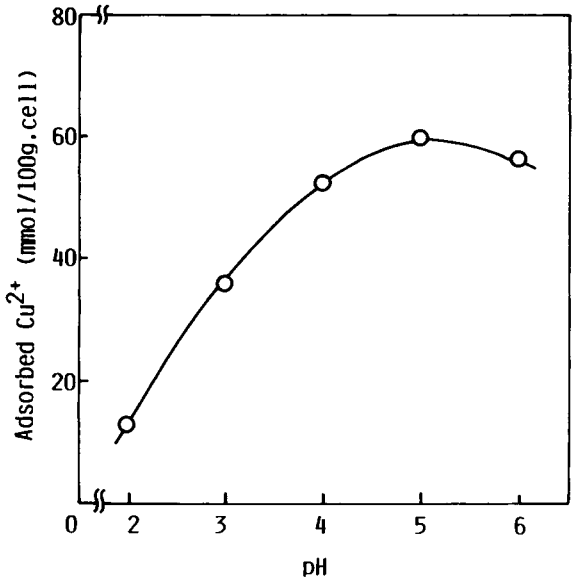


Figure 3 Effect of pH on the amount of adsorbed Cu^{2+} in TETTA-G-Cell. Concentration of TETTA ligand and $CuCl_2 \cdot 2H_2O$ are $8.0 \times 10^{-4}M$ and $1.0 \times 10^{-3}M$, respectively. Adsorption was carried out at 30°C for 24 h.

the phenomenon in terms of a loop structure of the grafted chains containing amidoximes. That is, some of the amidoximes, which exist in the middle of the loop, are not able to take part in the chelate formation. It is plausible that GMA-grafted chains have a structure unfavorable to the reaction with amines, such as a loop structure, resulting in the existence of epoxy groups which cannot contribute to the reaction. Based on the above examinations, epoxy groups of G-Cell were found to exhibit reactivity for amines though the proportion of aminated epoxy groups was lower than E-Cell.

Adsorption of Cu^{2+}

Each aminated cellulose prepared by reaction of E-Cell and G-Cell with amines has a pendant group containing nitrogen atoms with more than two on the cellulose chain or GMA-grafted chain. The nitrogen atoms may be expected to form a complex with the metal ions. Accordingly, adsorption reaction of Cu^{2+} with the aminated celluloses was studied to understand their ability to form complex with metal ions. Figure 3 shows the effect of pH on the amount of adsorbed Cu^{2+} in the aminated cellulose, TETTA-G-Cell, which is prepared by the reaction of G-Cell with TETTA. Denotation of each aminated cellulose is shown in Table II. The amount of adsorbed Cu^{2+} increased with increasing pH of the system and afforded a maximum amount at about pH = 5. Maekawa et al.[22] studied adsorption reaction of cupric ions with cellulose having hydroxamic acid groups and observed a maximum amount of adsorbed cupric ions around pH = 5. Accordingly, the system of pH = 5 was used for further adsorption reaction.

Table II presents the adsorption of Cu^{2+} with various aminated celluloses. The amount of adsorbed Cu^{2+} was expressed by mole number of adsorbed Cu^{2+} per one mole of amine residue in the sample. EDA-, DETA-, and TETTA-introduced samples showed an ability to adsorb Cu^{2+}, but TMDA- and HMDA-introduced samples did not. The amount of adsorbed Cu^{2+} was nearly equal for the aminated celluloses prepared from G-Cell and E-Cell. The

Table II. Adsorption[a] of Cu^{2+} with Various Aminated Celluloses

Epoxidized Cellulose	Amine	Aminated Cellulose	Adsorbed Cu^{2+} (mol/mol Amine)
G-Cell	Ethylenediamine	EDA-G-Cell	0.65
G-Cell	Tetramethylenediamine	TMDA-G-Cell	0.03
G-Cell	Hexamethylenediamine	HMDA-G-Cell	0.02
G-Cell	Diethylenetriamine	DETA-G-Cell	0.80
G-Cell	Triethylenetetramine	TETTA-G-Cell	0.98
E-Cell	Ethylenediamine	EDA-E-Cell	0.73
E-Cell	Tetramethylenediamine	TMDA-E-Cell	0.07
E-Cell	Hexamethylenediamine	HMDA-E-Cell	0.06
E-Cell	Diethylenetriamine	DETA-E-Cell	0.84
E-Cell	Triethylenetetramine	TETTA-E-Cell	1.03

