Preparations and Oil Absorptivities of Poly(stearyl methacrylate-*co*-cinnamoyloxyethyl methacrylate) and PET Nonwoven Fiber Photocrosslinked with It

SEUNG-HYUN KIM,[1] **IL-DOO CHUNG,**[1] **CHANG-SIK HA,**[1] **KYU-JIN KIM,**[2] **WON-JEI CHO**[1]

[1] Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, South Korea

[2] UNESCO Centre for Membrane Science and Technology, Department of Chemical Engineering, University of New South Wales, Sydney 2052, Australia

ABSTRACT: Cinnamoyloxyethyl methacrylate (CEMA) was synthesized by the reaction of cinnamoyl chloride (CMC) and 2-hydroxyethyl methacrylate (HEMA). Its copolymers with stearyl methacrylate (SMA) were synthesized using benzoyl peroxide (BPO) as an initiator. The synthesized copolymers, poly(SMA-*co*-CEMA)s (PSCMAs), were photocrosslinked by UV light irradiation. The structures of the products were confirmed by IR and NMR spectroscopies. The thermal properties of the synthesized polymers were determined by DSC. The crystalline melting temperature of crosslinked PSCMA was decreased with increasing CEMA content in the feed. The oil absorptivities of the synthesized polymers were evaluated by the ASTM method (F726-81). The highest oil absorptivity of crosslinked PSCMA on poly(ethylene terephthalate) (PET) nonwoven fiber (NWF) was 610% in 10% crude oil diluted with toluene when the mol percentage of CEMA to SMA in the feed was 7.5. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2349–2357, 1999

Key words: cinnamoyloxyethyl methacrylate (CEMA); poly(SMA-*co*-CEMA); thermal property; photocrosslinking; oil absorptivity; PET nonwoven fiber treated with polymer; morphology

INTRODUCTION

Many photosensitive polymers which can be crosslinked by UV light irradiation have been attracting academic and industrial interest because of their oil absorptivity.[1–7] One of the characteristics of oil-absorptive polymers is that they have crosslinked three-dimensional hydrophobic networks that do not dissolve in oil. The polymers containing the cinnamoyl moiety can be transformed to a crosslinked structure by UV light irradiation.[8] The cinnamate derivatives have been studied for a long time because of their photochemical importance. From the aspect of the photochemistry, for cinnamic acid and cinnamate esters, which have been investigated widely, the $[2\pi + 2\pi]$ photocycloaddition on UV light irradiation occurs at wavelengths over 290 nm, whereas the formed cyclobutane ring is preferentially cleaved to regenerate cinnamate at wavelengths below 260 nm.[9,10] In addition to reactions involving two cinnamate moieties, cinnamates undergo facile *trans–cis* photoisomerization.[11]

Crosslinking via photodimerization of polymeric systems has been utilized in various ap-

Scheme 1   Syntheses of CEMA(A) and PSCMA(B).

plications, such as in paint, adhesive, printing, dental industries, and photoresists.[12–15] In spite of the explosive development of photocrosslinking systems, there have been few reports on the preparation of a photocrosslinked poly(stearyl methacrylate-*co*-cinnamoyloxyethyl methacrylate) (PSCMA) to absorb oil.

The aim of this work was to synthesize new oil-absorptive polymers containing the cinnamoyl moiety which can be crosslinked by UV light irradiation. In this study, cinnamoyloxyethyl methacrylate (CEMA) was synthesized by the reaction of cinnamoyl chloride (CMC) and 2-hydroxyethyl methacrylate (HEMA). Its copolymers with stearyl methacrylate (SMA) were synthesized using benzoyl peroxide (BPO) as an initiator. The synthesized copolymers, PSCMAs with various contents of CEMA, were photocrosslinked by UV light irradiation. The structures of the polymers were identified by IR and NMR spectroscopies. The thermal properties of the synthesized polymers were determined by DSC. The oil absorptivities of the crosslinked PSCMAs synthesized in this study were evaluated by the ASTM method (F726-81).[16]

