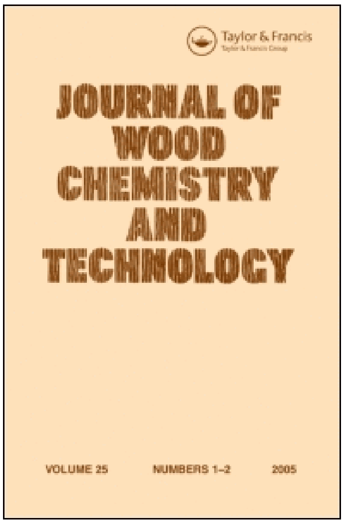

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Synthesis and Identification of Graft Copolymers of Wood Pulp and 4-Methyl-2-oxy-3-oxopent-4-ene

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SYNTHESIS AND IDENTIFICATION OF GRAFT COPOLYMERS OF WOOD PULP AND 4-METHYL-2-OXY-3-OXOPENT-4-ENE

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ABSTRACT

A set of graft copolymers of wood pulp and 4-methyl-2-oxy-3-oxopent-4-ene has been synthesized. The graft reaction is a free radical polymerization coinitiated by calcium chloride, hydrogen peroxide on wood pulp in dimethylsulfoxide at 30°C. The wood pulps used in this research are unbleached products produced by chemical, thermal and mechanical pulping. All of them contain 25 to 29 weight percent lignin. Separation of the grafted wood pulp from homopoly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) formed during the reaction was done by benzene extraction. The results show that after the reaction, virtually all the wood pulps have a weight increase and, for very high yield sodium bisulfite pulp, a weight increase of up to 92.7% of the original weight of pulp was obtained. The Fourier transform infrared spectra of the benzene unextractable fractions provide strong proof of grafting.

The grafted wood pulp is a surface-modified pulp. Grafting has changed the surface properties of the starting wood pulp from hydrophilic to hydrophobic. The importance of this change is that the grafted wood pulp has potential use as a reinforcing material without use of coupling agents in many hydrophobic polymer matrixes.

The reaction products contain homopoly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) and uniformly dispersed grafted wood pulp. Under ordinary thermal compression conditions, thermoplastic composite objects can be made directly from the reaction products which contain up to 56 weight percent wood pulp.

INTRODUCTION

The use of natural organic fillers such as wood fibers as a reinforcing agent has been limited to thermoset materials[1]. Wood fibers offer many advantages: lower density, higher specific strength and modulus, renewable resources, lower cost and less wear to the machinery during processing[1-2]. The major problem in preparing composite materials of wood fibers and thermoplastic polymers has been the poor interfacial adhesion between the hydrophilic wood filler and the hydrophobic polymer matrix[1,3,4]. One of the methods used to improve the adhesion is the use of coupling agents or adhesion promoting agents, such as maleic anhydride (MA)[2], maleic anhydride modified polypropene (MAPP)[1,2,4,5], polymethylene-poly(phenyl isocyanate) (PMPPIC)[3], polyethylene-poly(phenyl isocyanate) (PEPPIC)[1], ionomer modified polyethylene (Surlyn)[2,5], chlorinated polyethylene (CPE)[2,5], γ-aminopropyltriethoxysilane (A-1100)[3], and vinyltris(2-methoxyethoxy) silane (A-172)[1]. A related problem in making wood-thermoplastics composites is the poor dispersion of wood in the polymer matrix[3,5]. This problem can be solved by adding dispersing agents such as stearic acid, paraffin wax, polyethylene wax, mineral oil, etc.[2,4,5], elevating mixing temperature, and extending mixing period. However, extended mixing will break more wood fibers because of the strong shearing stress caused by high viscosity during the mixing stage.

An alternative method to overcome the problems of poor adhesion and dispersity is to graft short polymer segments to the fiber surface[1,2,3,6,7]. In this research, 4-methyl-2-oxy-3-oxopent-4-ene (MMA) has been polymerized and grafted on wood materials by free radical polymerization. Grafting changes wood surface properties[8,9], promotes the dispersity of wood in polymers and improves the adhesion of wood to polymers. Uniform wood-thermoplastics composites have been made directly from the copolymerization products. By adjusting reaction formulations and reaction conditions, wood materials with different amount of grafted polymer and copolymerization products with varied wood content have been made. Grafting provides a promising method to make wood-thermoplastic composite materials.

EXPERIMENTAL

Materials

Wood materials used in this research were wood pulp and wood filaments. The lignin content in wood pulp was 25 to 29% (% = weight percent), and in wood filaments 16%. Degreased cotton which is supposed to contain no lignin was used as a control. TABLE 1 shows data for wood pulp, wood filament and degreased cotton. Before reaction, all the materials were dried in an oven at 50°C to constant weight. 4-Methyl-2-oxy-3-oxopent-4-ene was purchased as inhibited monomer from Mallinckrodt Inc., Paris, Kentucky 40361 and E. I. Du Pont De Nemours & Co., Wilmington, Delaware. Before reaction, it was vacuum-distilled under nitrogen. The central portion was collected at 43°C, and stored at -15°C in a freezer. Anhydrous calcium chloride ($CaCl_2$) was 8 mesh chemical grade from J. T. Baker Chemical Co., Phillipsburg, N. J. Before reaction, it was ground to about 40 mesh in a dry atmosphere. Dimethylsulfoxide (DMSO) was from Baxter Healthcare Corporation, Muskegon, MI 49442. It was used as received. Hydrogen peroxide (H_2O_2) was purchased from East Kodak Company and was nominally defined as 30% of H_2O_2 in water (0.0097 mole/mL). H_2O_2 purchased from the Peroxygen People Co., 3333 Richmond Ave., Houston, TX 77098 was also used. It was a chemical grade reagent with 70% H_2O_2 in water. Before use, it was diluted to 30% H_2O_2 concentration with distilled water. Other chemicals used in this research