[a] Concentrations of $CuCl_2 \cdot 2H_2O$ and ligand are $1.0 \times 10^{-3}M$ and $8.0 \times 10^{-4}M$, respectively; pH = 5.0, temperature = 30°C, time = 24 h.

numbers of EDA, DETA, and TETTA necessary for complexation with one cupric ion are estimated as 2.0, 1.5, and 1.0, respectively. The amounts of Cu^{2+} adsorbed by EDA-introduced G-Cell and E-Cell were considerably higher than that (0.50) calculated from the number 2.0. This suggests that the complex formed by the reaction of epoxidized celluloses with EDA contains incompletely coordinated species (structure I) besides the complex with structure II. For example, structures I and II of complex prepared by EDA-E-Cell,

$$\begin{array}{l} ROCH_2CH-CH_2, \\ \quad\;\; |\quad\;\; | \\ \quad OH \quad NH(CH_2)_2NH_2 \end{array}$$

and Cu^{2+} are schematically shown in Figure 4. It was observed, thus, that the ability of the aminated cellulose to adsorb Cu^{2+} is not largely influenced by the type of epoxidized celluloses, E-Cell and G-Cell, though it depends on the nature of amine residue introduced into the substrate.

Decomposition of H_2O_2

It is reported that complexes[23] prepared by polymer ligands and Cu^{2+} exhibit higher catalytic activity for decomposition of H_2O_2 than free Cu^{2+}. Therefore, complexes prepared by reaction of the aminated cellulose with Cu^{2+} were subjected to the decomposition reaction of H_2O_2 to examine their catalytic activity, and the results are shown in Figure 5. The pseudo-first-order rate constant k_1 is used as a measure of catalytic activity. The values of k_1 for each complex were higher than that of $CuCl_2$, showing that all complexes have catalytic activity for the decomposition of H_2O_2. It is known that catalytic activity of metal complexes[24] for the decomposition of H_2O_2 originates in the complex species with incompletely coordinated structure. EDA-E-Cell–Cu^{2+} complex,

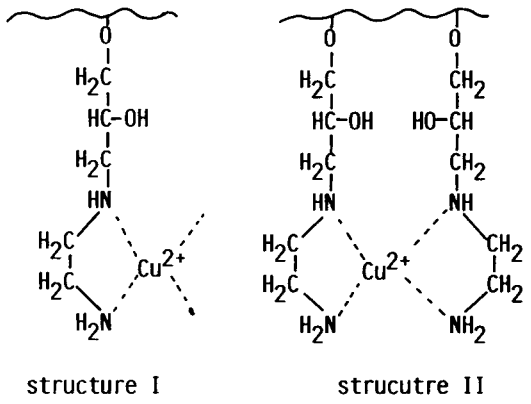


Figure 4 Complex formation of EDA-E-Cell with Cu^{2+}.

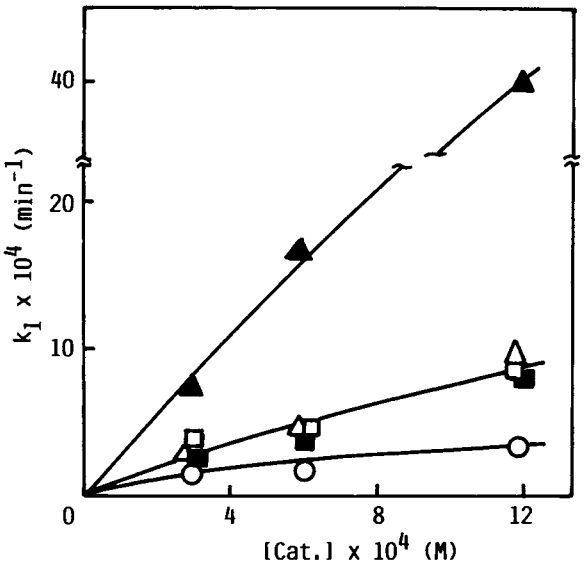


Figure 5 Relationship between pseudo-first-order rate constant and catalyst concentration. (○) $CuCl_2 \cdot 2H_2O$, (△) EDA-G-Cell/Cu^{2+}, (▲) EDA-E-Cell/Cu^{2+}, (□) TETTA-G-Cell/Cu^{2+}, (■) TETTA-E-Cell/Cu^{2+}. Concentration of $H_2O_2 = 2.5 \times 10^{-3}M$, molar ratio of Cu^{2+} to ligand = 1.6, temperature = 30°C.

