ABSTRACT

Photosensitive polymers have received considerable attention in the recent past owing to their applications as photoresists to make integrated circuits, photocurable coatings, photorecorders, printing plates, optical memory devices and energy exchange materials. Polymers employed for these applications should possess one of the photoreactive groups like cinnamoyl, coumaroyl, azide, arylidene, cyclic carbonate and stilbene. The photosensitivity of these materials is mainly based on the electron density of the photoactive chromophore. Photoresist materials are of two kinds: positive and negative photoresists. Positive photoresists become soluble in developers on exposure to UV light. In negative photoresists, the photochemistry that occurs on irradiation renders the material less soluble in the developer; the unirradiated parts of the coating are washed away and a negative polymer image of the original pattern remains on the substrate. Among many photosensitive polymers, polymers containing α, β-unsaturated ketones received greater attraction due to their high sensitivity towards UV radiation. Most of the photosensitive polymers reported in the literature possess poor solubility in common organic solvents and have high softening temperatures. Nevertheless, further research is necessary to develop new polymers with structural modifications in order to enhance the desirable properties and applications.

The photosensitive monomers, 3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl) propenone and 1, 3-bis (4-hydroxyphenyl) propenone

were prepared respectively by refluxing 3-methoxy-4-hydroxybenzaldehyde and 4-hydroxybenzaldehyde with 4-hydroxy acetophenone using borontrifluoride diethyletherate catalyst. 2,6-Bis (4-hydroxy-3-methoxybenzylidene) cyclohexanone, 2,6-bis (4-hydroxybenzylidene) cyclohexanone were prepared respectively by refluxing 4-hydroxybenzaldehyde and 3-methoxy-4-hydroxybenzaldehyde with cyclohexanone. Bis (4-hydroxy-3-methoxy benzylidene) acetone was prepared from 4-hydroxy-3-methoxy benzaldehyde and acetone. The structure of the monomers was confirmed by FT-IR, ^{1}H and ^{13}C-NMR spectroscopic techniques.

In the present investigation, photosensitive polymers were prepared by reacting the monomers 3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl) propenone, 1, 3-bis (4-hydroxy phenyl) propenone, 2, 6-bis (4-hydroxy-3-methoxy benzylidene) cyclohexanone, 2, 6-bis (4-hydroxy benzylidene)cyclohexanone and bis-(4-hydroxy -3-methoxy benzylidene) acetone with epichlorohydrin by solution polycondensation method. All the polymers were characterized systematically.

The reaction conditions and molar ratio of diol and epichlorohydrin were optimized. The synthesized polymers were characterized by UV, FT-IR, ^{1}H and ^{13}C -NMR spectroscopic techniques. The photosensitive property of the polymers in film and solution state was studied. The effect of solvents, photoinitiators, sensitizers and temperature on photoreactivity were investigated by ultraviolet spectroscopy. Curing kinetics of the synthesized epoxy resin was determined by differential scanning calorimetry technique.

The thermal properties of the polymers were studied by thermogravimetric analysis and differential scanning calorimetry under nitrogen atmosphere.

Most of the synthesized polymers are stable upto 350 ^{o}C. The glass transition temperature (T_g), melting temperature (T_m) and curing kinetics data were obtained from Perkin Elmer Pyris 6 Differential Scanning Calorimeter, heated from 40 to 400 ^{o}C with different heating rates (5, 10, 15 °C/min), in nitrogen atmosphere.

The photocrosslinking property of the polymers in solution and film state was studied by monitoring UV absorbance. The rate of conversion of C=C to C-C was calculated using the expression, $[(A_0\text{-}A_t)\ x100]\ /\ [A_0\text{-}A]$, where A_0, A_t and A are the absorption intensities of $>C=C<$ at irradiation times 0, t and a time after which there is no further significant change in the absorption respectively. All the polymers showed absorption maximum at around 350nm due to $\pi \rightarrow \pi$ transition of the olefinic double bond present in the polymer chain. A decrease in the intensity of absorbance was observed in all polymers during the successive irradiation with regular time intervals. This may be attributed to the disappearance of double bond leading to the formation of cyclobutane ring by the $2\pi+2\pi$ cycloaddition reaction of the olefinic double bond. Photopolymerising ability of the epoxy resin was studied in presence of triphenyl sulphonium photoacid generator. Photoreactivity studies revealed the dual functionality of the resin.

Inherent viscosity of the polymers was determined using Ubbelohde viscometer. The storage stability of the epoxy resin was studied

using Brookfield Viscometer and found that they are stable for more than 60 days. Gel permeation chromatography was used to determine the molecular weight of the polymers and found that the synthesized polymers are of low molecular weight. The epoxy content was determined by titration method using pyridinium hydrochloride and noticed that the epoxy equivalents of the synthesized polymers are in the range of 350 - 700. Studies on mechanical properties like tensile strength for chemically cured and photo cured epoxy resin were carried out. Satisfactory results were obtained in Photo lithographical study of the prepared polymer. Gel content, moisture absorption and chemical resistance of the prepared epoxy resin were determined and compared with the commercial bisphenol-A epoxy resin.

The results of this investigation indicate that the synthesized epoxy resins can be used as negative photoresist.