EXPERIMENTAL

Materials

SMA (Aldrich Chemicals, Milwaukee, WI) and HEMA (Junsei Chemicals, Toyko, Japan) were purified by washing with 5% aqueous sodium hydroxide, dried over anhydrous CaCl$_2$, and distilled under a vacuum. CMC (Aldrich) was used without further puification. Triethylamine (Junsei) was refluxed with acetic anhydride and with KOH and then distilled. BPO (Junsei) was dissolved in CHCl$_3$ and precipitated by adding an equal volume of MeOH. Crude oil was obtained from the Yukong Corp. (South Korea). Toluene (Junsei), THF (J.T. Baker Co., Phillipsburg, New Jersey), and other chemicals were purified by standard procedures.

Instruments

The structures of CEMA, PSCMA, and photocrosslinked PSCMA were identified by FTIR spectroscopy (Perkin–Elmer 1330). The ^{1}H-NMR spectra of CEMA and PSCMA were recorded on an FT-300 MHz Gemini 2000 spectrophotometer. The average molecular weights of the copolymers

were determined using THF as the eluent by GPC (Waters-Water 244) calibrated with polystyrene standards. The morphology of the samples was analyzed by an SEM instrument (JEOL JSM35-CF). In the examination of the copolymer surfaces, the samples before and after UV light irradiation were metallized by gold coating prior to the installation in the SEM chamber. The crystalline melting temperatures (T_m's) were measured using differential scanning calorimetry (DSC; DuPont 2100). The thermograms of the photocrosslinked PSCMAs were obtained at a heating rate of 10°C/min.

Synthesis of CEMA

CEMA (**III**) was prepared by the reaction of HEMA (**I**) and CMC (**II**) as shown in Scheme 1(A). A solution of HEMA (8.64 g, 66 mmol) and triethylamine (TEA; 6.68 g, 66 mmol) in THF of 100 mL was refluxed for 2 h with precaution being taken to exclude moisture from the atmosphere, and then the clear solution was cooled to 0°C in an ice bath. The prepared CMC solution (13.2 g, 79 mmol) in 50 mL dry THF was slowly added dropwise with vigorous stirring for 2 h at 0°C. The formed triethylamine hydrochloride salt was filtered out and the filtrate was concentrated on a rotary evaporator. The concentrated solution was slowly added to 500 mL *n*-hexane. After removing an insoluble part, the obtained dark yellow solution was fractional distilled in the presence of small amounts of sulfur as an inhibitor to obtain pure CEMA (yield: 72%). The IR spectrum of CEMA [Fig. 1(A)] exhibited characteristic absorption bands at 2926 cm^{-1} (stretching vibration of the aliphatic C—H bond), 1730 cm^{-1} (stretching vibration of the C=O bond), 1620 cm^{-1} (stretching vibration of the C=C), 1149 cm^{-1} (stretching of C—O), and 900–650 cm^{-1} (out-of-plane rotational vibration of aromatic C–H). In the ^{1}H-NMR spectrum [Fig. 2(A)], the peaks of CEMA indicated aromatic protons at 7.2–7.8 ppm, vinyl protons at 5.6–6.6 ppm, and methyl protons at 1.9 ppm.

Syntheses of PSCMA

PSCMA was synthesized according to Scheme 1(B) and the detailed procedures are described as follows: A mixture of SMA (10 g, 30 mmol) and CEMA (1.0–10.0 mol % based on SMA mol) was dissolved in 100 mL toluene, and the solution was poured into a round-bottom flask under a nitro-

Figure 1 IR spectra of CEMA(A), PSCMA(B) & photocrosslinked PSCMA(C).

gen atmosphere. The mixed solution was then placed in a regulated thermostat at 70 ± 0.05°C for 20 h. The products were poured into excess methanol with stirring. The obtained precipitate was filtered and dried *in vacuo* at 30°C to a constant weight. All preparations of the polymers were performed in the dark. The conversion data for each polymerization are listed in Table I.

