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SYNTHESIS AND CHARACTERIZATION OF CINNAMOYLOXYETHYL (METH)ACRYLATES AND THEIR COPOLYMERIC HYDROGELS

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ABSTRACT

Two unsaturated hydrophobic monomers, cinnamoyloxyethyl acrylate (CEA) and cinnamoyloxyethyl methacrylate (CEMA), were synthesized from hydroxyethyl acrylate (HEA) and hydroxyethyl methacrylate (HEMA), respectively, by the esterification reaction with cinnamoyl chloride. FT-IR, ^1H - and ^{13}C -NMR spectra were employed to characterize the monomers. These monomers were bulk copolymerized with HEA and HEMA, respectively, by free-radical polymerization using azobisisobutyronitrile (AIBN). Mechanical properties, thermal behavior, and surface morphology of the transparent copolymers were studied by Instron, differential scanning calorimeter (DSC), and scanning electron microscope (SEM), respectively.

INTRODUCTION

Wichterle and Lim developed the first synthetic polymeric hydrogels based on hydroxyethyl methacrylate (HEMA), for use as biomaterials [1]. Since then, there has been continuing interest in the development of novel types of hydrogel materials for biomedical applications [2, 3].

The surgical applications of synthetic hydrogels based on HEMA have been relatively unsuccessful as its homopolymeric hydrogels exhibit poor mechanical

properties which strongly reduces the possibilities for their application as materials in artificial implants. Several investigations have focused on the copolymers of HEMA with hydrophobic monomers like methyl acrylate, ethyl acrylate, methyl methacrylate, butyl acrylate, dodecyl methacrylate, styrene, etc., not only to enhance the mechanical properties but also to modify the release rate of drug materials in controlled drug-delivery systems [4-9]. Recently, hydrophobic monomers were also derived from the well-known hydroxyalkyl(meth)acrylates by reaction with several acyl chlorides [10, 11] and anhydrides [12], and the resultant monomers were copolymerized again with hydroxyalkyl(meth)acrylates.

This paper deals with the synthesis of two unsaturated hydrophobic monomers, cinnamoyloxyethyl acrylate (CEA) and cinnamoyloxyethyl methacrylate (CEMA), by the reaction of cinnamoyl chloride with HEA and HEMA, respectively. These monomers were characterized by FT-IR, ^1H - and ^{13}C -NMR spectral techniques. The above synthesized monomers were then bulk copolymerized with HEA and HEMA, respectively. Mechanical properties, thermal behavior, and surface morphology of these copolymers were studied by Instron, DSC, and SEM, respectively.

EXPERIMENTAL

Materials

2-Hydroxyethyl acrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA) (E. Merck) were purified by vacuum distillation, and the middle portion of the distillates were used. Cinnamic acid, thionyl chloride, triethylamine (TEA), dimethylformamide (DMF), petroleum ether (60-80°C), and dichloromethane (s.d. fine chem., India) were used as received. Azobisisobutyronitrile (AIBN, Aldrich) was used as radical initiator after recrystallization from methanol.

Synthesis of CEA and CEMA Monomers

Cinnamoyl chloride was prepared from cinnamic acid by refluxing it with thionyl chloride and a few drops of DMF for 2 hours. After evaporating the excess thionyl chloride, the cinnamoyl chloride was purified by vacuum distillation.

A 500-mL three-neck round-bottom flask was charged with HEA (26 mL, 0.2 mol), TEA (23 mL, 0.22 mol), and dichloromethane (50 mL). The flask was fitted with a glass stirrer and kept in an ice bath between 0 and 5°C. Freshly prepared cinnamoyl chloride (34 mL, 0.2 mol) was taken in a 100-mL addition column with 50 mL dichloromethane and added dropwise to the flask for 30 minutes. The stirring was continued for another 2 to 3 hours. The precipitated salt (TEA·HCl) was filtered off, and the filtrate was extracted with distilled water several times. The aqueous layer was discarded every time. Finally the organic layer was also extracted with 5% NaOH and 5% HCl. On evaporating the solvent from the organic layer, an oily monomer (CEA) was obtained.

