ABSTRACT

Photocrosslinkable prepolymer/monomers containing acrylate and methacrylate functional groups have been synthesized. These are listed below:

I Acrylated polyethylene diepoxymethylene tartramide
II Acrylated polybutyl diepoxymethylene tartramide
III Acrylated polyhexamethylene diepoxymethylene tartramide
IV Acrylated polyoctyl diepoxymethylene tartramide
V Acrylated diepoxymethylene diethyl tartrate
VI Methacrylated polyethylene diepoxymethylene tartramide
VII Methacrylated polybutyl diepoxymethylene tartramide
VIII Methacrylated polyhexamethylene diepoxymethylene tartramide
IX Methacrylated polyoctyl diepoxymethylene tartramide
X Methacrylated diepoxymethylene diethyl tartrate

The synthetic route is as follows: Polyalkyl tartramides containing free hydroxyl groups were prepared by the reaction of diethyl tartrate with the diamines, 1,2-diaminoethane, 1,4-diaminobutane, 1,6-diaminohexane and 1,8-diaminoocctane at room temperature without the use of any solvent or catalyst. The reaction of polyalkyl tartramides with epichlorohydrin yielded polyalkyl diepoxymethylene tartramides.

The photocrosslinkable acrylated and methacrylated prepolymer/monomers were synthesized by the ring-opening reaction of polyalkyl diepoxymethylene tartramide with acrylic acid and methacrylic acid respectively. In addition, the monomers acrylated and methacrylated diepoxymethylene diethyl tartrate without diamine moiety were synthesized by the reaction of diepoxymethylene diethyl tartrate with acrylic acid and
methacrylic acid to produce the respective monomers. All the synthesized compounds were characterized by IR, $^1$H-NMR and $^{13}$C-NMR techniques.

IR spectra of the prepolymers/monomers exhibit absorption band around 1610-1635 cm$^{-1}$ due to C=C functional group stretching of the monomers. Absorption band around 1690-1710 cm$^{-1}$ corresponds to ester C=O stretching in the monomers. The monomers show broad absorption bands around 3350-3136 cm$^{-1}$ owing to the -OH and -NH stretching vibrations. The absorption with respect to ether C-O-C is observed at around 1160-1149 cm$^{-1}$.

In the $^1$H-NMR spectra of the monomers, each proton in the alkenyl group appears at different frequencies as multiplet in the region 5.68-6.51 $\delta$. The methyl protons adjacent to the alkenyl group show as a singlet at 1.70-1.80 $\delta$. The resonates corresponding to -NH protons appear as triplet at around 7.05-7.15 $\delta$. In the $^{13}$C-NMR spectra of the monomers, the carbon of the alkenyl functional group resonates at around 124-133 ppm. The methyl carbon adjacent to alkenyl reactive centre resonates at 18 ppm.

The photocrosslinking properties of the prepolymers/monomers have been studied by irradiating the prepolymers/monomers in the presence of free radical photoinitiator, 1-hydroxycyclohexyl phenyl ketone using medium pressure mercury vapour lamp for different time intervals and different initiator concentration. The rate of disappearance of the acrylate and methacrylate functional group during irradiation have been studied by measuring the FT-IR absorption intensity due to C=C stretching frequency of the crosslinked polymers. The photocrosslinking studies indicate that the methacrylated prepolymers/monomers exhibit higher double bond conversion than the acrylate prepolymers/monomers.
The values of the hardness of the photocrosslinked polymers were measured and it was observed that the hardness values are higher for the polymers obtained from the methacrylated monomers than the acrylated monomers. The highest hardness value of 98 (d) was observed for the polymer MD$_{20}$ and lowest value of 36 (d) for the polymer E$_{1}$.

The densities of all the photocrosslinked polymers were measured. Among the crosslinked polymers obtained from acrylated and methacrylated monomers, the polymers from the methacrylated monomers show relatively higher density than those of the polymers from the acrylated monomers.

The solubility of the photocrosslinked polymers were tested and these polymers were found to be insoluble in most of the organic solvents. This observation indicates, all the polymers were swollen in N,N-dimethylformamide, dimethyl sulfoxide and methyl alcohol.

The swelling studies of the crosslinked polymers were carried out using N,N-dimethylformamide as a solvent to find out the swelling coefficient, crosslink density and molecular weight between crosslinks. These studies reveal that the swelling coefficient and molecular weight between crosslinks decreases with increasing irradiation time and initiator concentration but there is an increase in the crosslink density of the polymers. The percent gel content of the crosslinked polymers were studied and the results indicate that the percent gel content increases with increasing the irradiation time.

Thermal characterization of the crosslinked polymers were studied by thermogravimetric analysis and glass transition temperature ($T_g$) were determined by differential scanning calorimetry.