Composition of Methyl Methacrylate-Grafted Cellulose

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Synopsis

Graft copolymerization of methyl methacrylate on cellulose samples was carried out using various initiator systems, and extraction treatment was performed on the copolymers with 50% to 300% grafting by weight. Adding of ceric ion to a suspension of cellulose and methyl methacrylate in water resulted in more efficient grafting than other methods. That is, amount of extracted cellulose from graft copolymers obtained by the conventional ceric ion method was approximately 20%, whereas those obtained either by the hydrogen peroxide method or by the adsorbed ceric ion method amounted to 70% to 80%. However, the amount of extracted homopolymer was approximately proportional to that of extracted cellulose. The composition of refined samples ranged 20% to 30% of cellulose content and 70% to 80% of poly(methyl methacrylate) content throughout all samples, and it was recognized that the proportion of poly(methyl methacrylate) tended to increase slightly with higher per cent grafting. When the structure of refined graft copolymer was derived from these values, it was recognized that the extent of the grafted chain was at most 1 mole per 1 mole of cellulose molecule in the conventional ceric ion method and amounted to only 1/10 mole in the hydrogen peroxide and adsorbed ceric ion methods.

INTRODUCTION

Recently, graft copolymerization of vinyl monomers has been investigated extensively as a means to modify cellulosic materials. Studies on the composition of graft copolymers from cellulose and vinyl monomers have been also carried out widely. For example, Sumitomo et al.[1,2] repeatedly carried out extraction of graft copolymer of styrene on cellophane with cupriethylenediamine and benzene alternately to increase the purity of graft copolymer and assumed its structure by analyzing it. By similar methods, Imoto et al.[3] analyzed a graft copolymer from cellulose initiated by a water–carbon tetrachloride system, and Iwakura et al.[4] reported another method consisting of acetylation followed by extraction of the acetylcellulose. As the graft copolymerization on cellulose usually is carried out in a heterogeneous system, not only the reaction proceeds partly, but it is thought to be remarkably affected by the fine structure of cellulose itself. The effect of different grafting methods must also be taken into account, since they can result in remarkable differences in composition and structure of the resulting copolymers.

In this report the graft copolymerization of methyl methacrylate on wood pulps was carried out using various initiators, the purity of the graft co-

polymers was increased by alternate extraction with cupriethylenediamine and acetone, and the true structure of cellulose–methyl methacrylate graft copolymers was studied by examining their compositions.

EXPERIMENTAL

Using bleached softwood sulfite pulp (SP) and bleached hardwood semi-chemical pulp (SCP) as cellulosic materials, the graft copolymerization of methyl methacrylate was carried out according to the following three methods.

Conventional Ceric Ion Method.[5,6] A method in which the polymerization is initiated by the addition of ceric ammonium nitrate aqueous solution to a system containing cellulose, water, and monomer under nitrogen.

Adsorbed Ceric Ion Method.[7] A method in which ceric ion-adsorbing cellulose is prepared in advance by immersing cellulose sample in ceric salt aqueous solution and washing it, and then the polymerization is carried out by adding water and monomer to the sample under nitrogen.

Hydrogen Peroxide Method.[8,9] A method in which ferric or ferrous ion-adsorbing cellulose is prepared in advance and the polymerization is carried out by adding monomer and then hydrogen peroxide under nitrogen.

By either method the graft copolymerization is easily initiated, but as a special feature by the conventional ceric ion method the grafted chain of copolymer is short and its number is large, while longer but fewer grafted chains are observed in both the adsorbed ceric ion and the hydrogen peroxide methods. The polymer sample which was washed with water and extracted with acetone for 24 hr after polymerization was indicated as an unrefined graft copolymer. The polymerization conditions are summarized

TABLE I
Conditions of Graft Copolymerization

Initiation	Cellulose sample	Concn of initiator mmole/l	Polymer temp, °C	Polymer time, min
Conventional ceric ion method	SP and SCP	ceric ion, 1–10	45	60
Adsorbed ceric ion method	SP[a] and SCP[a]	—	45	60
Hydrogen peroxide method	SP[b] and SCP[b]	hydrogen peroxide, 0.5–10	60	60

[a] Cellulose samples were pretreated with an aqueous ceric ion solution of concentrations 2 to 10 mmoles per liter at 45°C for 60 min.