A similar procedure was followed for the preparation of CEMA by taking HEMA and cinnamoyl chloride. Petroleum ether (60-80°C) was used as the solvent instead of dichloromethane.

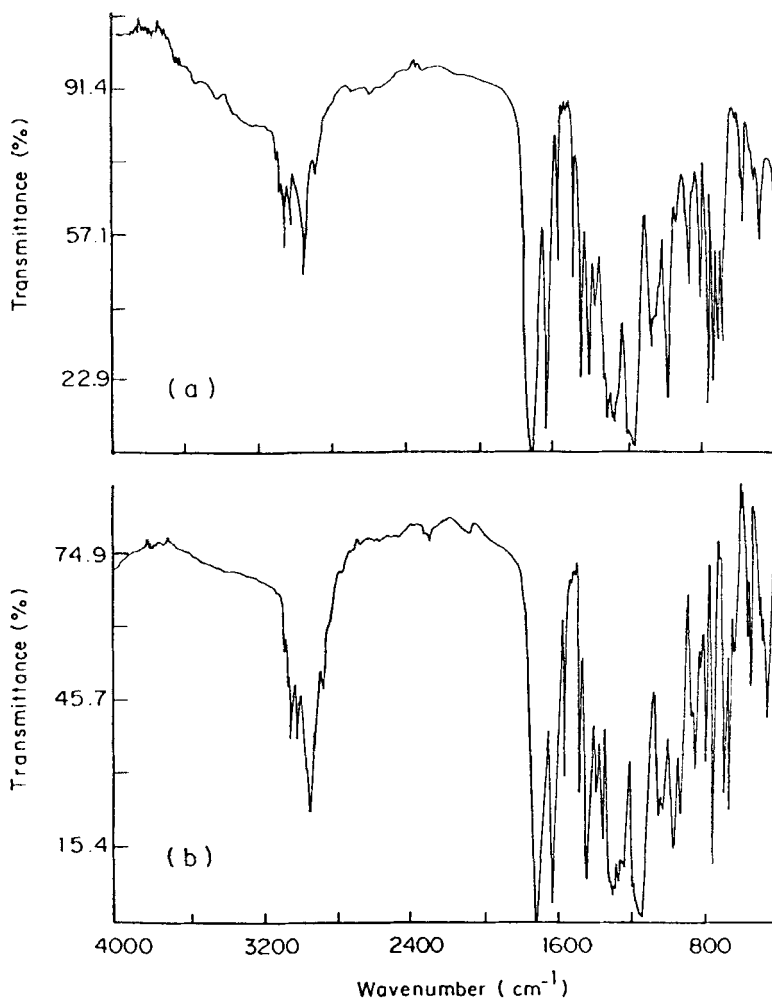


FIG. 1. FT-IR spectra of (a) CEA and (b) CEMA monomers.

Spectral Characterization of CEA and CEMA Monomers

FT-IR spectra of monomers were recorded using a Nicolet Impact 400 spectrometer. The liquid monomers were cast into a thin film between KBr windows. A Bruker MSP 300 MHz FT-NMR spectrometer was used to record the ¹H- and ¹³C-NMR spectra of the monomers using deuterated chloroform.

