

EFFECT OF MIXED SOLVENTS CONSISTING OF WATER AND ORGANIC SOLVENT ON PREPARATION OF MEDIUM-RESPONSIVE GRAFTED CELLULOSE FILM BY MEANS OF PHOTOGRAFTING

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Abstract

Cellulose having a medium-responsive function were synthesized by photografting of methacrylic acid (MAA) on regenerated cellulose film (thickness = 20 μm) at 60°C using mixed solvent consisting of water and organic solvents such as acetone and methanol. Xanthone was used as photoinitiator by coating on the film surfaces. A maximum percentage of grafting was observed at a certain concentration of organic solvent. MAA-grafted cellulose films produced showing homogeneous distribution of grafted chains, which was examined by scanning electron microscopy. The modified films also exhibit medium responsive character, it shrinks in acidic and swells in basic solution. Moreover, the grafted film exhibited the ability to absorb copper ion, which was not influenced by the solvent used in grafting processes.

Keywords: Photografting, mixed-solvent, regenerated cellulose film, methacrylic acid, pH-responsive character, absorption of cupric ion

1. Introduction

Cellulose is a cheap, renewable, biodegradable and raw material for the textile paper and packaging industry. In recent years, attempts to graft polymerize vinyl monomers onto cellulose have aroused considerable interest. By grafting of a monomer to the cellulose backbone, some of the drawbacks of cellulose such as low tensile strength, high moisture transmission and low strength against microbial attachment can be eliminated. Depending on the chemical structure of the monomer grafted onto cellulose, graft copolymers gain new properties such as hydrophilic or hydrophobic character, improved elasticity, absorption of basic dyes [1], water absorption [2,3], ion-exchange capability [4], and heat resistance [5].

It was reported that the use of mixed solvent consisting of water and organic solvent (mixed solvent) on photografting of vinyl monomers onto natural [3,6] and synthetic polymers [7,8] has been extensively studied. The component of the organic solvents such as acetone, methanol, ethanol, dimethylformamide, dioxane in the mixed solvent accelerates the diffusion of monomer by swelling the trunk polymer and the grafted chains. In our previous papers, we reported the photografting of methacrylic acid (MAA) [9] and N-isopropylacrylamide (NIPAAm) [10] on xanthone (XT)-coated linear low-density polyethylene (LLDPE) film in mixed solvents consisting of water and organic solvent. It was found that the type/kind of the organic solvent in the mixed solvent influenced both the photografting behaviors and the location of grafted chains in the LLDPE film substrate.

It is interesting to study the effect of mixed solvent on the photografting of MAA on regenerated cellulose film since cellulose is a hydrophilic polymer having three reactive hydroxyl groups per an hydroglucose unit. On the other hand, it is well known that hydrogels formed by poly(MAA) [11,12] exhibit shrinking and swelling behaviors according to the medium. Therefore, by grafting of poly(MAA) on the regenerated cellulose films, it is expected that resulted

MAA-grafted films exhibit a medium-responsive function, according to the aqueous medium. This article deals with application of photografting using mixed solvents consisting of water and organic solvent to introduce of poly(MAA) onto regenerated cellulose film. The effect of mixed solvent on this system was investigated in terms of photografting behaviors, distribution of the grafted chains and its characteristics such as medium-responsive function and the ability to absorb copper ion.

2. Experimental

2.1. Materials

Commercially available regenerated cellulose film (cellophane) with thickness of 20 μm was used as a film sample, which was extracted with hot methanol for 24 h to remove additives. The film sample (3 x 10 cm, ca. 0.05 g) was immersed in an acetone solution containing known quantity of xanthone (XT) and 0.5 wt % poly(vinyl acetate) (PVAc, weight-average molecular weight = 100,000) at room temperature for 5 min, removed from the solution, and then dried at room temperature for 2 h under reduced pressure of 5 Torr to prepare a XT-coated film. The quantity of XT on the film was gravimetrically estimated to be about 10^{-8} mol per unit surface area (cm^2). MAA was purified by distillation under reduced pressure (4 torr at 35°C). All chemicals such as XT, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Cu^{2+}), acetone and methanol (MeOH) were reagent grade and used without further purification.

