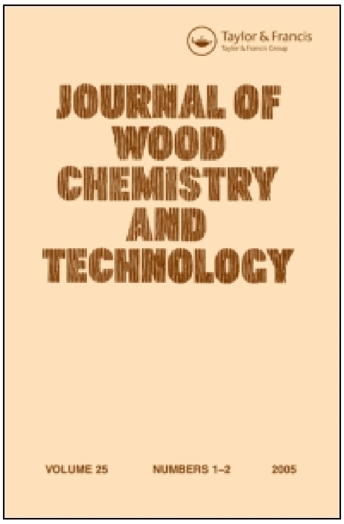

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GRAFTING OF MALEIC ANHYDRIDE COPOLYMERS ONTO CELLULOSE ACETATE AND METHYL CELLULOSE

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ABSTRACT

A high level of control over grafting reactions onto cellulose derivatives was achieved by an acyl transfer reaction mechanism. Ethylene/maleic anhydride copolymer (EMA) and styrene/maleic anhydride copolymer (SMA) were grafted onto cellulose acetate (CA) and methyl cellulose (MC) in a simple and effective way under homogeneous reaction conditions. While pyridine, a commonly used catalyst for the reaction of an anhydride with an alcohol to form an ester, gave an inconveniently long reaction time, N-methylimidazole (NMID) and 4-(N,N-dimethylamino)pyridine (DMAP) were found to increase greatly the rate of esterification.

INTRODUCTION

Grafting of synthetic polymers onto cellulose and cellulose derivatives is a useful way to improve the qualities of both materials and to expand the

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range of their applications[1]. To date, there are a few reaction schemes that attempt to prepare graft copolymers of cellulose with the goal of preparing a new material with the advantages of both starting materials. Most of the proposed grafting reactions are carried out by free radical mechanisms[1,2]. Some inherent disadvantages in these procedures are a high percentage of occluded homopolymer in the graft product, only a few high molecular weight graft molecules, reaction results that are not reproducible, and low levels of substitution. These problems have prevented significant commercialization of grafting processes and have been reviewed in detail by Stannett[3].

A high degree of control over the grafting process can be achieved by nucleophilic substitution reactions. Biermann *et al.* have reported that polystrylcarboxylate, polyamidecarboxylate, and poly(methylmethacrylate)carboxylate were grafted onto mesylated cellulose acetate with a high level of control by nucleophilic displacement of the mesylate groups by carboxylate anions[4,5]. Recently, Biermann and Narayan grafted poly(ethyleneimine) onto mesylated cellulose acetate by second order nucleophilic displacement of mesylated groups by amine groups[6]. It is known that anhydrides react with alcohols by the acyl transfer reaction mechanism in which -OOCR is replaced by another basic group such as RO^- of ROH. This study describes a simple and effective way to achieve a high level of control over the grafting reactions of ethylene/maleic anhydride copolymer (EMA) or styrene/ maleic anhydride copolymer (SMA) onto cellulose acetate (CA) or methyl cellulose (MC) by the acyl transfer reaction mechanism under homogeneous reaction conditions. The number of reaction sites per side chain is easily controlled by the amount of maleic anhydride copolymer employed. While the acyl transfer reaction itself is not new, its application to the formation of cellulose graft copolymers is novel. Pyridine is commonly used in acylation reactions where it serves as a nucleophilic catalyst[7] and base to accept the generated proton. More powerful catalysts like N-methylimidazole (NMID) and 4-(N,N-