Polymerization Procedure

The homopolymer of HEA and its copolymers with CEA were prepared in the form of small thin disks (approximately 70 mm length, 40 mm breadth, 1 mm thickness) by free-radical polymerization with AIBN initiator (0.1 wt%). For each copolymer composition the proper amount of monomer mixture, after degassing

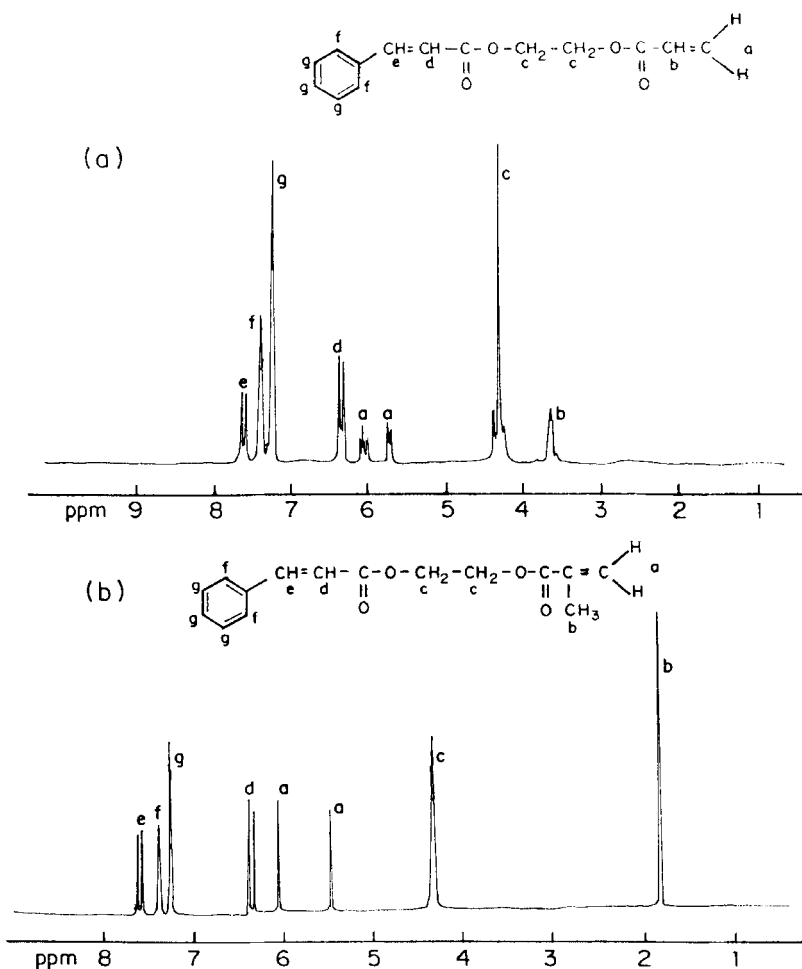


FIG. 2. $^1\text{H-NMR}$ (CDCl_3 solution) spectra of (a) CEA and (b) CEMA monomers.

with dry nitrogen for 10 minutes, was injected into a die obtained by inserting a silicon rubber gasket between two superimposed tempered glass plates. The inner surfaces of the glass plates were covered firmly with a thin polyethylene sheet for easy removal of the polymer sheet. In this polymerization procedure, no further crosslinking agent like ethylene glycol dimethacrylate (EGDMA) was added since hydrophilic monomer itself contains a sufficient amount of crosslinking agent as reported in the literature [13]. The total volume of the monomer mixture was adjusted to 3 mL in all the polymerization experiments.

The polymerization die setup was kept in a thermostatic water bath at 70°C for 5 hours. The copolymer sheets were taken from the glass die and again kept in a hot air oven at 90°C for another 7 to 8 hours to ensure complete polymerization. Finally, the copolymer sheets (xerogels) were allowed to swell in distilled water until they reached their equilibrium water content.

TABLE 1. ¹H-NMR Data of CEA and CEMA Monomers

CEA			CEMA		
δ, ppm	Multiplicity	Protons	δ, ppm	Multiplicity	Protons
3.7	m	1H	1.8	s	1H
4.3	m	4H	4.2	m	4H
5.7	m	1H	5.4	m	1H
6.1	m	1H	6.0	m	1H
6.3	d	1H	6.3	d	1H
7.2	m	3H	7.2	m	3H
7.5	m	2H	7.4	m	2H
7.6	d	1H	7.6	d	1H

