Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Retuert, J. and Yazdani-pedram, M.(1992) 'Graft Copolymerization of Dimethyl Itaconate onto Microcrystalline Cellulose', Journal of Macromolecular Science, Part A, 29: 1, 31 — 41
To link to this Article: DOI: 10.1080/10101329208054105
URL: http://dx.doi.org/10.1080/10101329208054105

J.M.S.—PURE APPL. CHEM., A29(1), pp. 31–41 (1992)

GRAFT COPOLYMERIZATION OF DIMETHYL ITACONATE ONTO MICROCRYSTALLINE CELLULOSE

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ABSTRACT

Dimethyl itaconate was grafted onto microcrystalline cellulose (MCC) by using ceric ammonium nitrate in dilute nitric acid as the redox initiator. The grafting reactions were carried out in the presence of an oxygen atmosphere. The percentages of grafting, grafting efficiency, and homopolymer were found to depend on monomer, nitric acid, and initiator concentrations as well as reaction time and reaction temperature. The thermal behavior of MCC and grafted MCC were studied by dynamic thermogravimetric analysis and differential scanning calorimetry. The results obtained show that the graft copolymer is thermally less stable than unreacted MCC.

INTRODUCTION

Graft copolymerization of various vinyl monomers with cellulose and its derivatives, as a way of modifying their properties, has been reported in the literature

[1-22]. A vast number of these publications refer to grafting reactions where redox initiating systems such as Fenton's reagent (Fe^{2+}-H_2O_2) and ceric ammonium nitrate (CAN), among other redox systems, are employed [1, 4-6, 10, 12-22]. Indeed, it has been shown that vinyl monomers such as acrylonitrile, acrylamide, vinyl acetate, styrene, and some esters of acrylic and methacrylic acids can be grafted successfully onto cellulosic substrates by using the CAN catalyst [1, 5, 13-22].

Dimethyl itaconate (DMI), which is structurally similar to methyl methacrylate (MMA), has not been previously used in grafting reactions with cellulose and its derivatives, although the free radical homopolymerization of this monomer has been reported [23]. This vinyl monomer is the first member of the aliphatic diesters of itaconic acid and differs structurally from MMA only in the carbomethoxy group which replaces a hydrogen of the MMA methyl group.

It is the aim of this work to study the different parameters which affect the graft copolymerization of DMI onto MCC by using CAN in nitric acid as the redox initiator. In addition, the thermal behavior of DMI-grafted MCC is examined and the results are compared with that of ungrafted MCC.

EXPERIMENTAL

Materials

MCC was purchased from E. Merck. DMI was prepared by acid catalyzed esterification of itaconic acid with methanol by using the method described by Baker et al. [24]. The pure monomer was obtained by vacuum distillation of the crude product and its purity was checked by melting point, IR, and ^{1}H-NMR spectroscopies. The initiator used was analytical grade ceric ammonium nitrate obtained from E. Merck Darmstadt and was used as received. Freshly prepared CAN solutions in dilute nitric acid were used to initiate the grafting reactions.

Graft Copolymerization

Graft copolymerizations were carried out in 50 cm^3 stoppered flasks by first dispersing an exact amount of previously dried MCC in the initiator solution. The flask was then closed and placed in a thermostated bath at the desired reaction temperature and shaken for 1 min. The monomer was then added. Polymerization was started and continued for a predetermined period, during which time the reaction mixture was shaken occasionally. At the end of the polymerization, the grafted cellulose was separated by filtration, washed with warm water, and dried under reduced pressure at 50°C to constant weight. The grafted copolymer was then extracted with benzene in a Soxhlet for 24 h in order to remove poly(dimethyl itaconate) (PDMI) homopolymer which also forms during the grafting reaction.

Some grafting reactions were also carried out by using Fenton's reagent (Fe^{2+}-H_2O_2) as the redox initiator. The experimental conditions were as described for CAN-initiated polymerizations with the exception that in this case 8 cm^3 of 0.2 M H_2O_2 and 8 cm^3 of 0.02 M solution of ferrous ammonium sulfate (FAS) were used instead of CAN solution in dilute nitric acid.

Evidence of Grafting

The increase in weight of the extracted copolymer samples, as compared with that of original unreacted MCC, and the existence of the carbonyl absorption band at 1730 cm^{-1} in the IR spectra of the copolymers after benzene extraction of the homopolymer were taken as evidence of polymer add-on.