TABLE 1. Wood Material Data

Pulp Name	Lig.%	Source	Manufacturer
RMP (Unbleached Refiner Mechanical Pulp)		Aspen PH=7.0	Mead Paper Co. P.O. Box 757 Escanaba, MI 49829
GWP-1 (Stone Ground Wood Pulp)	29	White Spruce, Balsam Fir, and Poplar(0-8%) PH=7.0	Research+Tech. Dept. Stone-Consolidated Inc. 55, 1st Street Grand'Mere, Quebec, Canada G9T 5L2
TMP (Thermomechanical Pulp)	25-29	ibid. PH=7.0	ibid.
VHYS (Very High Yield Sodium Bisulfite)	25	ibid. PH=6.0	ibid.
CTMP-1 (Chemithermomechanical Pulp)	25-29	ibid. PH=8.0	ibid.
MP (Mechanical Pulp)	29	Spruce(70%) Bulk(30%)	Stora Forest Industry Ltd., P.O. Box 59, PortHawkesburg Nova Scotia, B0E 2V0,Canada
CTMP-2 (Chemithermo-Mechanical Pulp)		Hemlock (Western) From British Columbia	Canada Pacific Forest Products Research Ltd., 179 Main Street West, Hawkesbury, Ontario K6A 2H4, Canada
GWP-2 (Ground Wood Pulp)			ibid.
Wood Filament	16	Aspen	American Excelsior Company, 1210 Manufacturers Drive Westland, MI 48185
Degreased Cotton	0	CB 340 Cotton Balls	Parke Davis, Inc. 201 Tabor Rd. Morris Plains, NJ 0795

such as nitrogen gas, benzene and poly(1-methyl-1-(2-oxy-1-oxopropyl) ethylene) (PMMA) were commercial products of chemical grade.

Synthesis

A mixture of previously dried wood pulp, $CaCl_2$, and DMSO was prepared in a conic flask. The mixture was stirred until uniform. The uniform mixture was stirred and bubbled with N_2 for 20 minutes at 30°C, and then H_2O_2 was added to it. The mixture was stirred and bubbled with N_2 for 20 minutes. At the same time, the 4-methyl-2-oxy-3-oxopent-4-ene in another conic flask was bubbled with N_2 for 1-2 minutes. It was then added to the above mixture. The reaction mixture was stirred and bubbled for 10 minutes, and the flask was sealed with a rubber stopper and placed in a water bath at 30°C. The reaction was carried out under agitation for 72 hours, and terminated by exposing the reaction mixture to air and adding it to 20-30 times of its own volume of distilled water. The precipitation mixture was stirred for 30 minutes and then let stand for 24 hours. The water-insoluble residue was recovered by filtration, and dried first in a hood at room temperature and then in a 60°C vacuum oven to constant weight. This product was named Product A. Product A was a white loose fluff which contained homopoly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) and uniformly dispersed grafted wood pulp. Based on the weight of 4-methyl-2-oxy-3-oxopent-4-ene and wood pulp added to the reaction and the weight of Product A recovered, conversion of monomer, yield of Product A, and wood pulp content in Product A were calculated.

Uniform mechanical mixtures were prepared as test materials for extraction studies by mixing one of three wood pulps (VHYS, CTMP-2 and GWP-1, respectively) with commercial poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) in DMSO to form a uniform mixture and precipitating it in water. The mechanical mixture was then recovered as if it were a reaction product.

Fractionation

A benzene extraction method was used to separate grafted wood pulp from homopoly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) formed during the reaction. Several grams of Product A were placed in a Soxhlet apparatus and extracted with 220mL benzene at a reflux rate of about 100 drops per minute for 48 hours to remove homopoly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene). The benzene-extractable fraction and the benzene-unextractable fraction were separately dried first in a hood at room temperature and then in a 60°C vacuum oven to constant weight. The dried benzene-extractable fraction was named Product Ben. Ex. It was homopoly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene. The benzene-unextractable fraction was named Product B. It was a white fibrous grafted wood pulp. The content of grafted poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene (g-PMMA) in Product B depended on the reaction formulations and other reaction conditions, especially the type of the wood pulp used. In this research, up to 48.1% of product B was thermoplastic sidechain. Based on the weight of Product A added and the weight of Product B recovered, weight increase of wood pulp, content of grafted poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) (g-PMMA) in product B, and grafting efficiency of 4-methyl-2-oxy-3-oxopent-4-ene were calculated. A diagram of synthesis and fractionation of the reaction product is shown in FIGURE 1.

Differential scanning calorimetry was run under nitrogen on copolymerization products and their benzene-unextractable fractions from a starting temperature of 20°C at a ramp rate of 10°C/min. Thermogravimetric analyses were done under nitrogen from a starting temperature of 20°C at a ramp rate of 20°C/min. All the samples tested by both methods were dried in a 60°C oven for about 15 hours before testing.

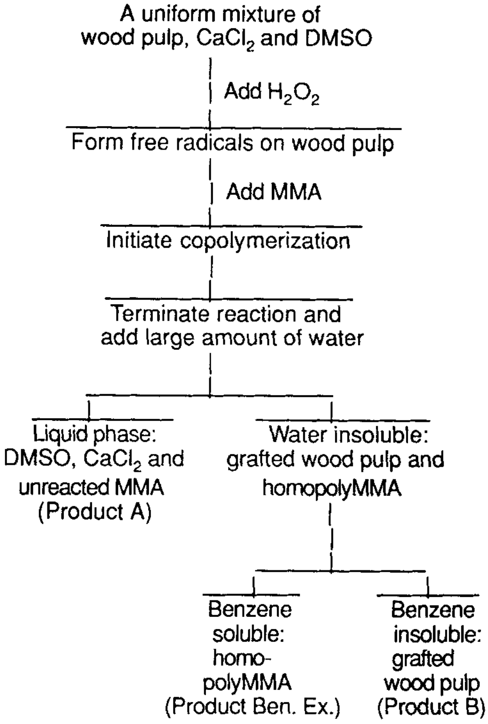


Figure 1. A Diagram of Synthesis and Fractionation of Copolymerization Reaction Product

Formation of Thermoplastic Composites

Product A and Product B were thermally compressed into plastic sheets with a Carver laboratory press. Product A or Product B was placed between two Teflon sheets and the Teflon sheets were placed between the two metal plates of the press. The thermal compression conditions used were: temperature of 150-180^{o}C; pressure of 2-3 metric tons; and pressure-holding time of 1-2 minutes. Under the above conditions, yellow to light brown, translucent, uniform thermoplastic composite sheets were made from the copolymerization product (Product

A) which contained up to 56% wood pulp and from the benzene-unextractable fraction (Product B) which contained more than 45% grafted polymer. Thermoplastic composite sheets were also prepared by mixing Product A with commercial homopoly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene).