UV Crosslinking of PSCMA

One gram of PSCMA was dissolved in 9 mL THF, and then the solution was cast over a poly(ethylene terephthalate) nonwoven fiber (PET NWF) at room temperature under an air atmosphere. The PET NWF treated with PSCMA was irradiated with the wavelength of 290 nm[9,10] using a 400-W high-pressure mercury lamp (WAKO H-400A/B; Tokyo, Japan). The irradiated PET NWF was extracted with THF to remove the uncrosslinked part of the polymer which is soluble in THF and

Figure 2 ¹H-NMR spectra of CEMA(A) and PSCMA(B).

dried *in vacuo* at 30°C until a constant weight. The crosslinking ratio was calculated by the following equation:

Crosslinking ratio (%)

$$= \frac{\text{weight of the PSCMA attached to PET NWF after extraction with THF}}{\text{weight of total PSCMA coated on PET NWF}}$$

(1)

The crosslinking ratio at a given CEMA mol percentage in the feed is listed in Table II.

Oil Absorption Test

The PET NWF samples photocrosslinked with PSCMA which have a highly porous structure were prepared by rapid evaporation to remove THF from the samples swelled with it at room temperature *in vacuo*. After immersion of the PET NWF samples with a porous structure in

Table I   Effect of Mole Percentage of CEMA to SMA on the Copolymerization, Conversion, Average Molecular Weight, and Crystalline Melting Temperature

CEMA Content (mol %)	Conversion (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n/\bar{M}_w$	T_m of Photocrosslinked PSCMA (°C)
1.0	88	56,000	139,000	2.5	—
2.5	86	49,000	173,000	3.5	28
5.0	85	42,000	142,000	3.4	26
7.5	85	47,000	158,000	3.3	24
10.0	85	53,000	172,000	3.3	22

Solvent: toluene; time: 20 h; temperature: 70; BPO: 1 wt %.

toluene or 10% crude oil diluted with toluene for given time periods at room temperature, the samples were picked up from the oil and the excess oil on the samples surfaces were removed by tissue paper. The samples absorbed oil were then weighed. The equation $(W_s - W_p)/W_p$ was used to evaluate the oil absorptivity, where W_s is the weight of the sample absorbed oil and W_p is that of the sample before immersion.

RESULTS AND DISCUSSION

Characterization

The FTIR spectrum [Fig. 1(B)] of PSCMA indicated characteristic absorption peaks at 2926 cm^{-1} (stretching vibration of the aliphatic C—H bond), 1730 cm^{-1} (stretching vibration of the C=O bond), 1620 cm^{-1} (stretching vibration of the C=C), 1149 cm^{-1} (stretching of C—O), and 900–650 cm^{-1} (out-of-plane rotational vibration of aromatic C—H). The ^{1}H-NMR spectrum [Fig. 2(B)] of PSCMA shows methyl protons in the polymer backbone at 1.1 ppm, aromatic protons at 7.2–7.8 ppm, vinyl proton in the cinnamoyl moiety at 6.4–6.6 ppm, and methylene protons at 1.9 ppm together with the disappearance of vinyl protons in the acryloyl group of CEMA at 5.6–6.2 ppm.

The FTIR spectrum [Fig. 1(C)] of PSCMA crosslinked by UV irradiation indicated absorption at 2926 cm^{-1} (stretching vibration of the aliphatic C—H bond), 1730 cm^{-1} (stretching vibration of the C=O bond), 1149 cm^{-1} (stretching of C—O), and 900–650 cm^{-1} (out-of-plane bending vibration of aromatic C—H) with the disappearance of the vinyl stretching vibration peak at 1620 cm^{-1}.

Conversion and Average Molecular Weights

Table I represents the conversion percentage for the copolymerization and the number (M_n)- and weight (M_w)-average molecular weights of PSCMAs

Table II   Oil Absorptivities of Photocrosslinked PET NWF After Treatment with PSCMA and Untreated PET NWF

Sample	CEMA Content in PSCMA (mol %)	Crosslinking Ratio (%)	Oil Absorptivity (%) for 10 min	
			Toluene	Diluted Crude Oil (10%)[a]
Untreated PET NWF	0	0	390	410
PET NWF photocrosslinked with PSCMA	2.5	33	550	500
	5.0	40	580	550
	7.5	80	610	610
	10.0	100	440	520

[a] 10% crude oil diluted with toluene.