The grafting parameters were calculated as follows:

$$\%\ \text{Grafting}\ (\%\text{G}) = \frac{W_2 - W_1}{W_1} \times 100$$

$$\%\ \text{Grafting efficiency}\ (\%\text{E}) = \frac{W_2 - W_1}{W_3} \times 100$$

$$\%\ \text{Homopolymer}\ (\%\text{H}) = \frac{W_4 - W_2}{W_3} \times 100$$

where W_1, W_2, W_3, and W_4 denote, respectively, the weight of MCC, grafted MCC after benzene extraction, DMI, and grafted MCC before benzene extraction.

Gel Permeation Chromatography (GPC)

The weight-average molecular weights (M_w) of some DMI homopolymer samples, separated from grafted MCC by extraction with benzene, were determined by a GPC technique. A Bruker model LC-21B Liquid Chromatograph equipped with a refractive index detector and an IBM column packed with μ-Styragel of pore size 10 μm (molecular weight range 4×10^3 to 4×10^5) was used. The elution solvent was tetrahydrofuran, and a flow rate of 1 cm^3/min was used. Column calibration was carried out with standard polystyrene samples of narrow molecular weight distributions obtained from Waters Associate.

Thermal Analysis

Dynamic thermogravimetric analysis was carried out by using a Perkin-Elmer model TGS-1 thermobalance with a Perkin-Elmer UU-1 temperature program control. Samples (5-10 mg) were placed in the platinum sample holder, and the thermal degradation measurements were carried out in nitrogen atmosphere between 20 and 450°C at a heating rate of 20°C/min.

Differential scanning calorimetry (DSC) was carried out by using a Mettler model TA-3000 differential scanning calorimeter. Polymer samples (4-7 mg) were weighed into aluminum DSC pans and dried under vacuum at 50°C prior to measurements. Dry nitrogen was used as the purge gas, and thermograms were obtained in the temperature range 25-370°C at a scan rate of 20°C/min.

RESULTS AND DISCUSSION

Optimization of Conditions for the Grafting of DMI on MCC

Preliminary grafting copolymerizations were carried out by examining the influence of reaction temperature and reaction time on grafting percentage and efficiency. This was done by performing four sets of experiments where the concentrations of MCC, CAN, nitric acid, and DMI were kept constant. In the first three sets of experiments, the variations in grafting percentages and efficiencies were determined by carrying out copolymerizations at 50, 60, and 70°C for reaction periods ranging from 30 to 180 min. The effect of the variation of reaction temperature on grafting yield for a constant polymerization time was determined in the last set of experiments. From the results of these studies, it was observed that maximum grafting occurred when the grafting reaction was carried out at 60°C for 90 min.

A systematic investigation of the graft copolymerization of DMI, based on the results obtained from these preliminary experiments, was then carried out by taking into consideration other reaction parameters such as variations in CAN, DMI, and nitric acid concentrations, reaction time, and reaction temperature.

Influence of CAN Concentration on Grafting

The effect of ceric ion concentration on the graft yield obtained with MCC is shown in Table 1. The maximum percentage of grafting was obtained when 0.0548 g of CAN in 10 cm^3 of 10^{-4} *M* nitric acid was used. A further increase in CAN concentration, which is also accompanied with an increase in liquor-to-material ratio, has little effect on grafting yields. The grafting percentage increases up to 56.9% and then decreases to 18.5%. This could be due to the heterogeneous nature of the grafting reaction but more probably to the dual role of CAN as initiator and terminator. This postulate is supported by the fact that with increasing CAN concentration and liquor-to-material ratio, there is an increase in monomer solubility and hence an increase in homopolymer formation. It is also possible that with increasing total volume of the reaction, there is a decrease in the amount of monomer adsorbed onto cellulose, which results in lowering the extent of grafting. A similar decrease in grafting yield with increasing CAN concentration has been observed by other investigators when they grafted acrylic and methacrylic monomers onto cellulose [13, 19, 25].

TABLE 1. Effect of CAN Concentration on the Grafting of DMI on MCC[a]

Sample	CAN, g	%G	%H	%E
1	0.0183	10.8	8.9	1.6
2	0.0369	14.3	3.1	2.2
3	0.0465	23.9	11.7	3.6
4	0.0548	56.9	6.0	8.5
5	0.0639	40.7	6.4	6.1
6	0.0731	31.7	9.4	4.8
7	0.0914	27.9	14.2	4.2
8	0.1097	20.8	14.1	3.1
9	0.1281	18.5	14.8	2.8

[a] Reaction conditions: MCC, 0.3 g; DMI, 2.0 g; *T*, 60°C; reaction time, 90 min.