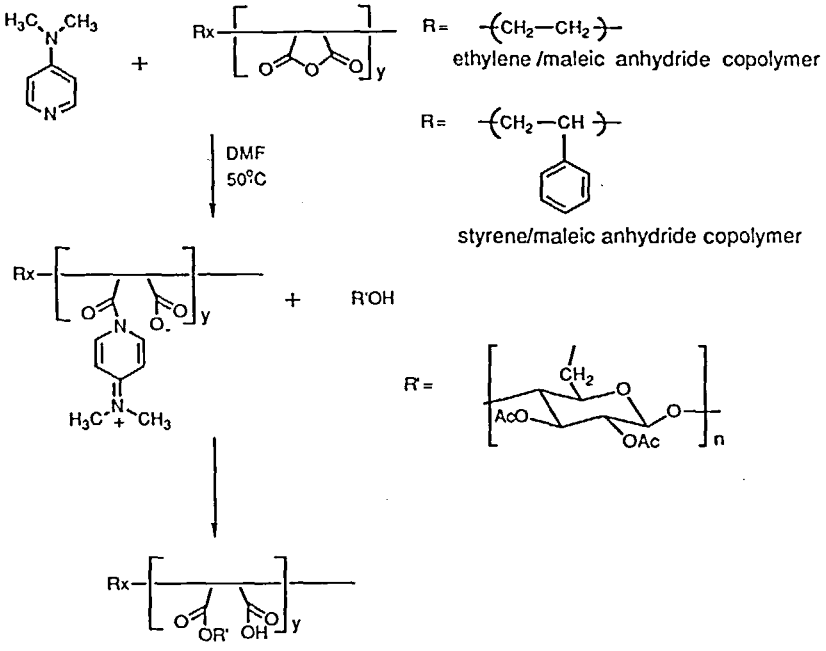

FIGURE 1. Reaction Mechanism for the Grafting of the Maleic Anhydride Copolymers onto Cellulose Acetate in the presence of DMAP

dimethylamino)-pyridine (DMAP) can be employed to accelerate the acylation rate. The relative catalytic efficiency of pyridine, NMID, and DMAP for the catalyzed acetylation of isopropyl alcohol is 1:360:17000 (pyridine:NMID:DMAP, respectively)[7,8]. Figure 1 shows the mechanism for the DMAP-catalyzed grafting reaction.

Crosslinking is to be expected since many reaction sites on the maleic anhydride copolymers could potentially react with the numerous hydroxyl groups on the cellulose derivatives. The crosslinks will principally involve the C-6 hydroxyl groups, since cellulose acetate often has many of the free hydroxyl groups at the C-6 position and there is less steric hindrance for formation of ester linkages at this position. Rowland found that C-6 hydroxyl groups are favored in esterification reactions[9]. Figure 2 shows the formation

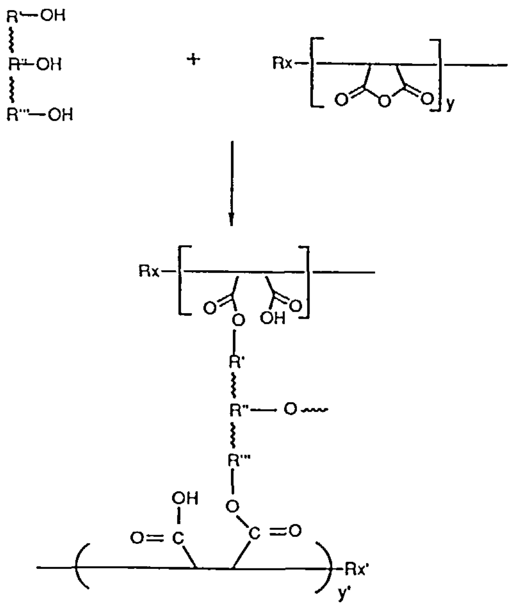

FIGURE 2. Formation of the Cross-linked Graft Copolymer by Reaction of Maleic Anhydride Copolymer with Cellulose Derivative

of crosslinks by the reaction of maleic anhydride copolymers with cellulose derivatives.

RESULTS AND DISCUSSION

Grafting reactions were accomplished by reacting either cellulose acetate (CA) of 2.4 degree of substitution(DS) or methyl cellulose (MC) of 1.8 degree of substitution(DS) with high molecular weight ethylene/maleic anhydride copolymer (EMA) or high molecular weight styrene/maleic anhydride copolymer (SMA) by the acyl transfer reaction mechanism (Figure 1). In order to achieve high grafting efficiencies, these grafting reactions were carried out under strictly anhydrous conditions to avoid hydrolysis of the anhydrides. The addition of 0.1% and 0.2% water in dry DMF did not change the gelation time significantly of the EMA-CA system; however, the use of reagent grade, DMF of unknown moisture content that was not dried did increase the gelation time and lead to a softer gel.