Figure 3 DSC thermograms of photocrosslinked PSCMAs prepared with several mol percentages in the feed.

prepared with various mol percentages of CEMA to SMA in the feed. The conversions were more than 85% regardless of the CEMA content in the feed. The number-average molecular weight of PSCMA decreased with increasing CEMA content up to 5 mol % in the feed but it again increased at above that content. However, the weight-average molecular weight did not exhibit a constant trend according to the CEMA content. The polydispersity of the obtained polymers was found to be in the range of 2.5–3.5.

Thermal Property

Figure 3 shows the DSC thermograms of photocrosslinked PSCMA prepared from various mol percentages of CEMA in the feed and the T_m values of the polymers are listed in Table I. The T_m values decreased with an increasing mol ratio of CEMA in the feed. This decreasing phenomenon means that the degree of disorder caused by long side chain of CEMA in the polymer increases with increasing content of CEMA.

Morphology

Figure 4 shows scanning electron micrographs of the (A) uncrosslinked PSCMA, (B) crosslinked PSCMA, (C) untreated PET NWF, (D) PET NWF treated with PSCMA, and (E) crosslinked PET NWF after treatment with PSCMA. Figure 4 shows several distinct structures as follows: a smooth surface for (A), a crack and pore structure for (B), crossed staples in PET NWF for (C), PSCMA incorporated into the crossed staples of PET NWF for (D), and an extensive pore struc-

ture for (E), which was formed by the extraction of uncrosslinked PSCMA and evaporation of THF.

Crosslinking Ratio

The crosslinking ratios of PSCMA in PET NWF were calculated by eq. (1) and are listed in Table II. The viscosity in the crosslinking reaction increases very rapidly at some extent of the reaction as the reaction proceeds, and the reaction product begins to form an infinite molecular weight network called the gel point. In the gel state, chemical reaction can proceed and chains form the network by crosslinking. The crosslink density or degree of crosslinking is a measure of the total links between chains in a given mass of substance. In a crosslinking system, there are a soluble portion and a insoluble portion; the former can be extracted with suitable solvents and the latter cannot be extracted with any solvents due to crosslinking[17,18]—it only swells in good solvents to give a gel. As can be seen in Table II, the crosslinking ratio increased slowly with increasing CEMA contents up to 10 mol % in the feed. This reveals that the double bond of CEMA in the copolymer participates in the crosslinking.

Oil Absorptivity

The absorptivities of toluene and 10% crude oil diluted with toluene are summarized in Table II for PET NWF photocrosslinked with PSCMA prepared from various mol percentages of CEMA in the feed. The oil absorptivities of PET NWF photocrosslinked with PSCMAs on the mol percentage of CEMA to SMA in the feed were in the following order: 7.5 > 5.0 > 2.5 > 10.0 > untreated PET NWF for toluene and 7.5 > 5.0 > 10.0 > 2.5 > untreated PET NWF for 10% crude oil diluted with toluene. However photocrosslinked PSCMA which was prepared from 1 mol % of CEMA to SMA at 70°C for 20 h was soluble in toluene; thus, we cannot obtain oil absorptivity from it. Figures 5 and 6 show the absorptivities of toluene and 10% crude oil diluted with toluene for photocrosslinked PSCMA, untreated PET NWF, and photocrosslinked PET NWF after treatment with PSCMA as a function of time. The used PSCMA was prepared from 7.5 mol percentage of CEMA to SMA in the feed at 70°C for 20 h. The highest oil absorptivity of photocrosslinked PSCMA was 875% for toluene and 700% for 10% crude oil diluted with toluene when the weight of PSCMA used in the measurement of oil absorptivity was 2 g. For the photocrosslinked PET NWF after being

Figure 4 Scanning electron micrographs of (A) uncrosslinked PSCMA, (B) crosslinked PSCMA, (C) untreated PET NWF, (D) PET NWF treated with PSCMA, and (E) PET NWF photocrosslinked with PSCMA by UV irradiation (medium-pressure mercury lamp) (×1000).

coated with PSCMA, the highest absorptivities were found to be 610% for toluene and 10% crude oil diluted with toluene, when the weight of coated PSCMA was 1.4 g. Also, the oil absorptivity for PET NWF photocrosslinked with PSCMA increased to

about 10 min and thereafter leveled off without regard to the CEMA content.