which was prepared by the reaction of EDA-E-Cell and Cu^{2+}, showed the highest activity. The activity of EDA-G-Cell–Cu^{2+} complex was lower than that prepared from EDA-E-Cell. It is supposed that the result is ascribed less to formation of the complex

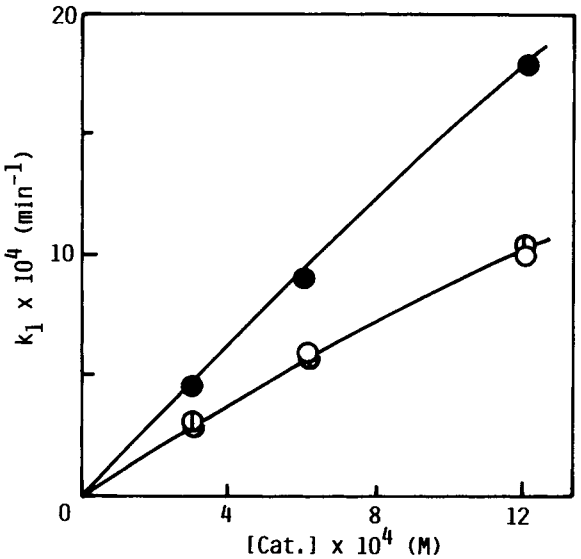


Figure 6 Effect of ratio of adsorbed amount of Cu^{2+} to EDA ligand content on catalytic activity of EDA-G-Cell–Cu^{2+} complex. Molar ratio of Cu^{2+} to ligand: (○) 1.0, (◐) 1.6, (●) 2.5. Concentration of $H_2O_2 = 2.5 \times 10^{-3}M$, temperature = 30°C.

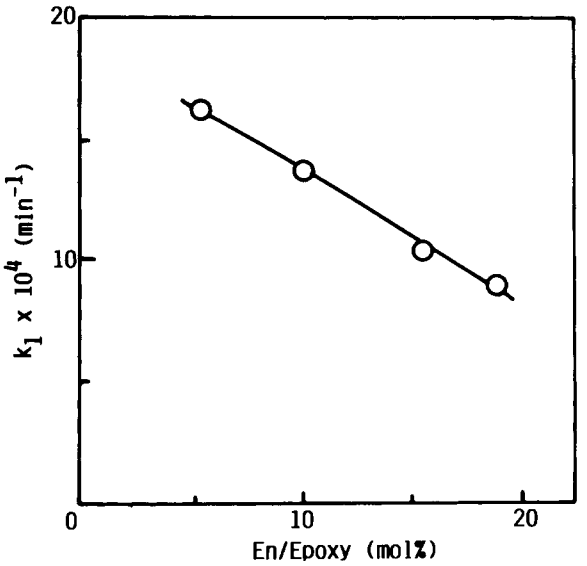


Figure 7 Effect of ratio of EDA ligand to epoxy content on catalytic activity of EDA-G-Cell–Cu^{2+} complex. Concentrations of H_2O_2 and catalyst are $2.5 \times 10^{-3}M$ and $6.0 \times 10^{-4}M$, respectively. Molar ratio of Cu^{2+} to ligand = 1.0, temperature = 30°C.

species with structure I in EDA-G-Cell–Cu^{2+} complex than that prepared from EDA-E-Cell.

Factors influencing catalytic activity of EDA-G-Cell–Cu^{2+} complex were examined in order to improve the activity; the effect of the ratio of the amount of adsorbed Cu^{2+} to EDA ligand content is shown in Figure 6. The activity increased with decreasing the ratio. At lower ratio, the complex species with structure I seem to be easily formed. Figure 7 shows the effect of the ratio of EDA ligand to epoxy content. The activity increased with decreasing the ratio. This suggests the existence of distribution of ligand molecules appropriate for the formation of complex species with structure I. When the distance between the ligand molecules on grafted chains increases, the molecules are not able to participate in complex formation. This leads to the formation of complex species with structure I. Thus, it was found that complexes prepared by reaction of aminated G-Cell with Cu^{2+} exhibit catalytic activity for decomposition of H_2O_2, and it is possible to improve the catalytic activity by controlling the preparation conditions of the complex.

Based on the above investigations, it is concluded that photografting is useful for introducing epoxy groups into the cellulose substrate, and the reactivity of the introduced epoxy groups toward amines can be utilized for the attachment of the ability to form complex with metal ions and the catalytic activity for decomposition of H_2O_2 to the substrate. However, the reactivity of G-Cell for amines is lower than E-Cell, and further studies are necessary to prove the reason why epoxy groups, which do not contribute to amination, exist on grafted chains.

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