Equilibrium Water Content

The water absorbed by the homo- and copolymeric hydrogel networks is quantitatively represented by the equilibrium water content (EWC) which is represented as the ratio of the weight of water in the hydrogel to the weight of the hydrogel at equilibrium hydration. The EWC was measured by the weight difference between the swollen hydrogel and the dehydrated polymer as described earlier [14]. This is expressed as

$$\text{EWC (\%)} = \frac{\text{weight of water in hydrated gel}}{\text{total weight of hydrated gel}} \times 100$$

Differential Scanning Calorimetry

Differential scanning calorimetry of swollen homo- and copolymers was performed in a DuPont 2910 differential scanning calorimeter. Samples weighing not more than 20 mg were cut from the hydrated gel sheet, and surface water was carefully removed with tissue paper. The weighed samples were placed in pre-weighed aluminum sample pan. The samples were cooled to -75°C using liquid nitrogen and then heated up to 250°C at a rate of 10°C per minute.

Mechanical Properties of CEMA-co-HEMA

The mechanical properties of the swollen samples were studied using an Instron 1112 model. The samples were cut into a dumbbell shape according to ASTM D 638 Type 5 with an extension rate of 20 mm per minute. The samples were taken from the swelling medium (distilled water) just before the test and utilized immediately for analysis.

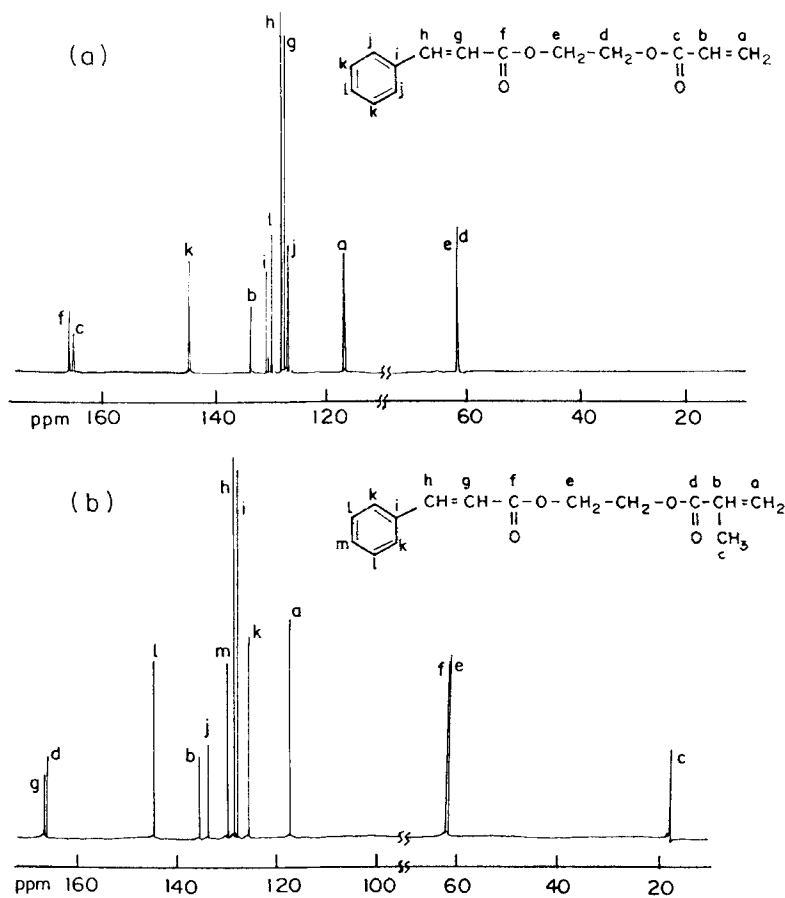


FIG. 3. ^{13}C -NMR (proton decoupled) spectra of (a) CEA and (b) CEMA monomers.