2. Photografting

Photografting was carried out in a Pyrex glass tube containing the XT-coated film sample and 30 ml water or mixed solvent, in which a given concentration of MAA (0.39 mol/l) was dissolved, under a nitrogen atmosphere. Irradiation with 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), around which the Pyrex glass tubes were rotated. Polymerized films were extracted for 24 h with hot methanol to remove the homopolymer of poly(MAA), and then dried at room temperature for 24 h under reduced pressure of 5 torr. Grafted samples with different percentage of graftings in each system were prepared by varying irradiation time. The percentage of grafting and the percentage of homopolymer were calculated by the following equations :

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

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

2.3. Measurements of attenuated total reflectance-infrared (ATR-IR) spectra

The ATR-IR spectra of the surface layer of grafted film were measured with an infrared microscope (AIM-800, FTIR-8700) of Shimadzu Co., Ltd. Kyoto, Japan.

2.4. Scanning Electron Microscope (SEM) Measurements

Carboxylic acid groups in a grafted poly(MAA) were converted to the potassium salts by immersing the grafted film in an aqueous solution of 1.0 wt % potassium hydroxide at 25°C for 24 h and then washed with water. The distribution profile of potassium ions in the cross section of the grafted film was measured with a scanning electron microscope (JSM-5600LV, JED-2200) of JEOL Co., Ltd. Tokyo, Japan.

2.5. Measurements of medium-responsive characters

The medium-responsive character of the grafted regenerated cellulose film was evaluated by measuring the dimensional change of the grafted films. Dimensional change of MAA-grafted regenerated cellulose film was examined as follows: Grafted film (surface area, $S_0 \text{ mm}^2$) was immersed in pH=4 or pH=8 solutions at 25°C for 24 h, alternately, whose pH were adjusted by Clark-Lubs buffer solution. After treatment, any excess of water on the film surface was removed using a filter paper and then, the surface area ($S_1 \text{ mm}^2$) of the treated film was measured. The surface area was determined by the length and width of the grafted film using standard ruler. The dimensional change of the grafted film was defined as follows:

$$\text{Dimensional change (\%)} = \frac{S_1 - S_0}{S_0} \times 100$$

2.6. Absorption of copper ion

A known amount of grafted film was added to 40 mL aqueous $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution (0,02 M), whose pH was adjusted to known values by Clark-Lubs buffer solution, and then absorption reaction was carried out at 25°C for 24 h. After the reaction, the grafted film sample was removed from the solution, and the remaining concentration of Cu^{2+} in the solution was determined by chelate titration¹³ using EDTA standard solution and (2-pyridylazo)-2-naphthol indicator.

3. Results and Discussion

3.1. Effect of solvents

Photografting is known to be useful for the introduction of various functional groups into polymeric substrates by selecting the type of monomers [14,15]. This paper deals with application of photografting using mixed solvent to introduce of polymethacrylic acid (MAA)-grafted chains into regenerated cellulose. The effect of mixed solvent on photografting of MAA onto XT-coated regenerated cellulose film was investigated at 60°C , and the results are shown in Fig. 1. The organic solvents used are acetone and MeOH.

The solvent composition give an effect on the percentage of grafting and showed a maximum (percentage of grafting) at a certain concentration of organic solvent. The effect of mixed solvent on polyethylene substrate described in previous study [9], was similar observed for cellulose substrate system. In our previous article [9] on photografting of MAA on LLDPE film the use of a mixed solvent was supposed to increase the solubility of MAA monomer in the system. As a result it will stimulate monomer supply for the radicals on the growing grafted polymer chains, and finally it will increase the percentage of grafting. A high concentration of organic solvent, the percentage of grafting decreases because of the chain transfer from growing grafted polymer radicals to organic solvent and/or termination reaction proceed. A similar effect may be observed on regenerated cellulose film.

3.2. Distribution of MAA-grafted chains

The surface layer of the original and grafted films was subjected to measurements of ATR-IR spectra and the results are shown in Figure 2. In the spectrum of polyMAA-grafted regenerated cellulose film, a sharp peak at 1710 cm^{-1} assigned to the carbonyl group of MAA-grafted chains is shown in Fig. 2b, confirming that grafting of MAA on regenerated cellulose film has occurred.

The observation was done using the grafted films treated with potassium hydroxide. Accordingly, the curve in the figure represents distribution profile of potassium atoms, that is, the MAA-grafted chains, in the cross section of the MAA-grafted regenerated cellulose film.