Equipment

Agitation of the reaction mixture at a controlled stirring speed and stirring force was carried out with an immersible magnetic stirrer, Telemodul 40 S. Benzene extraction was done with a Soxhlet apparatus. Spectra of Fourier trasform infrared (FTIR) were run on a Nicholet 5 DX FTIR. Differential scanning calorimeter (DSC) thermograms were run on a Du Pont Instrument Model 910. Thermogravimetric analysis (TGA) was run on a Du Pont Instrument Model 951.

Calculations

Data about the synthesis were calculated by the following formulas:

(a) Conversion of MMA (Conversion) = (wt. of Product A - wt. of wood pulp added) / wt. of MMA added

(b) Yield of Reaction Product A (Yield) = wt. of Product A / (wt. of MMA added + wt. of wood pulp added)

(c) Wood Pulp Content in Product (Pulp/A) = wt. of wood pulp added / wt. of Product A

(d) Weight Increase of Wood Pulp After Reaction and Benzene Extraction (g-PMMA / Pulp) = wt. of grafted PMMA / wt. of wood pulp added = (wt. of Product B - wt. of wood pulp added) / wt. of wood pulp added

(e) Grafted PMMA content in benzene-unextracted fraction (g-PMMA / B) = wt. of grafted PMMA / wt. of Product B = (wt. of Product B - wt. of wood pulp added) / wt. of Product B

TABLE 2. Typical Reaction Formulations

Pulp/(Pulp+MMA), wt.%	36,	30,	25,	20,	15,	10
MMA (monomer), g	3.5,	4.7,	6.0,	8.0,	11.3,	18.0
Wood Pulp (backbone), g	2.0					
$CaCl_2$ (coinitiator), g	3.0					
DMSO (solvent), g	50.0					
H_2O_2 (coinitiator), mL	3.0					

(f) Grafting Efficiency of MMA (g-PMMA / PMMA) = wt. of grafted PMMA / (wt. of grafted PMMA + wt. of homo-PMMA) = (wt. of Product B - wt. of wood pulp added) / (wt. of Product A - wt. of wood pulp added)

RESULTS AND DISCUSSION

Typical Reaction Formulations

Typical reaction formulations for the copolymerization of wood pulp and 4-methyl-2-oxy-3-oxopent-4-ene are given in TABLE 2. Before reaction, the wood pulp and $CaCl_2$ must be thoroughly dispersed in DMSO. Starting temperature for the mixture has an important effect on the reaction results. Poor dispersity and starting temperatures above 35°C will cause low conversion and low grafting of monomer.

The macromolecular free radicals of the wood pulp are formed during mixing wood pulp, $CaCl_2$, DMSO, and H_2O_2 together. For all reactions run in this research, the weight percent wood in the polymerizable material is one of 36, 30, 25, 20, 15, and 10 %. The polymerizable material is wood pulp plus 4-methyl-2-oxy-3-oxopent-4-ene. The content of wood pulp in the reaction product (Product A) depends on reaction formulations and other reaction conditions which affected conversion of monomer. As 4-methyl-2-oxy-3-oxopent-4-ene added to the reaction increased, the content of wood pulp in Product A decreased because more polymer was formed. In this research, Product A with 12 to 70% wood pulp was obtained.

In order to explore the reaction rules, the copolymerization was run under different conditions. The results will be discussed below.

Effect of 4-methyl-2-oxy-3-oxopent-4-ene

Synthesis results from eight wood pulps, MP, TMP, VHYS, CTMP-1, CTMP-2, GWP-1, GWP-2, and RMP, show a common trend. That trend is, as the 4-methyl-2-oxy-3-oxopent-4-ene added to the reaction increases, (1) conversion of monomer and yield of reaction product go up; (2) weight increase of wood pulp goes up; and (3) grafting efficiency of monomer increases to a maximum. An example of these trends is shown in FIGURE 2.

The "gel effect" controls yield of these polymerizations. The wood pulp is well dispersed in the liquid medium, forming a gel-like slurry. In this system, the mobility of the polymer radicals is limited and their diffusion is reduced. This reduces the termination of the growing chains but the small monomer molecules still can react with the polymer radicals by diffusing to the radicals. When termination rate drops sharply but propagation rate remains essentially constant, yield and conversion of monomer increase.

Effect of Wood Pulp

The wood pulps used here are made from different species of tree by different processes, contain different amount of cellulose, hemicellulose and lignin, and may contain residual processing chemicals. It is predictible that different wood pulps will have different reactivity in the copolymerization.

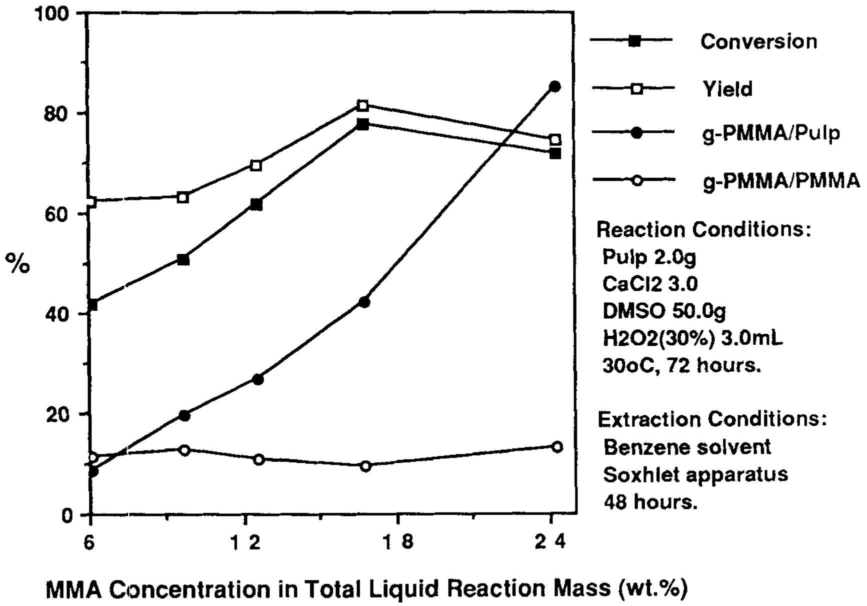


FIGURE 2. Copolymerization of Chemithermomechanical Pulp (CTMP-2) and MMA

In this research, eight kinds of wood pulps, denoted RMP, GWP-1, GWP-2, MP, TMP, VHYS, CTMP-1, and CTMP-2, were used. All of the wood pulps copolymerize with 4-methyl-2-oxy-3-oxopent-4-ene to form graft copolymer. After copolymerization with 4-methyl-2-oxy-3-oxopent-4-ene and extraction with benzene, the wood pulps weighed more (TABLE 3) and the surface properties of the pulps changed from very hydrophilic to very hydrophobic. TABLE 4 gives reaction results for the different wood pulps in reactions that contain 10 % wood pulp in the polymerizable material.