TABLE 2. Equilibrium Water Content (EWC) of CEA-co-HEA and CEMA-co-HEMA Copolymer Hydrogels

Composition in copolymeric hydrogels, wt%		Equilibrium water content (EWC), %	
CEA/CEMA	HEA/HEMA	CEA-co-HEA	CEMA-co-HEMA
0.0	100.0	42.0	39.7
5.0	95.0	29.3	33.3
10.0	90.0	24.6	28.1
15.0	85.0	20.1	25.1
20.0	80.0	17.7	21.6
30.0	70.0	12.4	16.7
50.0	50.0	6.6	10.8

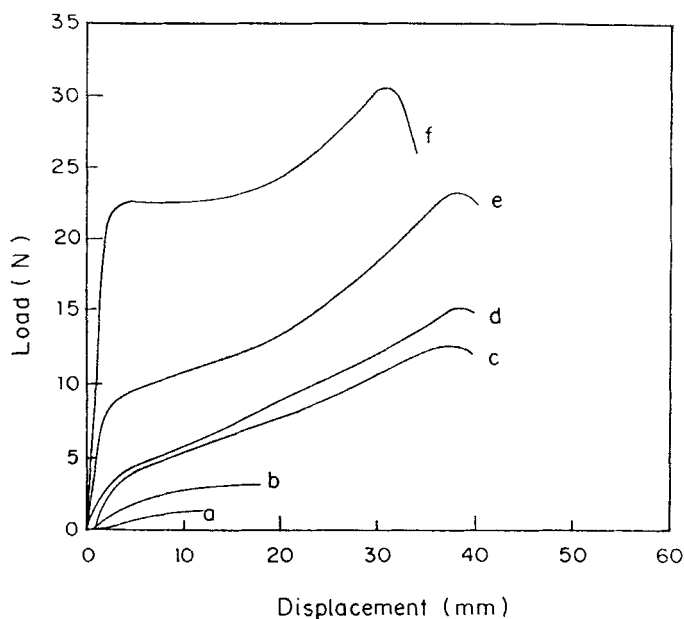


FIG. 4. Tensile (load displacement) curves of P(HEMA) (a) and CEMA-*co*-HEMA 5:95 (b); 10:90 (c); 15:85 (d); 20:80 (e); and 30:70 (f) copolymer hydrogels.

Scanning Electron Microscopy

Surface morphologies of the dried samples of hydrophilic homopolymers and copolymers were examined after slightly etching the sample surface using a Jeol JSM CF36 scanning electron microscope (SEM). A very thin gold film (approximately 200 Å) was coated on the samples before analysis.

RESULTS AND DISCUSSION

The FT-IR spectra of CEA and CEMA are shown in Fig. 1. CEA showed the characteristic peaks at 1720 cm^{-1} for conjugated carbonyl group, and at 3030, 3065, and 3084 cm^{-1} for aromatic C-H stretching. Similarly, CEMA showed the

TABLE 3. Mechanical Properties of CEMA-*co*-HEMA Copolymers

Composition in copolymeric hydrogels, wt%		Tensile strength, MPa	Elongation, %	Initial modulus, MPa
CEMA	HEMA			
0	100	0.15	115	0.36
5	95	0.34	205	0.53
10	90	0.90	460	1.60
15	85	1.09	507	1.90
20	80	1.74	483	2.90
30	70	2.20	416	9.57