The reaction of 2.5% (w/vol) ethylene/maleic anhydride copolymer or styrene/maleic anhydride copolymer with 5% (w/vol) cellulose acetate or 3.3% (w/vol) methyl cellulose in DMF at 50°C resulted in the formation of a solid gel, indicating crosslinking of the chains of the cellulose derivatives and the maleic anhydride copolymers. There is no method given for observing the crosslinking other than gelation. Size exclusion chromatography (SEC) cannot be used to determine the molecular-weight distribution because the gelled product is not soluble. Similarly, NMR techniques available to us could not be used for the same reason. Even FT-IR characterization of the products was inconclusive due to the small extent of reaction during the grafting process. Solvent extraction was used to remove unreacted maleic anhydride copolymer as an indication of grafting.

The gelation time of ethylene/maleic anhydride copolymer onto cellulose acetate is much shorter than that of styrene/maleic anhydride copolymer. This difference in gelation time may be due to steric hindrance and the slightly lower viscosity of the styrene/maleic anhydride copolymer. The styrene/maleic anhydride copolymer contains a bulky phenyl group where ethylene/maleic anhydride copolymer has a hydrogen atom. The gelation times are reported in Table 1.

Two cellulose acetates (lot# A8A and A18B of the same commercial product of Kodak co.) were used for the acylation reaction with EMA and showed different acylation reaction time of 3 minutes and 20 minutes, respectively. Although no readily apparent explanation for these discrepancies is available, lot# A18B was used for further experimentation because of unavailability of additional samples of lot# A8A. Even though these two cellulose acetates have been reported to have the same nominal molecular weight (61,000), the viscosity measurements were substantially different

TABLE 1.
Results of the Grafting Reaction at 50°C in DMF

Catalyst	Copolymer	Substrate	Gelation time
Pyridine	EMA	CA	12 hrs
	SMA	CA	>10 days
NMID	EMA	CA	65 min
	SMA	CA	570 min
DMAP	EMA	CA_k	20 min
	EMA	CA_a	60 min
	SMA	CA	210 min
DMAP	EMA	MC	15 min
	SMA	MC	90 min

EMA : Ethylene/maleic anhydride copolymer
SMA : Styrene/maleic anhydride copolymer (average M.W. 50,000)
DMAP: 4-(N,N-dimethylamino)pyridine
NMID : N-methylimidazole
CA_a : Cellulose acetate (Aldrich co, catalog # 18,085-5)
CA_k : Cellulose acetate (Kodak co, lot # A18B)
MC : Methyl cellulose (Kodak co.)

between these lots. Because the gelation time of EMA onto CA of the Aldrich co. is inconveniently much longer(60 minutes) than that of EMA onto CA of the Kodak co., only the Kodak CA was used to compare the acylation reaction time using different catalysts. The acylation reactions of 3.3% (w/vol) MC in DMF with maleic anhydride copolymers occurred faster than that of 5% (w/vol) CA, as would be expected, because of the higher viscosity and lower degree of substitution of the methyl cellulose, which gives more reactive sites for copolymerization. Table 2 shows the results of viscosity measurements of the starting materials.

TABLE 2.
Viscosities of Starting Materials

Material	MW	Concentration	Viscosities (cps)
CA (Kodak-A)	61,000	2.7% in Acetone	245
CA (Kodak-B)	61,000	7.6% in Acetone	137
CA (Aldrich)	30,000	7.6% in Acetone	20
MC (Kodak)	86,000	1.1% in DMSO	249
EMA (Aldrich)	Unknown	12.3% in DMF	130
SMA (Aldrich)	350,000	12.3% in DMF	108

MW : Molecular weight
Kodak-A : Lot# A8A
Kodak-B : Lot# A18B

Considering the high molecular weights of the polymers involved, an extent of reaction of less than 10% would likely give a crosslinked product. For example, while the 1700 molecular weight SMA has about 6 reactive anhydride units per molecule, even after 7 days of reaction at 50°C with DMAP catalyst gelation was not observed. Considering that the acylation of isopropyl alcohol is complete within 5-10 min at 54-70°C with 2% DMAP, one would expect crosslinking with the low molecular weight SMA.[8] The fact that gelation occurs within 3.5 hours with the 350,000 molecular weight SMA indicates a slow reaction with a low extent of reaction.