Among the wood pulp materials, CTMP-1, CTMP-2, GWP-1, and GWP-2 gave the highest conversion and yield, and MP gave the lowest. VHYS and CTMP-2 were the two most active wood pulps because they

TABLE 3. Weight Increase of Wood Pulp After Copolymerization with 4-Methyl-2-oxy-3-oxopent-4-ene

MMA	g-PMMA/Pulp (%)							
(g)	MP	TMP	VHYS	CTMP-1	CTMP-2	GWP-1	GWP-2	RMP
3.6	0.00	0.00	4.99	4.89	8.67	5.29	4.62	0.00
4.6	4.26	0.00	13.46	9.15	19.32	7.00	7.00	0.00
6.0	4.85	3.65	32.14	17.25	19.59	15.06	9.32	1.99
8.0	11.62	13.99	37.98	22.92	27.00	21.06	12.34	11.86
11.3	16.55	13.90	63.63	29.03	42.33	21.60	16.43	15.60
18.0	26.77	33.40	92.68	50.83	85.02	51.19	25.89	32.44

TABLE 4. Copolymerization of Wood Pulp and 4-methyl-2-oxy-3-oxopent-4-ene

Expt. No.	Pulp Type	Conversion (%)	Yield (%)	g-PMMA/Pulp (%)	g-PMMA/PMMA (%)
48-22-6	MP	55.28	59.77	26.77	5.41
48-26-6	TMP	65.11	68.63	33.40	5.75
48-48-1	VHYS	62.69	66.43	92.68	16.50
48-32-6	CTMP-1	71.94	74.76	50.83	7.92
48-30-6	CTMP-2	71.63	74.49	85.02	13.28
48-34-6	GWP-1	79.83	81.85	51.19	7.14
48-50-6	GWP-2	75.71	78.15	25.89	3.82
48-52-6	RMP	70.56	73.49	32.44	5.09

gave the highest grafting. In one of the graft copolymers of VHYS, almost half of the weight of the copolymer (48.1%, Table 4, 48-48-1) was contributed by grafted poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene). MP, TMP, RMP and GWP-2 were less reactive than the other wood pulps. When the weight percent of these pulps in the polymerizable material was higher than 30%, little, sometimes even zero grafting was obtained;

as the weight percent of these pulps in the polymerizable material decreased, the grafting went up. However, maximum grafting was 33.4%.

In addition to wood pulp, aspen wood filaments and degreased cotton were reacted. Aspen filaments contained 16% lignin and were about 10 mm long and 0.5 mm thick. Unlike wood pulp, aspen could not form a gel-like mixture in the reaction. The results show that as the 4-methyl-2-oxy-3-oxopent-4-ene added to the reaction increases, conversion of monomer, yield of reaction product, and weight increase of the filaments increase but grafting efficiency of monomer remains constant. After reaction, the weight increase of the filaments ranged from 8.50% to 47.50% and the surface properties changed from hydrophilic to hydrophobic. These data clearly show that not only wood pulp but also wood filaments can be used to conduct graft copolymerization with 4-methyl-2-oxy-3-oxopent-4-ene.

Reactions with degreased cotton and 4-methyl-2-oxy-3-oxopent-4-ene failed. Before reaction, the degreased cotton fibers were cut into about 3 mm long pieces. Monomer conversion of 23.88% to 76.65% was obtained but, after benzene extraction, no weight increase of the original cotton was found for any reaction. The recovered cotton was still very hydrophilic, which confirmed that no grafting reactions had occurred. The failure of the copolymerization of cotton and 4-methyl-2-oxy-3-oxopent-4-ene shows that lignin is a necessary component in any material to be grafted by this technique.

Effect of $CaCl_2$

FIGURE 3 shows data from the copolymerization of CTPM-2 and 4-methyl-2-oxy-3-oxopent-4-ene in the presence of different amounts of $CaCl_2$. When no $CaCl_2$ is added, neither homopolymerization nor copolymerization occurs. However, when $CaCl_2$ concentration in the total liquid reaction mass increases to 1.52%, conversion of monomer

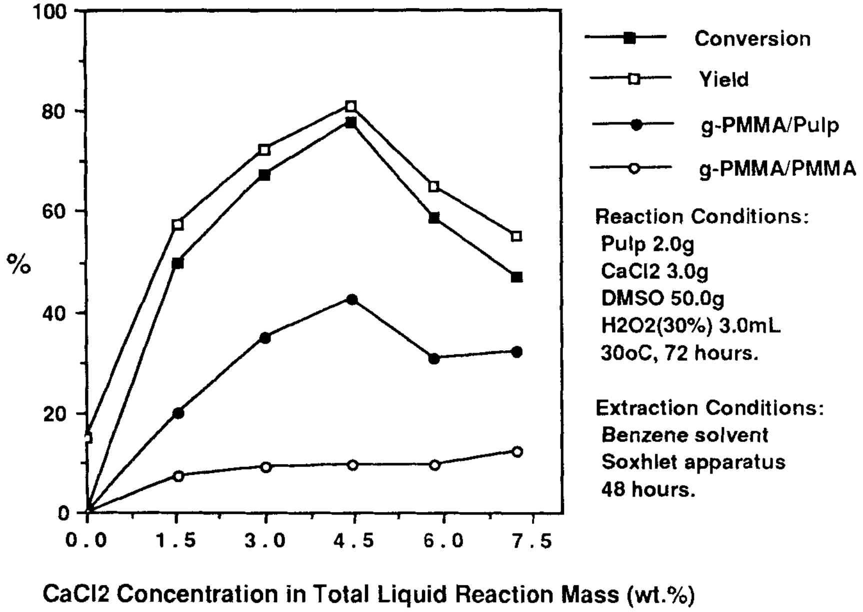
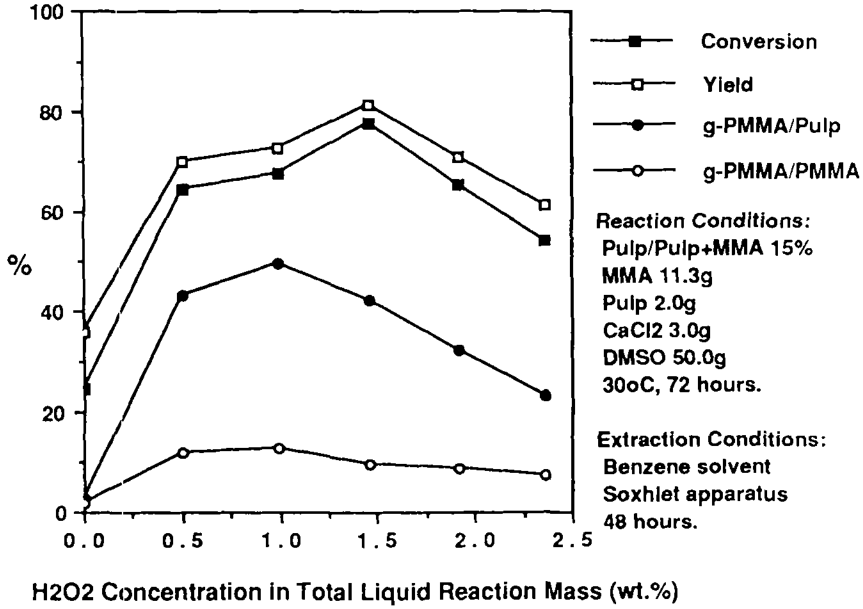