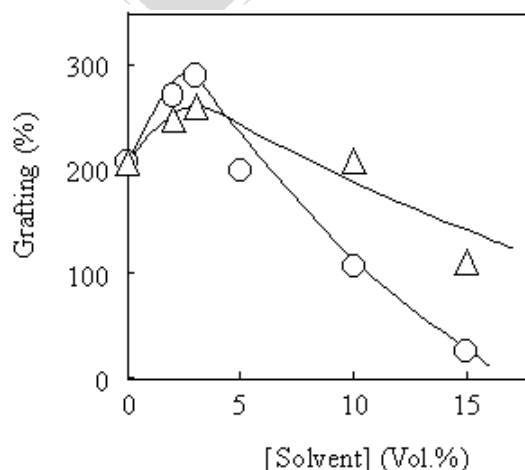


Figure 1. Photografting of MAA XT-coated regenerated cellulose film in mixed solvent. [MAA] = 0.39 mol/L. Irradiation at 60°C for 60 min: (○) acetone, (△) methanol.

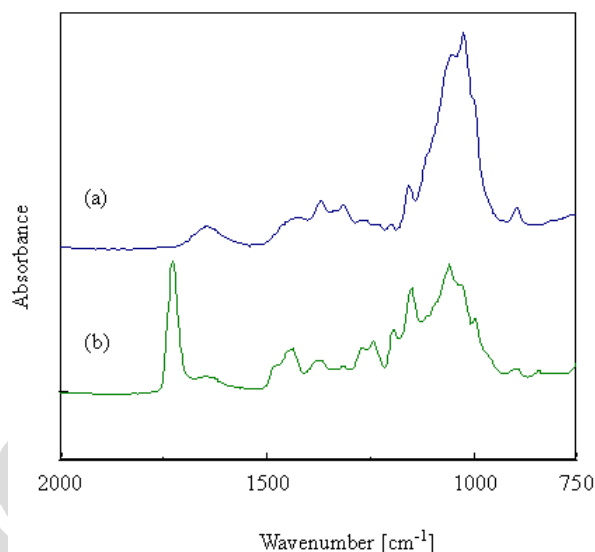


Figure 2. ATR-IR spectra of (a) regenerated cellulose film and (b) MAA-grafted regenerated cellulose film. The percentages of grafting are (a) 0% dan (b) 76%, respectively.

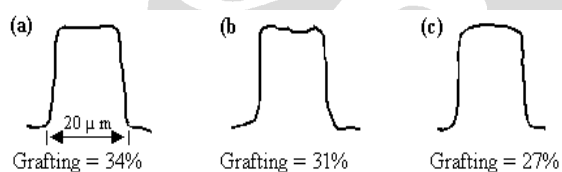


Figure 3. Distribution profile of potassium atoms in the cross-section of MAA-grafted regenerated cellulose films prepared in (a) water, (b) water/acetone (10% (v/v)) mixed solvent and (c) water/methanol (10% (v/v)) mixed solvent.

The vertical and horizontal directions in the figure correspond to the relative concentration of potassium atom and the cross section of the films, respectively. As seen from the results of SEM measurements in Figure 3, the MAA-grafted chains were found to distribute homogeneously inside the film sample even in the grafted films with lower percentage of grafting prepared in water and water/acetone (10 % (v/v)) mixed solvent. It is inferred that, higher affinity of cellulose substrate against water and mixed solvent, and thickness of the regenerated cellulose film used, resulted in grafted chains distribute homogeneously inside the films sample even in the grafted films with lower percentage of grafting.

3.3. Medium-responsive characters

It is known that MAA-grafted polymer films [8,16] exhibit medium responsive character, it shrinks in acidic and swells in basic solution. This behavior [17] is due to electrostatic repulsions between the carboxylic acids and ions present in the buffered solutions. At high pH values, the pendant carboxylate side chains are repelled each other and expand to minimize charge concentration.

The pH-responsive character of the resulting MAA-grafted regenerated cellulose film was evaluated by measuring a dimensional change of the grafted films. Fig. 4 shows the dimensional change of polyMAA-grafted regenerated cellulose films prepared in water and water/acetone-mixed solvents when immersed in pH 4 and pH 8 solutions at 25°C for 24 h,

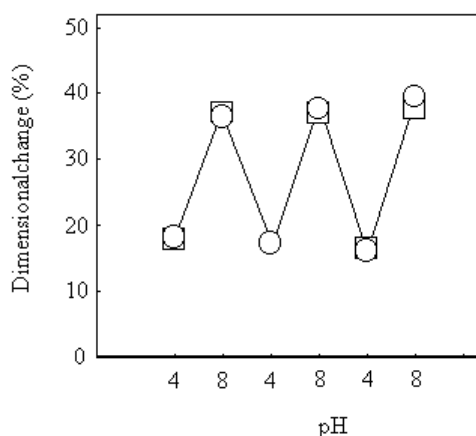


Figure 4. pH-responsive character of MAA-grafted regenerated cellulose film prepared in (□) water and (○) water/acetone (10 vol.%) mixed solvent. The percentages of grafting are (□) 83% and (○) 79%, respectively