TABLE 2. Effect of Initial DMI on the Grafting of DMI on MCC[a]

Sample	DMI, g	%G	%H	%E
10	0.5	4.1	3.9	2.5
11	1.0	22.4	5.9	6.7
12	1.5	32.3	6.2	6.5
13	1.75	26.4	8.5	4.5
14	2.0	49.3	5.5	7.4
15	2.25	36.1	6.4	4.8
16	2.5	43.0	3.4	5.2

[a] Reaction conditions: MCC, 0.3 g; CAN, 0.0548 g/10 mL HNO_3 ($10^{-4}M$); *T*, 60°C reaction time, 90 min.

Effect of Monomer Concentration on Grafting

Table 2 shows the influence of DMI concentration on graft copolymerization with MCC. Although the data in Table 2 are scattered, it can be seen that increasing monomer concentration is accompanied by a significant increase in grafting up to 2 g of DMI. However, at a higher monomer concentration, the percentage of grafting begins to decrease. This could be attributed to the substantial amount of poly(dimethyl itaconate) (PDMI) grafted onto the cellulose backbone, which inhibits the diffusion of monomer and ceric ions to initiate further grafting.

Influence of Nitric Acid Concentration on Grafting

Table 3 shows the values obtained for grafting percentages, percent homopolymer, and efficiencies when different concentrations of nitric acid are used. The percentage of homopolymer shows small variation with nitric acid concentration. According to Ogiwara et al. [27] and Varma et al. [28], the concentration of nitric

TABLE 3. Effect of the Concentration of HNO_3 on the Grafting of DMI on MCC[a]

Sample	HNO_3 concentration	%G	%H	%E
17	10^{-4} *M*	46.7	5.9	7.0
18	10^{-3} *M*	42.0	6.6	6.3
19	5×10^{-2} *M*	23.2	7.0	3.5
20	10^{-2} *M*	34.9	6.7	5.3
21	5×10^{-1} *M*	22.6	6.9	3.4
22	10^{-1} *M*	26.6	6.3	4.0

[a] Reaction conditions: MCC, 0.3 g; DMI, 2.0 g; CAN, 0.0548 g/10 mL HNO_3 (10^{-4} *M*); reaction time, 90 min.

acid can affect both initiation and termination reactions. The roughly constant percentage of homopolymer obtained here is probably due to the rather narrow concentration range of nitric acid used. On the other hand, the grafting yield shows a maximum value when the concentration of nitric acid is 10^{-4} *M*. A further increase in nitric acid concentration resulted in lower percentages of grafting. Similar results were obtained by other research groups [13, 26-28] when they carried out grafting of some acrylic and methacrylic acid derivatives onto cellulose by using CAN catalyst. Ogiwara et al. [27] and Varma et al. [28] discussed this phenomenon in detail in terms of the kinetics of graft copolymerization.

Effect of Reaction Temperature on Grafting

The results of grafting reactions carried out at six different temperatures between 50 and 80°C are presented in Table 4.

The maximum percent grafting was obtained at 60°C while keeping the concentrations of the reagents constant. At temperatures above 60°C, the grafting yield decreases rapidly. This could be due to chain transfer and termination reactions which are favored at higher temperatures and do not contribute to grafting. The percentage of homopolymer remains nearly constant. This could be due to the mechanism of the initiation reaction which is independent of changes in temperature.

Influence of Reaction Time on Grafting

Table 5 shows the influence of reaction time on the percentages of grafting obtained with MCC. The optimum reaction time for maximum grafting was 90 min. A further increase in reaction time slightly decreases the percentage of polymer add-on, while the amount of the homopolymer increases. We think that the slight decrease in percent grafting for longer reaction times is due to partial hydrolysis of the copolymer.

TABLE 4. Effect of Reaction Temperature on Grafting of DMI on MCC[a]

Sample	Temperature, °C	%G	%H	%E
23	50	13.9	5.3	2.1
24	55	34.6	5.3	5.2
25	60	45.1	6.7	6.8
26	65	30.7	5.4	4.6
27	70	12.3	6.8	1.9
28	80	6.2	5.8	0.9

[a] Reaction conditions: MCC, 0.3 g; DMI, 2.0 g; CAN, 0.0548 g/10 mL HNO_3 (10^{-4} *M*); reaction time, 90 min.