FIGURE 3. Copolymerization of Chemithermomechanical Pulp (CTMP-2) and MMA with Varied Amounts of CaCl2

jumps up from zero to 49.73% and weight increase of wood pulp jumps from zero to 19.94%. It is evident that $CaCl_2$ is one of the critical reagents which can initiate the reaction. As the $CaCl_2$ concentration in the reaction increases, conversion of monomer, yield of reaction product and weight increase of wood pulp go through a maximun at 4.44% total liquid reaction mass. FIGURE 3 also shows that when $CaCl_2$ added to the reaction increases, grafting efficiency of monomer increases. This means that as $CaCl_2$ concentration increases, so does graft copolymerization.

Effect of H_2O_2

FIGURE 4 shows data from the copolymerization of CTPM-2 and



Reaction Conditions:
Pulp/Pulp+MMA 15%
MMA 11.3g
Pulp 2.0g
CaCl2 3.0g
DMSO 50.0g
30oC, 72 hours.

Extraction Conditions:
Benzene solvent
Soxhlet apparatus
48 hours.

FIGURE 4. Copolymerization of Chemithermomechanical Pulp (CTMP-2) and MMA with Varied Amounts of H2O2

H_2O_2. When no H_2O_2 is added, a little homopolymerization and almost no graft copolymerization occur. However, when H_2O_2 concentration in total liquid reaction mass increases to 0.50%, conversion of monomer jumps from 24.58% to 64.54% and weight increase of wood pulp jumps from 2.50% to 43.21%. It is evident that H_2O_2 is one of the critical reagents which can initiate the reaction. When H_2O_2 concentration in the reaction increases, conversion of monomer and yield of reaction product pass through a maximun at 1.46% of total liquid reaction mass, and weight increase of wood pulp and grafting efficiency of monomer pass through a maximun at 0.99%of total liquid reaction mass. Blank reactions with CTMP-2 but without H_2O_2 still produce a limited amount of homopolymerization of 4-methyl-2-oxy-3-oxopent-4-ene. The cause and

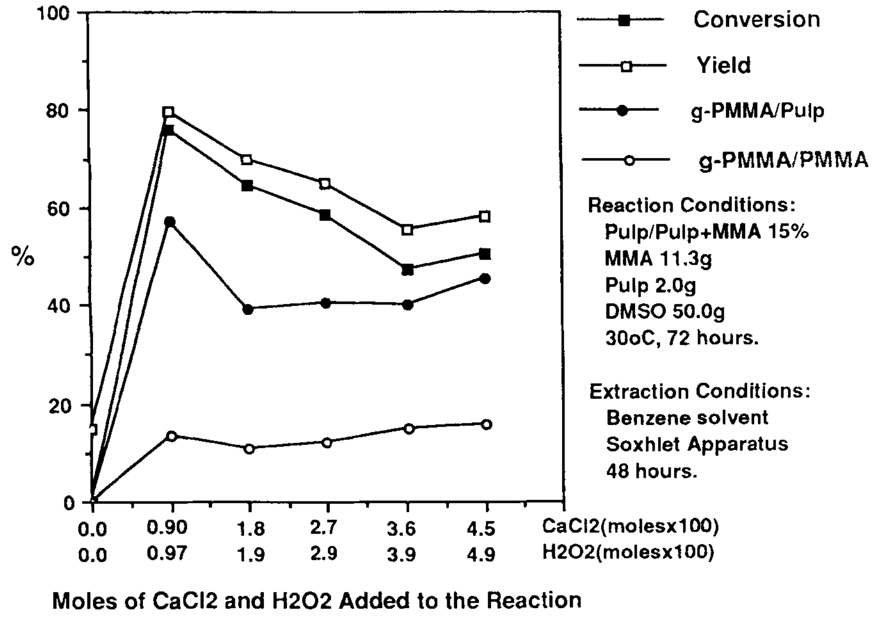
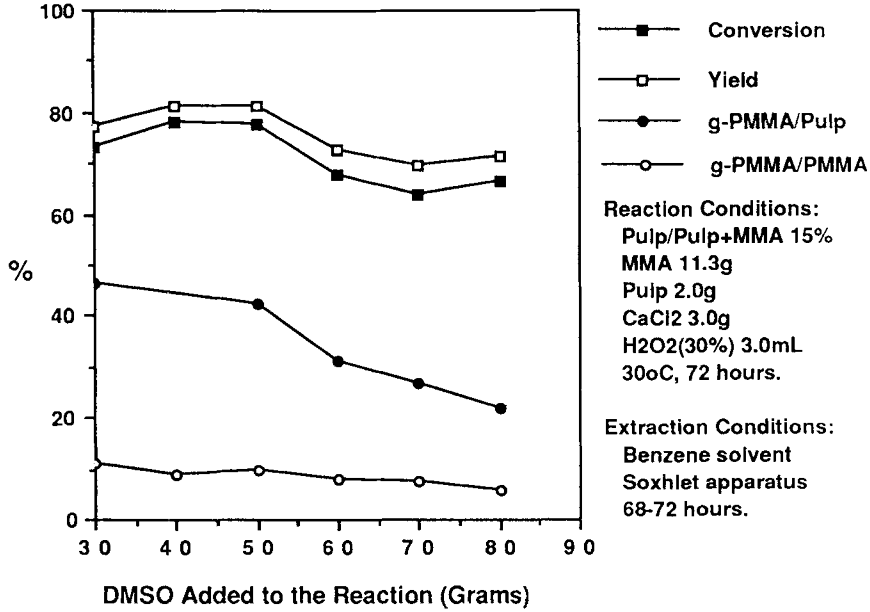