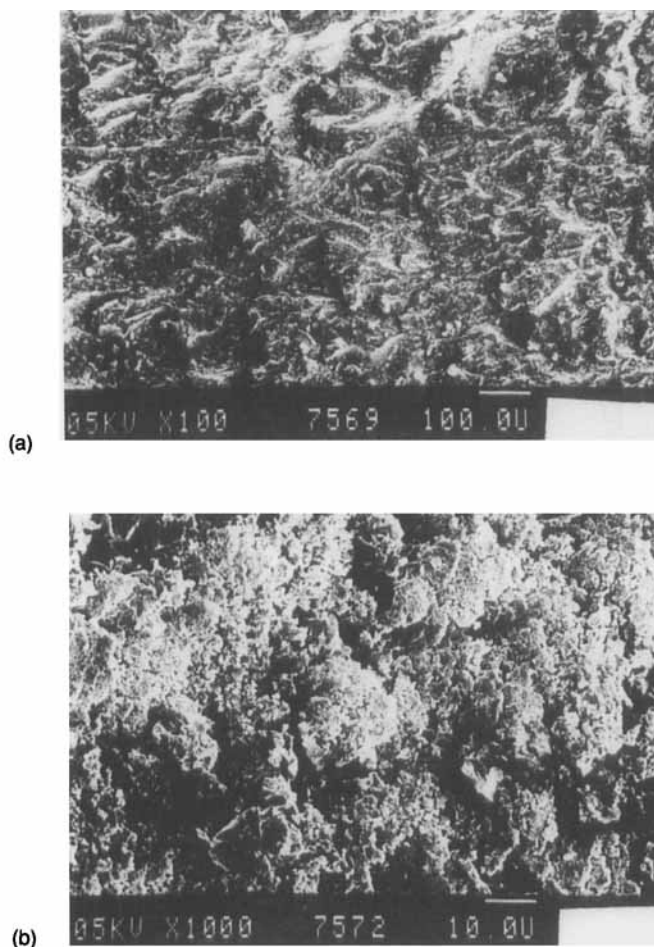


FIG. 5. SEM photographs of P(HEA) (a); CEA-co-HEA 50:50 (b); P(HEMA) (c); and CEMA-co-HEMA 50:50 (d).

carbonyl peak at 1719 cm^{-1} and aromatic C—H stretching peaks at 3023 , 3065 , and 3078 cm^{-1} . The absence of a broad peak at 3450 cm^{-1} for the —OH stretching frequency and the presence of peaks around $3000\text{--}3100\text{ cm}^{-1}$ due to aromatic —CH stretching confirm the formation of monomers.

$^1\text{H-NMR}$ peaks give good agreement with the structures of the monomers. The proton NMR spectra of CEA and CEMA are shown in Fig. 2, and the observed chemical shift values are given in Table 1. Seven multiplets were observed for CEA and CEMA; they are easily assignable to seven different types of protons. Both monomers showed two characteristic absorption peaks for trans —CH=CH— of cinnamoyl moiety at 6.3 and 7.6 ppm. All the other peaks were assigned to their corresponding hydrogen atoms as shown in Figs. 2(a) and 2(b).

The proton decoupled $^{13}\text{C-NMR}$ spectra of CEA and CEMA also confirm the structures of the monomers. The spectra are shown in Fig. 3. The CEA spectrum