It is known that weak bases are effective catalysts for the reaction of an anhydride with an alcohol to form an ester[10]. Acylation reactions often use pyridine as a catalyst. Acylation reactions in the presence of pyridine probably involve initial acylation of pyridine followed by a reaction with the alcohol[11,12] and the reaction times tend to be inconveniently long. DMAP was used as catalyst to accelerate the rate of esterification since it forms a more stable pyridinium ion by resonance stabilization[8,13]. The formation of this stable ion results in an effective increase of the alkoxide ion concentration. As shown in Table 1, the reaction times are considerably decreased with NMID and DMAP catalysts. The acylation reactions of CA (1.0 g) with EMA (0.5 g) in the presence of DMAP (0.4 g) in DMF (20 ml) with, or without, pyridine (0.5 g) did not change the gelation time significantly, meaning the amount of DMAP used was sufficient to act as an acid scavenger.

Grafting yields (%) were calculated as the weight percentage of copolymer that is covalently linked to the cellulose backbone of the graft copolymer, determined after DMF extraction. The DMF extraction removes unreacted maleic anhydride copolymers and DMAP present in the reaction products. The increase in weight of the products obtained after DMF extraction, compared to the original weight of CA and MC, indicates that grafting has occurred. Grafting yields increased with the use of NMID and DMAP compared to pyridine, and most of the yields were 70-95%.

EXPERIMENTAL

Materials

N,N-dimethylformamide (DMF) was freshly distilled under vacuum over CaH_2 before use and transferred by syringe technique under dry nitrogen. Cellulose acetate of 2.4 degree of substitution (Eastman Kodak co., Rochester, NY, catalog no. 1173335) was used for this experiment. Methyl cellulose of 1.6 to 1.9 degree of substitution (Eastman Kodak co., Rochester, NY, catalog no. 1374875) was used. Ethylene/ maleic anhydride copolymer (EMA)(Aldrich co., Milwaukee, WI, catalog no. 18,805-0) and styrene/maleic anhydride copolymers (SMA) (Aldrich co., catalog no. 18,293-1, average M.W. 350,000, styrene content 50% and catalog no. 30,267-4, average M.W. 1,700, anhydride content 33%) were dried in a vacuum desiccator over phosphorous pentoxide. The viscosities of the starting materials were measured with the Brookfield Viscometer (Model DV-1).

Grafting Reaction

The grafting reactions were carried out using 0.5 g of maleic anhydride copolymers, either 1 g of cellulose acetate in 20 ml of N,N-dimethylformamide (DMF) or 1 g of methyl cellulose in 30 ml of DMF, and the catalysts. Pyridine (0.5 ml), N-methylimidazole (NMID) (0.5 ml), and 4-(N,N-dimethyl amino)pyridine (DMAP) (0.3 g) were employed as catalysts and gelation time was determined for each reaction. The grafting reactions were carried out under strictly anhydrous conditions to avoid hydrolysis of the anhydrides. The reaction mixtures were reacted at 50°C with shaking. After the reaction periods, several of the reaction mixtures were extracted several times with DMF to remove unreacted copolymers and DMAP. The extract was dried in a vacuum oven at 50°C and weighed. Extractions were carried out until no further copolymers and DMAP were obtained. An extraction period of 72 hours at 50°C was sufficient to extract completely. Grafting yields were calculated as the weight percentage of the copolymers that are attached to the cellulose acetate substrate, which is given by:

$$\textit{Grafting yield} = \frac{\textit{weight of copolymer in grafts}}{\textit{weight of copolymer used}} \times 100\%$$

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