[b] Cellulose samples were pretreated with an aqueous ferrous or ferric ion solution of concentration 3 mmoles per liter at 60°C for 60 min.

in Table I. Weight of poly(methyl methacrylate) isolated from graft copolymer by treating with 72% H_2SO_4 expressed by percentage of cellulose was indicated as per cent grafting. The molar number of grafts per 100 g of cellulose was calculated from the per cent grafting and average molecular weight of grafts.

RESULTS AND DISCUSSION

Refinement

It is supposed that, in addition to true graft copolymer, unreacted cellulose and unextracted homopolymer is included in unrefined graft copoly-

Polymerization product

    → Soxhlet extraction with acetone for 24 hr

Unrefined graft copolymer

    → Extraction with cupriethylenediamine under
        nitrogen at room temperature for 60 min

Unextracted residue

    → Soxhlet extraction with acetone for 48 hr

Refined graft copolymer (first extraction)
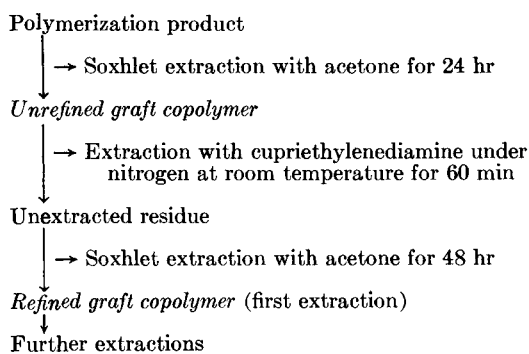
Further extractions

Fig. 1. Refinement of graft copolymer.

mers. If these samples are treated with cupriethylenediamine and acetone to extract cellulose and homopolymer, respectively, the purity of graft copolymer in the samples will be gradually increased. The refinement was carried out in the manner shown in Figure 1, and a pair of cupriethylenedi-
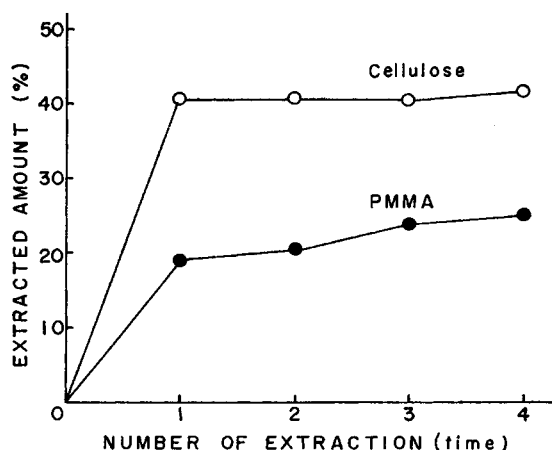

Fig. 2. Extracted amounts of unreacted cellulose and poly(methyl methacrylate).

amine–acetone extraction procedures was indicated as a set of extraction. The result of extractions for a sample with 325% grafting obtained from SCP by the conventional ceric ion method is shown in Figure 2. From this figure, it must be assumed that most of unreacted cellulose and homopolymer of methyl methacrylate is extracted by the first extraction procedure. The amount of cellulose extracted by the second and subsequent extractions was extremely small and also the amount of extracted poly(methyl methacrylate) was not so considerable. Accordingly, in the discussion below the sample treated by the first extraction is indicated as a refined graft copolymer.

Changes Due to Refinement

The changes of per cent grafting and average molecular weight of grafts with the number of extraction are shown in Figure 3. As a result of the first extraction, the per cent grafting remarkably increases from 325% to 450%, but after the second extraction it seems to decrease slightly. It is confirmed from the figure that the average molecular weight of grafted poly(methyl methacrylate) obtained by viscometry[10] is hardly affected at all by the extraction procedure.