TABLE 5. Effect of Reaction Time on the Grafting of DMI on MCC[a]

Sample	Reaction time, min.	%G	%H	%E
29	30	4.3	6.3	0.7
30	60	8.1	8.1	1.2
31	75	36.6	6.8	5.5
32	90	45.1	6.7	6.8
33	105	42.9	5.9	6.4
34	120	36.4	10.7	5.5
35	150	33.0	11.8	5.0
36	180	30.3	9.8	4.6

[a]Reaction conditions: MCC, 0.3 g; DMI, 2.0 g; CAN, 0.0548 g/10 mL HNO_3 (10^{-4} *M*); *T*, 60°C.

FAS-Initiated Copolymerization

The results obtained from FAS-initiated copolymerization of DMI with MCC show that the grafting percentages obtained with this redox initiator are similar to those obtained with ceric ion. The amount of homopolymer formed in this case was higher and the molecular weights of the homopolymers as determined by GPC showed a bimodal distribution with values between 15,000 and 85,000. We cannot explain these results, but we think that they are probably due to simultaneous initiation by both cellulosic and hydroxyl radicals.

Characterization of Graft Copolymer and PDMI Homopolymer

Infrared spectroscopy (IR), differential scanning calorimetry (DSC), and dynamic thermogravimetric analysis (TGA) were used to characterize the grafted microcrystalline cellulose with poly(dimethyl itaconate). The IR spectra of the grafted cellulose, microcrystalline cellulose, and poly(dimethyl itaconate) are shown in Fig. 1. The grafted material showed a carbonyl absorption band at 1730 cm^{-1} due to the carbonyl group of poly(dimethyl itaconate). This was taken as evidence for grafting.

The weight-average molecular weight of PDMI homopolymers, separated from CAN-initiated copolymerizations, were determined by a GPC technique. They range from 20,000 to 35,000 with rather broad molecular weight distributions.

The thermal decomposition behavior of microcrystalline cellulose and a sample of microcrystalline cellulose grafted with dimethyl itaconate (56.9% grafting yield) are shown in Fig. 2. The thermal decomposition temperature (TDT), taken as the temperature at which the samples have lost 10% of their initial weights, for the graft copolymer is slightly lower than the TDT value for microcrystalline cellulose. Generally, all the copolymer samples showed slightly decreased thermal stability as compared with pure microcrystalline cellulose. From Fig. 2 it is evident that both microcrystalline cellulose and grafted copolymer show similar profiles when they are heated from 20 to 450°C. However, the thermal decomposition temperature at which 50% weight loss is observed ($T_D^{50\%}$) for grafted cellulose is only 10°C lower

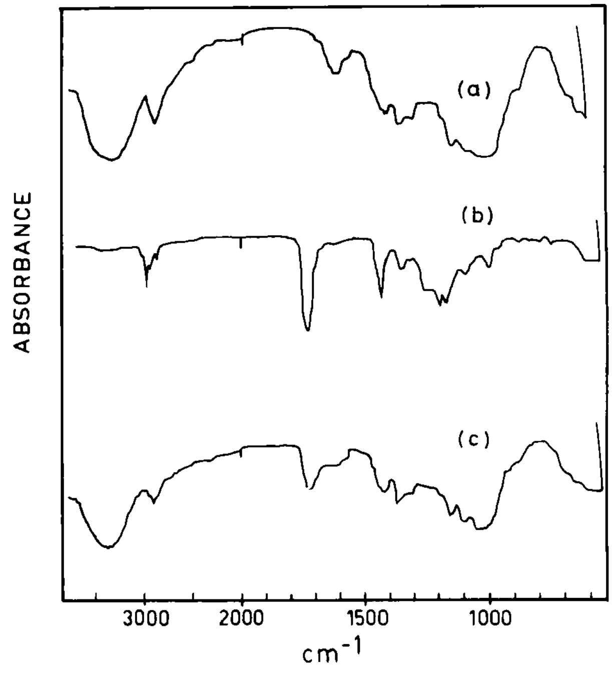

FIG. 1. IR spectra of MCC (a), PDMI homopolymer (b), and grafted MCC with PDMI (c).

than the $T_D^{50\%}$ value for microcrystalline cellulose. In the case of cotton cellulose grafted with acrylic and methacrylic monomers, Hurduc et al. [29] observed that the thermal behavior of grafted cotton with methyl acrylate and methyl methacrylate is lower than that of the initial cellulose. Later, Varma and Narasimhan [28] found that the thermal stability of grafted cellulose, with different acrylic monomers and methyl methacrylate, increases with an increase in percent graft-on. They also observed that the thermal stabilities of natural cotton and cotton grafted with