The higher oil absorptivity for crosslinked PSCMA than for the photocrosslinked PET NWF can be explained by the amount of the oil-absorp-

Figure 5 Toluene absorptivities of crosslinked PSCMA, untreated PET NWF, and photocrosslinked PET NWF after treatment with PSCMA prepared from different CEMA contents in the feed as a function of time.

Figure 6 Ten percent crude oil absorptivities of crosslinked PSCMA, untreated PET NWF, and photocrosslinked PET NWF after treatment with PSCMA prepared from different CEMA contents in the feed as a function of time.

Figure 7 Oil absorptivities of photocrosslinked PET NWF after treatment with PSCMA as a function of the crosslinking ratio.

tive PSCMA used. For the crosslinking ratio on the oil absorptivity, the toluene and 10% crude oil absorptivities were increased up to an 80% crosslinking ratio and thereafter they decreased rapidly as shown in Table II and Figure 7. The decreasing oil absorptivities at a higher crosslinking ratio may be ascribed to the size of the microporosity which cannot preferably contain oil. It has been reported[19-23] that the excellent oil absorptivity of materials depends on the bulkiness and length of the alkyl substituents, especially the porosity of the microstructure which can be controlled by crosslinking and the foaming agent. Because the driving force for oil absorption is caused mainly by the van der Waals force between the material and the oil, therefore, the materials with the proper porosity can effectively contain oil in their structures. The highest oil absorptivity of 610% was obtained at an 80% crosslinking ratio. The highest absorptivity of 610% for PET NWF photocrosslinked with PSCMA was about 1.5 times greater than that of untreated PET NWF of 410% for 10% crude oil. This result may be interpreted as an interaction between PSCMA and oil in the porous structure of the photocrosslinked polymer coated on the PET NWF, as manifested in the micrograph [Fig. 4(E)].

CONCLUSIONS

The photocrosslinkable monomer, CEMA, was prepared by the reaction of cinnamoyl chloride

and HEMA and the copolymers of SMA with CEMA were synthesized at 70°C using BPO as an initiator. The PET NWF photocrosslinked with synthesized PSCMAs was prepared by UV light irradiation.

The following conclusions are drawn from this study:

1. Uncrosslinked PSCMA was soluble in toluene and 10% crude oil diluted with toluene; thus, oil absorptivity cannot be measured.
2. The highest oil absorptivity of photocrosslinked PSCMA prepared from 7.5 mol percentage of CEMA to SMA was 875% for toluene and 700% for 10% crude oil diluted with toluene. For PET NWF photocrosslinked with PSCMA which has an 80% crosslinking ratio, the highest oil absorptivities were 610% for toluene and 10% crude oil diluted with toluene.
3. The absorptivities of toluene and 10% crude oil diluted with toluene for photocrosslinked PET NWF after treatment with PSCMA increased up to about 10 min and thereafter they leveled off without regard to CEMA content.
4. The oil absorptivities of PET NWF photocrosslinked with PSCMA were dependent on the mol percentage of the CEMA to SMA used in the preparation of PSCMA. The order of oil absorptivity on the mol percentage of CEMA to SMA was as follows: 7.5 > 5.0 > 2.5 > 10.0 > untreated PET NWF for toluene and 7.5 > 5.0 > 10.0 > 2.5 > untreated PET NWF for 10% crude oil diluted with toluene.
5. The highest oil absorptivity of 610% for photocrosslinked PET NWF after treatment with PSCMA was about 1.5 times greater than that of 400% for untreated PET NWF. This effect is attributed to the oil-absorptive PSCMA and the porous structure produced by the partial photocrosslinking of PSCMA coated on the PET NWF.

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