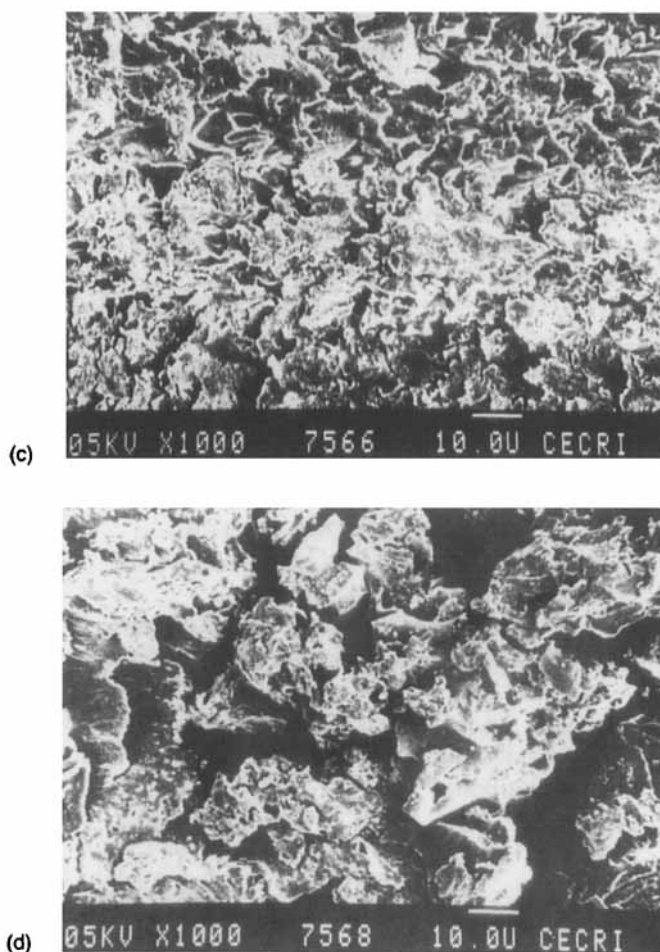


FIG. 5. (continued)

displayed 12 peaks, corresponding to 12 different carbons, whereas CEMA displayed 13 peaks. The additional peak is due to the methyl carbon of the vinyl group. All the other peaks were assigned to their respective carbon atoms as shown in Figs. 3(a) and 3(b).

The EWC values determined from swelling studies of the homo- and copolymeric hydrogels are listed in Table 2, which reveals the decrease in EWC value on increasing the addition of hydrophobic monomers. The synthesized monomers are multifunctional in nature, which could also induce additional crosslinking apart from their hydrophobicity on polymerization. Hence, further addition of crosslinking agents like EGDMA was avoided in the present studies. It was also observed that the sol fraction was negligible, which confirms the almost complete polymerization of monomers.

The thermograms of hydrated samples of homopolymeric HEA and HEMA, and copolymeric CEA-*co*-HEA and CEMA-*co*-HEMA (not shown) revealed their

glass transitions (T_g). The incorporation of CEA to HEA shifts the T_g of HEA from the negative temperature to positive temperature but did not give any multiple T_g s, which confirms the good compatibility until the copolymer composition consists of approximately 50% of each monomer. On increasing the hydrophobic monomer content, a decrease in freezing water content has been observed in terms of diminishing peak area of the endothermic peak at about 0°C. A broad endothermic peak starting about 100°C was also observed due to the loss of water absorbed when the polymers were hydrated. Similar observations were noticed in both the HEMA and its copolymers CEMA-*co*-HEMA.

Homopolymer of HEMA and its copolymers with CEMA were analyzed for their mechanical properties. The results are shown in Fig. 4 and Table 3. These copolymers are rigid in dehydrated form and flexible when hydrated. The steep rise in load during the initial displacement and the increase in initial modulus on increasing the amount of CEMA indicated a rise in rigidity. Even though enhancement in elongation was observed initially, further incorporation of CEMA diminished the elongation, resulting in high strength copolymers. Unlike P(HEMA) and CEMA-*co*-HEMA, P(HEA) and its copolymers CEA-*co*-HEA did not have measurable amounts of flexibility due to their highly fragile nature, even though they are relatively soft in the dehydrated state.

The surfaces of dehydrated homopolymeric and copolymeric polymers were scanned by SEM. A continuous phase morphology was noticed in the homopolymers of both HEA and HEMA, as seen from Figs. 5(a) and 5(c). From Figs 5(b) and 5(d) it is observed that the surfaces of both copolymers containing 50% of their respective hydrophobic monomers were perturbed and showed a phase separation indicating their poor compatibility.

CONCLUSION

Copolymerization of HEA and HEMA with CEA and CEMA, respectively, shows a wide variety of properties. It is possible to prepare copolymers with the required equilibrium water content and mechanical strength except in the case of CEA-*co*-HEA copolymers due to the fragile nature of P(HEA). From the present studies it was observed that the initial softness and fragile nature of P(HEA) could be improved gradually by the addition of CEA, but there is no appreciable improvement in flexibility. The absence of multiple T_g s in DSC indicated the good compatibility of copolymers having less than 50% of each monomer in their composition, which was further reflected by the continuous phase morphology in SEM.

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