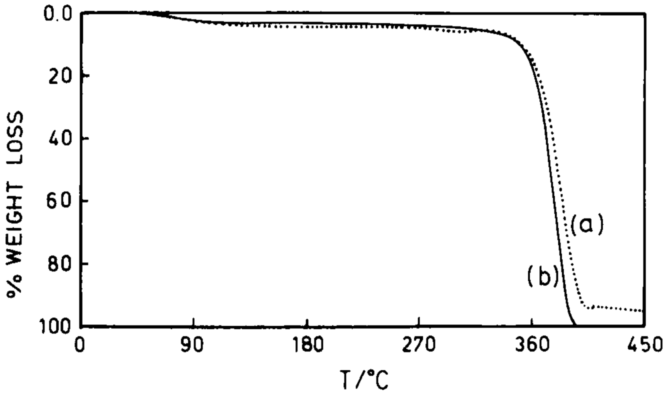

FIG. 2. TGA curves of MCC (a) and grafted MCC with PDMI (b).

methyl, ethyl, *n*-butyl acrylate, and methyl methacrylate are in the order ethyl > natural cellulose > methyl methacrylate > *n*-butyl acrylate. However, Sharma and Daruwalla [30] found that graft copolymerization of acrylamide and acrylonitrile makes cotton cellulose thermally more stable, while in the case of methyl acrylate and methyl methacrylate-grafted cottons, the initial decomposition starts at higher temperatures, but subsequent decomposition is faster and the overall thermal stability is lower. Recently, Fernandez et al. [31] reported that graft copolymerization of vinyl acetate makes cotton thermally less stable, while in the case of methyl acrylate-grafted cotton samples having 33, 83, and 174% grafting yield, the initial decomposition starts at lower temperatures but decomposition beyond 360°C takes place at higher temperatures than those for ungrafted cotton. In the case of the sample with 430% grafting yield, the thermal stability is higher than that of the original cotton. These authors also concluded that the thermal stability of cotton grafted with methyl acrylate is higher than that of cotton grafted with vinyl acetate.

From the results obtained in this study and by considering the findings of other investigators, it is evident that the thermal stability of grafted cellulose with synthetic polymers depends not only on the nature of the monomer used but also on the extent of grafting.

Therefore, the lower thermal decomposition temperatures observed for grafted microcrystalline cellulose with dimethyl itaconate could be due to both the lower thermal stability of poly(dimethyl itaconate) [32] and to the low percent grafting yield obtained. It should be noted that the small effect on thermal stability could be due to the grafting process that occurs mainly on the surface of microcrystals of MCC.

DSC thermograms of microcrystalline cellulose and a sample of grafted cellulose with 56.9% polymer add-on are presented in Fig. 3. These traces show similar features for both grafted material and unreacted cellulose. The shallow endotherm found by DSC in the temperature range 140 to 170°C could be due to dehydration, and the deeper endotherm in the temperature range 300 to 360°C for MCC and 340 to 370°C for grafted material could be due to the depolymerization process. The peak maximum temperature of the second endotherm for the grafted copolymer (358°C) is higher than the value for microcrystalline cellulose (337°C), probably due to crosslinking of cellulose chains with PDMI linkages. The glass transition

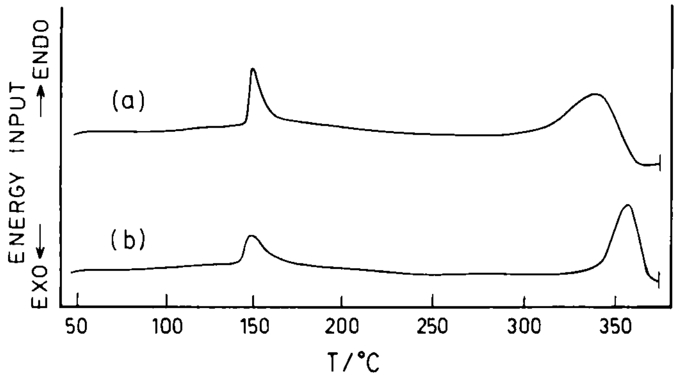

FIG. 3. DSC thermograms of MCC (a) and grafted MCC with PDMI (b).

temperatures of the two PDMI homopolymer samples obtained from CAN and FAS initiation systems were determined by DSC. The T_g values (87 and 82°C, respectively) for these homopolymers are in agreement with the value found previously by Cowie et al. [33] for this polymer with comparable molecular weight.

ACKNOWLEDGMENTS

The authors thank the FONDECYT (Project 1265/88) and Alexander von Humboldt-Foundation for financial support.

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Received February 18, 1991
Revision received May 7, 1991