FIGURE 5. Copolymerization of Chemithermomechanical Pulp (CTMP-2) and MMA with Varied Amounts of CaCl2 and H2O2

initiation sequence for this unique capacity to created homopolymer without H_2O_2 is unknown. But CTMP-2 is a chemithermomechanical pulp so the remaining chemicals that make this pulp so reactive in grafting may also initiate polymerizaiton without H_2O_2.

Effect of $CaCl_2$ and H_2O_2.

FIGURE 5 shows data from the copolymerization of CTMP-2 and 4-methyl-2-oxy-3-oxopent-4-ene in the presence of different amounts of $CaCl_2$ and H_2O_2. In each reaction, the molar ratio of $CaCl_2$ to H_2O_2 is about 1.0. The results show that when neither $CaCl_2$ nor H_2O_2 is added, neither homopolymerization nor graft copolymerization occurs; when 0.0090 mole of $CaCl_2$ and 0.0097 mole of H_2O_2 are added, conversion



Reaction Conditions:
Pulp/Pulp+MMA 15%
MMA 11.3g
Pulp 2.0g
CaCl2 3.0g
H2O2(30%) 3.0mL
30oC, 72 hours.

Extraction Conditions:
Benzene solvent
Soxhlet apparatus
68-72 hours.

FIGURE 6. Copolymerization of Chemithermomechanical Pulp (CTMP-2) and MMA with Varied Amounts of DMSO

of monomer rises from zero to 76.15% and weight increase of wood pulp rises from zero to 57.26%. It is evident that $CaCl_2$ and H_2O_2 are two of the critical reagents which can coinitiate the reaction. As $CaCl_2$ and H_2O_2 reaction content continues to increase, the conversion, the yield, and the weight increase of CTMP-2 go through a maximum. For this set of reactions, the optimum combination of $CaCl_2$ and H_2O_2 seems to be 0.0090 mole of $CaCl_2$ and 0.0097 mole of H_2O_2.

Effect of DMSO

FIGURE 6 shows data from the copolymerization of CTMP-2 and 4-methyl-2-oxy-3-oxopent-4-ene in different amounts of DMSO. As DMSO added to the reaction increases, conversion of monomer, yield of reaction product, weight increase of wood pulp, and grafting efficiency of monomer all decrease. The reason for this trend is that more DMSO produces lower concentration of monomer and coinitiators, thus reducing the gel effect and initiation. This reduces polymerization, chain length, and radical lifetime. Grafting efficiency data from benzene extracted products show that as more DMSO is added, homopolymerization predominates over graft copolymerization. A possible cause for increased homopolymerization might be chain transfer.

Poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) is readily dissolved in DMSO, but can not be dissolved in water. DMSO - H_2O mixtures were tried as a reaction medium with reduced polymer solubility and increased gel effect. In these reactions, the total mass of DMSO and H_2O was unchanged, but the proportion of the two solvents was varied. The results show that as the amount of water increases and the amount of DMSO decreases, conversion of monomer, yield of reaction product , and weight increase of wood pulp all decrease sharply, but the grafting efficiency gradually goes up. On the whole, water is not a good solvent for this reaction and inhibits both homopolymerization and graft copolymerization. However, it inhibits homopolymerization more than graft copolymerization.

Effect of Reaction Time

FIGURE 7 shows data from the copolymerization of CTMP-2 and 4-methyl-2-oxy-3-oxopent-4-ene run in various reaction periods. As the reaction time increases, conversion of monomer, yield of reaction product, weight increase of wood pulp, and grafting efficiency of monomer increase but then plateau after about 72 hours of reaction. In this research, 72 hours was used to run the reactions.

Proof of Grafting

FIGURE 8 shows the results of the weight change of two copolymerization products (Product A) during benzene extraction. After

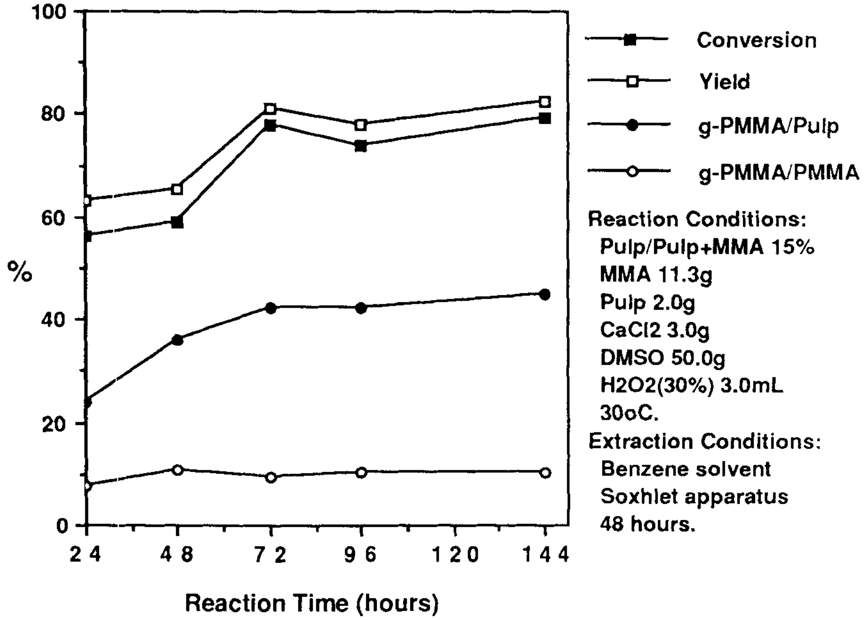


FIGURE 7. Copolymerization of Chemithermomechanical Pulp (CTMP-2) and MMA in Varied Reaction Time