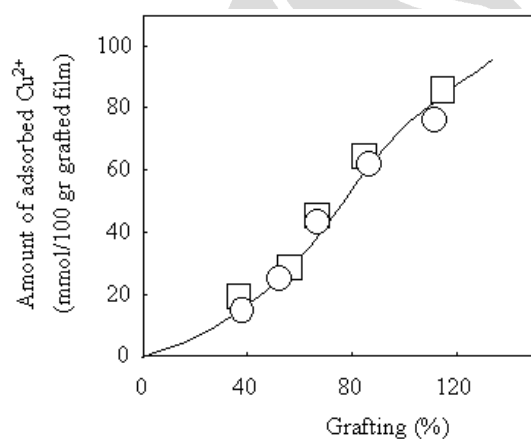


Figure 5. Adsorption of Cu^{2+} with MAA-grafted regenerated cellulose film prepared in (□) water and (○) water/acetone (10 vol.%) mixed solvent. $[\text{Cu}^{2+}] = 0.02 \text{ M}$, $\text{pH} = 5.0$, temperature = 25°C , time = 24 h.

alternately. The grafted film showed a medium-responsive character, where the film shrinks in acidic medium and swells in alkaline region. Moreover, the character was reversible between $\text{pH} = 4$ and $\text{pH} = 8$, and there was no large difference in the pH-responsive characters between the grafted films prepared in water and water/acetone (10 % (v/v)) mixed solvent. This is described in the fact that the distribution of MAA-grafted chains between the grafted films prepared in water and water/acetone (10 vol.%) mixed solvent, show similarity as shown in Figure 3.

3.4. Absorption of Cu^{2+}

It is conceivable that the carboxylic of polyMAA-grafted chains have to use as an ion exchange¹⁸ since polyMAA is known to form complex with copper (II) ion [19,20]. Absorption reaction of Cu^{2+} with the carboxyl groups in MAA-grafted films was studied to understand their ability to form complex with metal ions, and the results are shown in Figure 5.

The absorption was measured at $\text{pH} = 5.0$ using a Clark-Lubs buffer solution, since the pH is suitable for the absorption [21,22] of Cu^{2+} . The amount of absorbed Cu^{2+} increased with the increasing percentage of grafting due to the high content of carboxyl groups, and did not depend on the solvent used. This might be ascribed the grafted chains is distributed in the film based irrespective of polymerization conditions.

4. Conclusions

From above investigations it is concluded that by using a mixed solvent, a maximum percentage of grafting afforded at a certain concentration of organic solvent. The MAA-grafted chains penetrated the regenerated cellulose film substrate, which was commonly observed for the grafted films prepared in water and mixed solvent, even in the grafted films with lower percentage of grafting. The medium-responsive functions can be attached to the cellulose film by means of photografting MAA. The resulting grafted celluloses films were characterized by a medium-responsive character, in which they shrink in acid and swells in basic solution and showed absorption Cu^{2+} , which were not influenced by solvent composition in basic solution.