It is thought that the larger the number of grafts of graft copolymer, the larger the fraction of cellulose molecules participating in the formation of grafts. In this case the fraction of extractable unreacted cellulose may be thought to be smaller. This relation is shown in Figure 4 for unrefined samples (50% to 300% grafting) obtained by various initiator systems, using SP and SCP as cellulosic materials. As expected, the amount of extracted cellulose becomes smaller with increasing number of grafts. However, a linear relation is not found between these two values, and no definite difference is observed in the curves for different initiator systems.
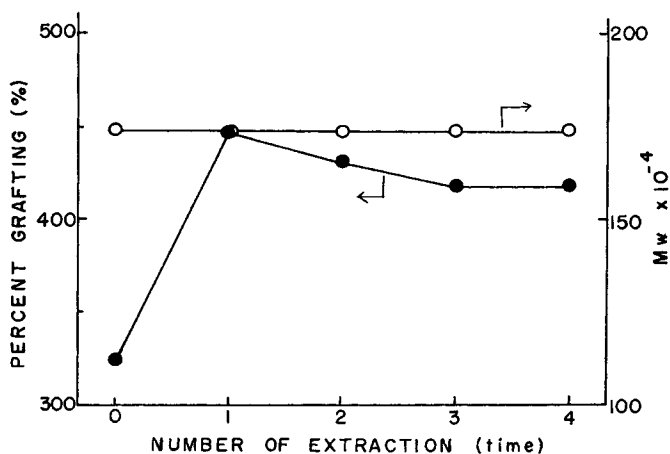

Fig. 3. Changes of per cent grafting (●) and average molecular weight of grafts (O) with number of extraction.
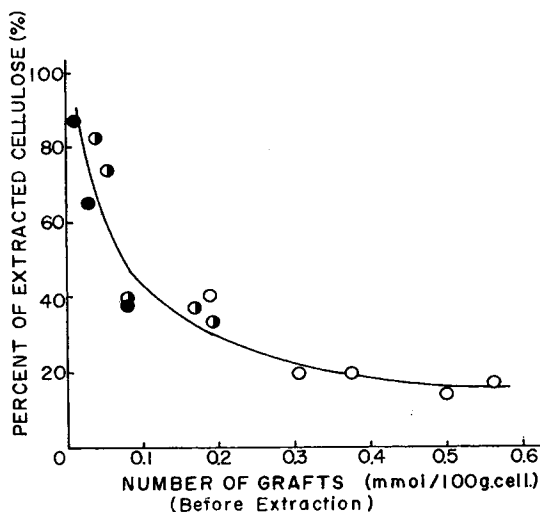
Fig. 4. Relation between extracted amount of unreacted cellulose and number of grafts of unrefined graft copolymer: (O) conventional ceric ion method; (●) adsorbed ceric ion method; (◐) hydrogen peroxide method.
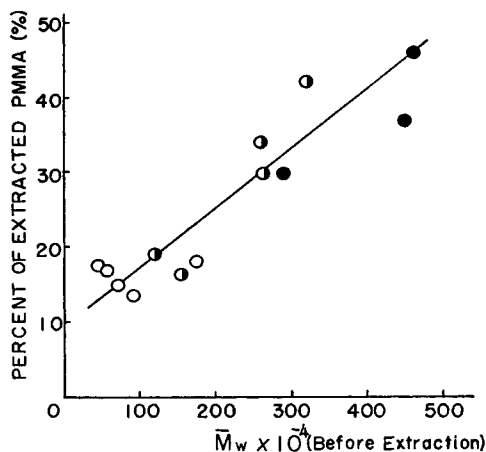

Fig. 5. Relation between extracted amount of poly(methyl methacrylate) and average molecular weight of unrefined graft copolymer: (O) conventional ceric ion method; (●) adsorbed ceric ion method; (◐) hydrogen peroxide method.

The average molecular weight of grafts for unrefined samples has a wide range in each initiator system, depending on the polymerization conditions, and the relation shown in Figure 5 exists between this value and the amount of poly(methyl methacrylate) extracted by the first extraction. The difference resulting from different initiator systems is hardly found and the amount of extracted poly(methyl methacrylate) is observed to increase linearly with increasing average molecular weight. This fact is

supposed to be closely connected with the increasing amount of extractable cellulose, because of the smaller number of grafts and the larger amount of unreacted cellulose with increase of the average molecular weight of grafts.