24 hours of extraction, the weight of the unextractable fraction keeps constant. That implys that homopoly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) has been removed. For virtually all the copolymerization reactions conducted in this research, after benzene extraction, the weight of the unextractable fraction (Product B) was larger than the weight of the wood pulp added to the reaction (TABLE 3 and FIGURE 9). On the contrary, after 48 hours of benzene extraction of uniform mechanical mixtures, no weight increase of the original wood pulp was found. Thus, 48 hours of benzene extraction is enough to remove all the homopoly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) unbound to the wood surface and the weight increase of the original wood pulp must be caused by chemically bound poly(1-methyl-1-(2-oxy-

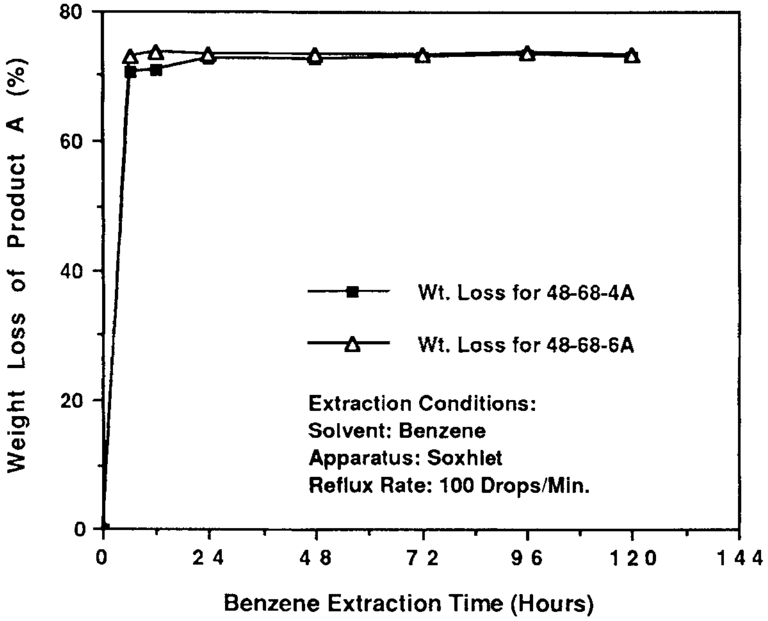


FIGURE 8. Weight Loss of Product A During Extraction with Benzene

1-oxopropyl)ethylene), that is, grafted poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) (g-PMMA). The results of the copolymerization of degreased cotton and 4-methyl-2-oxy-3-oxopent-4-ene also support the above viewpoint. In that set of blank reactions, conversion of monomer ranged from 23.88% to 76.65%, but after benzene extraction, the weight increase of the original cotton was zero. It is clear that no grafted poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) (g-PMMA) was formed in the reaction, and no homopoly(1-methyl-1-(2-oxy-1-oxopropyl) ethylene) was trapped inside the cotton fibers.

Wood pulp is a very hydrophilic material because 16 to 25% of its dry weight is hydroxyl groups. When pure wood pulp, or the wood pulp recovered from blank reactions (either H_2O_2 or $CaCl_2$ missing), or the

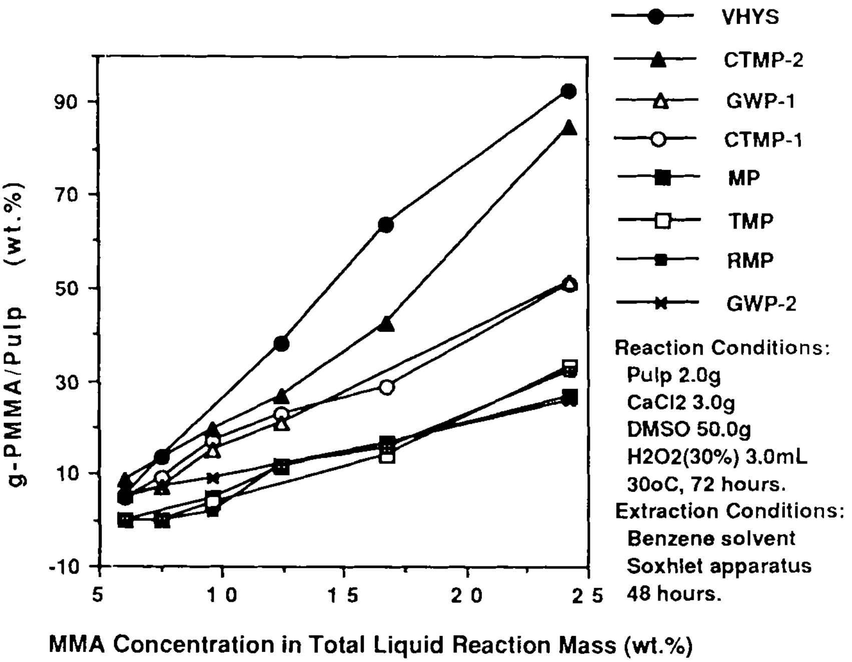


FIGURE 9. Weight Increase of Wood Pulp after Copolymerization with MMA and Extraction with Benzene

wood pulp recovered from uniform mechanical mixtures of wood pulp and poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) is put into water, it will wet, absorb water, and sink. But Product B, the "wood pulp" which has experinced copolymerization with 4-methyl-2-oxy-3-oxopent-4-ene and extraction with benzene, is a very hydrophobic material. When Product B is put into water, it will not wet, will not absorb water, and will not sink. Samples of grafted wood have not imbibed water after six months of floating on distilled water. It is evident that the surface properties of the original wood pulp have been completely changed by grafting.

Product B's which contained more than 45% of benzene-unextractable poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) were successfully thermally compressed into yellow to light brown, translucent, uniform thermoplastic sheets. When one of the thermoplastic sheets (48-48-1B) was extracted again with benzene at room temperature for 90 hours, the plastic sheet disintegrated and became powder. After the powder product was recovered, it was found that during this process, the total weight loss was 2.36% and the weight loss of the original benzene-unextractable poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) was 4.90%. When the recovered powder was thermally compressed, it again formed a thermoplastic sheet. This experiment shows that the benzene-unextractable poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) must be grafted poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene). The small loss of the original benzene-unextractable poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) might be caused by the thermal compression process, during which heat energy and very strong compression and shearing forces might cause the breakage of some grafted polymer sidechains. These newly formed homopolymer chains can be removed by benzene extraction.