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References

- [1] D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. Wagenknecht (Ed), *Comprehensive Cellulose Chemistry*, Vol. 2, Functionalization of Cellulose, Wiley—VCH Verlag GmbH, Weinheim, (1998). Chapter 4.
- [2] F. L. Buchholz, A. T. Graham (Ed), *Modern Superabsorbent Polymer Technology*, Wiley VCH, (1998).
- [3] S. Kuwabara and H. Kubota, Water-Absorbing Characteristics of Acrylic-Acid Grafted Carboxymethyl Cellulose Synthesized by Photografting, *J. Appl. Polym. Sci.* 60 (1996) 1965–1970.
- [4] A. Hebeish and Z. H. El-Hilw, Preparation of DEAE Cotton-g-Poly(methacrylic acid) for Use as Ion Exchange. *J. Appl. Polym. Sci.* 67 (1998) 739–745.
- [5] F. A. Abdel-Mohdy. Graft Copolymerization of Nitrogen- and Phosphorus- Containing Monomers onto Celluloses for Flame-Retardant Finishing of Cotton Textiles. *J. Appl. Polym. Sci.* 89 (2003) 2573–2578.
- [6] F. Khan, S. R. Ahmad, E. Kron, UV-Radiation induced Preirradiation Grafting of Methyl Methacrylate onto Lignocellulose Fiber in an Aqueous Medium and Characterization, *J. Appl. Polym. Sci.* 91 (2004) 1667–1675.
- [7] H. Wang and H. R. Brown, Ultraviolet Grafting of Methacrylic Acid and Acrylic Acid on High-Density Polyethylene in Different Solvents and the Wettability of Grafted High-Density Polyethylene. I. Grafting, *J. Polym. Sci. Part A: Polym. Chem* 42 (2004) 253–262.
- [8] G. S. Irwan, S. Kuroda, T. Kondo, H. Kubota, Examination of the Role of Oxygen in the Photografting of Methacrylic Acid on a Polyethylene Film with a Mixed Solvent Consisting of Water and Organic Solvents. *J. Appl. Polym. Sci.* 89 (2003) 992–998.
- [9] G. S. Irwan, S. Kuroda, T. Kondo, H. Kubota, Photografting of Methacrylic Acid on Polyethylene Film: Effect of Mixed Solvents Consisting of Water and Organic Solvent. *J. Appl. Polym. Sci.* 83 (2002) 2454–2461.
- [10] G. S. Irwan, S. Kuroda, T. Kondo, H. Kubota, Photografting of N-Isopropylacrylamide on Polyethylene Film in Mixed Solvents Composed of Water and Organic Solvent. *J. Appl. Polym. Sci.* 87 (2002) 2454–2461.
- [11] T. G. Park and A. S. Hoffman, Synthesis and Characterization of pH- and/or Temperature-Sensitive Hydrogels. *J. Appl. Polym. Sci.* 46 (1992) 659–671.
- [12] N. A. Peppas, Y. Huang, M. Torres-Lugo, J. H. Ward, and J. Zhang, Physicochemical Foundations and Structural Design of Hydrogels In Medicine and Biology. *Annu. Rev. Biomed. Eng.* 02 (2000) 9–29.
- [13] K. Ueno, *Chelatometry*. Tokyo: Nankodo, 1989, p. 143.
- [14] H. Kubota, Catalytic Activity of 4-Vinylimidazole-Grafted Polyethylene: Effect of Method of Introduction of Grafted Chains by Means of Photografting. *Eur. Polym. J.* 3 (1992) 267–270.
- [15] T. Rohr, D. F. Ogletree, F. Svec, and M. F. Fréchet, Surface Functionalization of Thermoplastic Polymers for the Fabrication of Microfluidic Devices by Photoinitiated Grafting, *Adv. Funct. Mater.* 13 (2003) 264–270.
- [16] M. A. Islam, A. Dimov, A. L. Malinova, Environment-Sensitive Properties of Polymethacrylic Acid-Grafted Polyethylene Membranes. *Journal of Membrane Science*, 66 (1992) 69–78.
- [17] N. A. Peppas, Y. Huang, M. Torres-Lugo, J. H. Ward, and J. Zhang, Physicochemical Foundations and Structural Design of Hydrogels In Medicine and Biology. *Annu. Rev. Biomed. Eng.* 02 (2000) 9–29.
- [18] A. Hebeish and Z. H. El-Hilw, Preparation of DEAE Cotton-g-Poly(methacrylic acid) for Use as Ion Exchange, *J. Appl. Polym. Sci.* 67 (1998) 739–745.
- [19] M. Mandel and J. C. Leyte, Interaction of Poly(methacrylic acid) and Bivalent Counter Ions. I. *J. Polym. Sci. A.* 2 (1964) 2883–2899.
- [20] H. P. Gregor, L. B. Luttinger and E. M. Loebel, Metal-Polyelectrolyte Complexes. II. Complex of Copper With

Cross-linked Polyacrylic and Polymethacrylic Acids, *J. Phys. Chem.* 59 (1995) 366–368.

- [21] G. Güclü, G. Gürdağ and S. Özgümüş, Competitive Removal of Heavy Metal Ions by Cellulose Graft Copolymers, *J. Appl. Polym. Sci.* 90 (2003) 2034–2039.
- [22] G. S. Irwan, S. Kuroda, T. Kondo, H. Kubota, Effect of Monomer Concentration on Characteristics of Methacrylic Acid-Grafted Polyethylene Film Prepared by Photografting. *Eur. Polym. J.* 38 (2002) 1145–1150.