In Figure 6, the average molecular weight of unrefined samples is compared with that of refined samples for various graft copolymers. If there is no difference between them, their relation can be expressed by a straight line in the figure, which is extremely well satisfied by the samples with
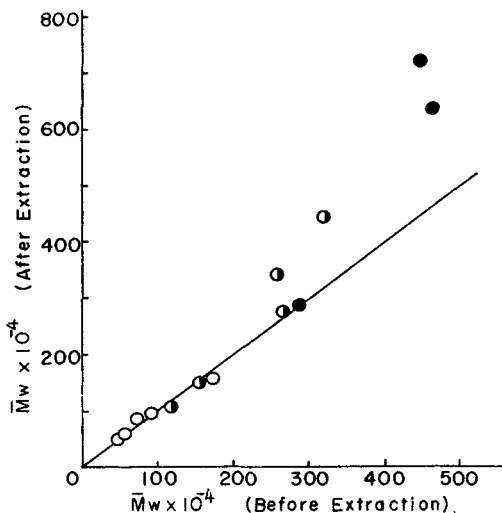

Fig. 6. Changes of average molecular weight of grafts due to refinement: (O) conventional ceric ion method; (●) adsorbed ceric ion method; (◐) hydrogen peroxide method.
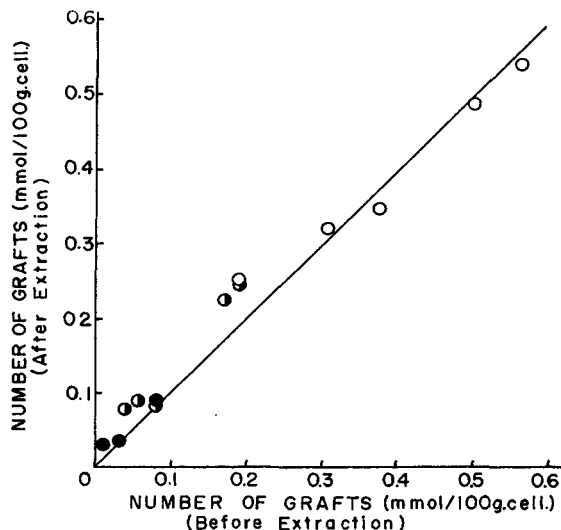

Fig. 7. Changes of number of grafts due to refinement: (O) conventional ceric ion method; (●) adsorbed ceric ion method; (◐) hydrogen peroxide method.
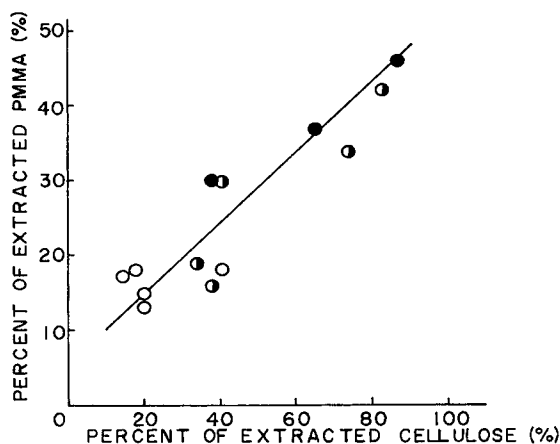
Fig. 8. Relation between extracted amount of poly(methyl methacrylate) and extracted amount of unreacted cellulose: (O) conventional ceric ion method; (●) adsorbed ceric ion method; (◑) hydrogen peroxide method.

average molecular weight of less than 2×10^6. However, in the case of average molecular weight of more than 2×10^6, their relation somewhat deviates from the straight line, and this result indicates that the lower molecular weight fraction is selectively extracted by the extraction procedure. As described above, it was clarified that the amounts of unreacted cellulose and homopolymer of methyl methacrylate which can be removed by the extraction procedure became larger in the following order: conventional ceric ion method < hydrogen peroxide method < adsorbed ceric ion method. The indications were also given about the changes accompanied by the refinement of graft copolymers.