The Fourier transform infrared (FTIR) spectra show that Product B's contain benzene-unextractable poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene). A set of FTIR spectra is given in Figure 10. The absorbance peaks at 1160, 1110, 1058, and 1033 cm^{-1} are typical absorbance peaks of the wood pulps, and the absorbance peaks at 1730 (main peak), 1200, and 750 cm^{-1} are typical absorbance peaks of poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene). The FTIR results show:

(1) In the spectra of the wood pulp recovered from mechanical mixtures of wood pulp and poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene), no absorbance peaks of poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) have been found,

(2) In the spectra of the benzene-unextractable fractions of the reaction products of degreased cotton and 4-methyl-2-oxy-3-oxopent-4-

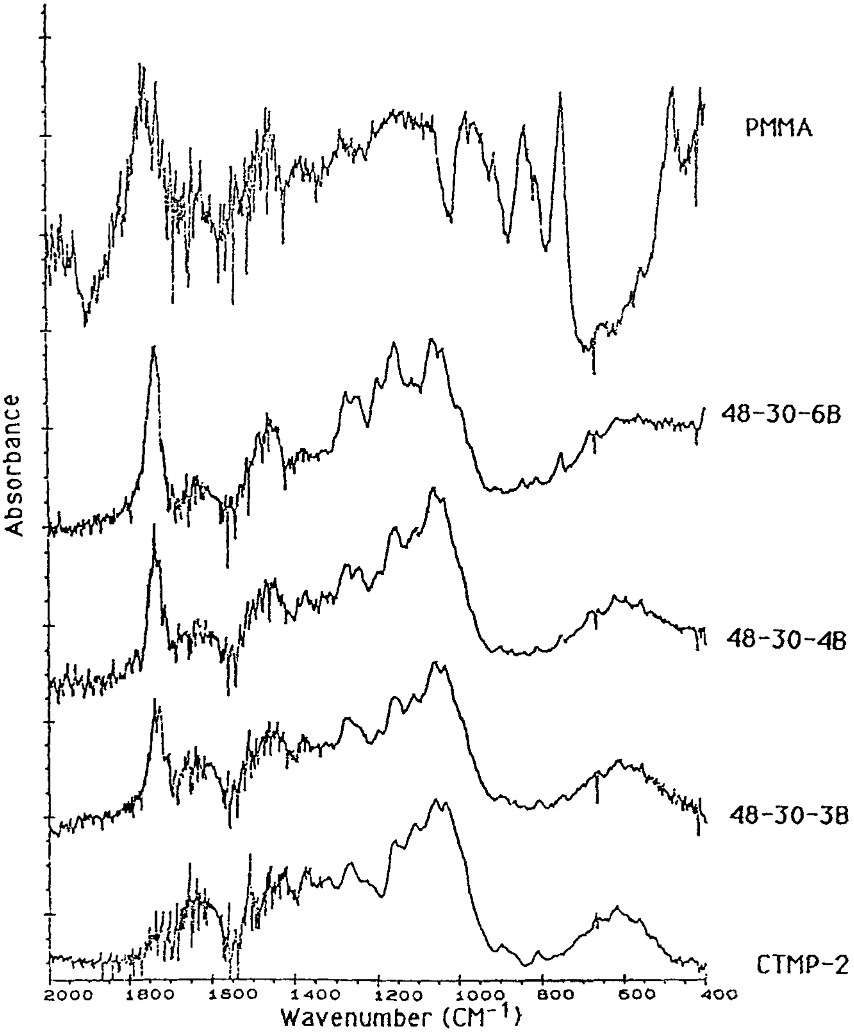


FIGURE 10. FTIR Spectra of the Benzene-unextractable Fraction

Sample Number	48-30-6B	48-30-4B	48-30-3B
g-PMMA/Product B (wt.%)	45.95	21.26	16.38

ene, no absorbance peaks of poly(1-methyl-1-(2-oxy-1-oxopropyl) ethylene) have been found, and

(3) In the spectra of the benzene-unextractable fractions of the reaction products of wood pulp and 4-methyl-2-oxy-3-oxopent-4-ene, the absorbance peaks of both wood pulps and poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) have been found.

The FTIR results provide strong proof of grafting.

CONCLUSIONS

Lignin-containing materials such as wood pulp and wood filaments have been successfully grafted with polymerized 4-methyl-2-oxy-3-oxopent-4-ene. The graft copolymerization of wood materials and 4-methyl-2-oxy-3-oxopent-4-ene can be conducted at 30°C for 72 hours using $CaCl_2$ and H_2O_2 as coinitiators and DMSO as a medium. The reaction formulation, the reaction temperature and the reaction time can be varied to obtain the products with different levels of conversion and different amounts of grafted monomer. Before reaction, the wood materials and $CaCl_2$ must be dispersed in the medium to form a uniform mixture. Gel effect plays a very important part in the reaction.

Among the wood pulp materials used in this research, very high yield sodium bisulfite pulp from white spruce and balsam fir and chemithermomechanical pulp from Western Hemlock have the highest grafting activity. The highest weight increase for VHYS is 92.7%, and for CTMP-2, 85.0%. The reason for this high activity is still unkown, but very possibly, it is related to the pumping process and the chemicals remaining in the wood pulp.

The copolymerization reaction product is a composite material, which contains homopoly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) as a polymer matrix and grafted wood pulp as a reinforcing material. The grafting of wood pulp with poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) changes the surface properties of the original wood pulp, improves the compatibility of wood pulp with poly(1-methyl-1-(2-oxy-1-oxopropyl) ethylene), and promotes the dispersibility of wood pulp in a poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) matrix. After thermal compression of the copolmerization products which contain up to 56% wood pulp, uniform translucent thermoplastic sheets can be formed. By this method, a thermoplastic composite material can be made without coupling agents or dispersing agents and without complicated processing procedures.

The separation of grafted wood pulp from homopoly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) formed during the reaction was done by benzene extraction of the reaction product in a Soxlet apparatus. The weight increase of the wood pulp after the reaction and benzene extraction, the infrared spectra of the reacted pulp, and the results of wettability tests of the benzene-unextractable pulp provide strong proof of grafting.

The benzene-unextractable fraction of the reaction product is a grafted wood pulp. The grafted wood pulps which contain more than 45% grafted poly(1-methyl-1-(2-oxy-1-oxopropyl)ethylene) have been successfully thermally compressed to plastic sheets in which no wood fibers can be seen. That implies that the wood pulp component in the graft copolymer has been plasticized.

ACKNOWLEDGMENT

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