The number of grafts before and after refinement is compared in Figure 7 for each sample. We expected that the number of grafts would markedly be increased by the refinement, whereas, as observed in the figure, the number of grafts hardly changes before and after refinement. However, the situation is a little different for the samples with smaller number of grafts obtained by the adsorbed ceric ion and the ferric ion–hydrogen peroxide methods; namely, the number of grafts increased threefold (from 0.01 to 0.03 mmole per 100 g of cellulose) for the sample obtained by the adsorbed method. This firmly indicates that the composition of true graft copolymer exists in the region of higher number of grafts than unrefined copolymer, and it is not difficult to expect that this value would become higher by repeated extractions. Using the results after the first extraction, it is difficult to attain to sound conclusions in our study. However, inasmuch as the extracted amount by the first extraction reached 80% for cellulose and 40% for poly(methyl methacrylate) for these samples, such samples are considered to be fairly far from the concept of graft copolymer from the viewpoint of composition. As indicated above, even if refinement was carried out, the number of grafts did not remarkably vary

TABLE II
Composition of Refined Graft Copolymer

Initiation	Cellulose sample	Per cent grafting, %		Average mol wt of grafts $\times 10^{-4}$	No. of grafts $\times 10$, mmole/100 g cellulose	Composition of copolymer	
		unrefined copolymer	refined copolymer			Cellulose, %	Grafted PMMA, %
Conventional ceric ion method	SP	282	306	95	3.22	24.6	75.4
	SP	268	285	82	3.48	26.0	74.0
	SCP	325	447	174	2.57	18.3	81.7
	SCP	274	273	60	4.55	26.8	73.2
	SCP	271	271	50	5.43	26.9	73.1
Adsorbed ceric ion method	SP	46	181	644	0.281	35.7	64.3
	SP	134	235	726	0.324	29.9	70.1
	SCP	235	267	293	0.912	27.3	72.7
Fe^{2+}–H$_2$O$_2$ method	SP	214	249	281	0.887	28.7	71.3
	SCP	229	271	109	2.49	27.0	73.0
	SCP	261	350	156	2.24	22.2	77.8
Fe^{3+}–H$_2$O$_2$ method	SP	122	355	450	0.790	22.0	78.0
	SP	143	314	350	0.897	24.2	75.8

from that for unrefined samples, and was larger for the conventional ceric ion method than for the hydrogen peroxide and the adsorbed ceric ion methods. A fairly definite difference was observed depending on the method of initiation.

The relation between the amount of extracted cellulose and that of extracted poly(methyl methacrylate) is shown in Figure 8 for the samples obtained with various initiator systems and with different per cent grafting. A common linear relation is observed in the figure and, although the correlation between these amounts is not so high irrespective of the method of initiation and per cent grafting, several indications about the composition of graft copolymer could be obtained from this relation.

Composition of Refined Graft Copolymers

The numerical values for all refined graft copolymers used in this study are shown in Table II. Comparing the kind of pulps, the number of grafts of refined samples is higher for SCP than for SP, and as a tendency of initiation methods, it becomes higher in the following order: adsorbed ceric ion method < ferric ion–hydrogen peroxide method < ferrous ion–hydrogen peroxide method < conventional ceric ion method. The number of grafts ranged from 0.03 to 0.55 mmole per 100 g of cellulose throughout the samples. Now, if the average degree of polymerization of cellulose is assumed to be 1000, then 100 g of cellulose corresponds to approximately 0.6 mmole and the maximum number of grafts obtained in this study corresponds to at most 1 mole of grafts per 1 mole of cellulose. In the case of the hydrogen peroxide and the adsorbed ceric ion methods, the number of grafts amounts to only $1/10$ mole. When the composition of refined samples was examined throughout all samples with 200% to 400% grafting, cellulose content ranged from 20% to 30% and poly(methyl methacrylate) content from 70% to 80%, and it was recognized that the ratio of the latter tended to increase slightly with the higher percentage of grafting. Why further refinement is difficult and whether the structure of the graft copolymer is essentially of the block type or not still remains unsolved and must be examined in the future.

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