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NEW PREPOLYMER FOR UV CURABLE COATINGS : SYNTHESIS, CHARACTERIZATION AND PHOTOCROSS LINKING OF 2-HYDROXY-3-[*p*-(1-[2-HYDROXY-3-(ISOPROPHENYL CARBONYLOXYPROPOXY] PHENYL} CYCLO PENTYL) PHENOXY] PROPYLACRYLATE

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ABSTRACT

The new ultraviolet curable prepolymer, 2-hydroxy-3-[*p*-(1-{2-hydroxy-3-(isoprophenyl carbonyloxypropoxy]phenyl}cyclopentyl) phenoxy] propylacrylate (BISCEDA) was synthesized by the reaction of *p*-[1-(*p*-hydroxyphenyl) cyclopentyl] phenol with cyclopentanone, epoxidation with epichlorohydrin followed by addition reaction with acrylic acid. All synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR and FTIR spectroscopy. An ultraviolet (UV) curable formations were prepared by the prepolymer, BISCEDA (75%), diluent, tri(ethyleneglycol)dimethacrylate (25%) and different concentrations of a photoinitiator, 1-hydroxycyclohexylphenyl ketone and irradiated at 365 nm. The kinetics of the photopolymerization, percent double bond conversion and rate of photopolymerization was studied by FTIR spectroscopy. The results show that, increasing photoinitiator concentration, increase percent double bond conversion whereas, rate of photopolymerization increase suddenly and then decrease. The swelling measurement was carried out by using N, N'-dimethyl formamide as a solvent.

Key words: Prepolymer, UV curable formulation, FTIR, Percent double bond conversion, Rate of polymerization.

INTRODUCTION

An ultraviolet (UV) curable coating contains prepolymer, diluent and photoinitiator. Generally bisphenol vinyl ester compounds are used as a prepolymer in coating industries. A bisphenol vinyl ester resins were first introduced commercially in the year 1960's[1]. Today, it

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*Author for correspondence; E-mail: kumar.jsec@gmail.com; Mo.: +91-8939273733 is one of the most important photocrosslinkable materials. It has excellent chemical resistance to a wide variety of chemicals and chemical environments, low water absorption and low cost when compared with polyester resins, polyether resin and polyurethane acrylate. It is well known that bisphenol epoxy vinyl ester resins have very good mechanical properties and are used to fabricate a variety of reinforced structures[2-9]. A structural modification of vinyl ester resins was studied by many researchers to alter their properties in order to satisfy specific application requirements. The vinyl esters with considerable structural modification can be synthesized by the combination of different epoxide resins with acrylic acid. Today, vinyl ester epoxy resins are becoming more important in industry and the research on vinyl epoxy ester resins is expanding. The development and application of vinyl epoxy ester resin include the synthesis of vinyl epoxy ester resins with structural modification is an effort to improve toughness, to reduce viscosity and to decrease shrinkage.

In the present work, a new UV curable prepolymer, 2-hydroxy-3-[*p*-(1-{2-hydroxy-3-(isoprophenylcarbonyloxypropoxy]phenyl}cyclopentyl)phenoxy]propylacrylate (BISCEDA) was synthesized and characterized. The prepolymer, BISCEDA is irradiated by UV radiation and kinetics of the photocrosslinked polymer, percent double bond conversion and rate of polymerization was studied by FTIR. The crosslink density, swelling coefficient and molecular weight between crosslinks of the photocrosslinked polymers were studied by swelling measurement using DMF as a solvent.

EXPERIMENTAL

Materials

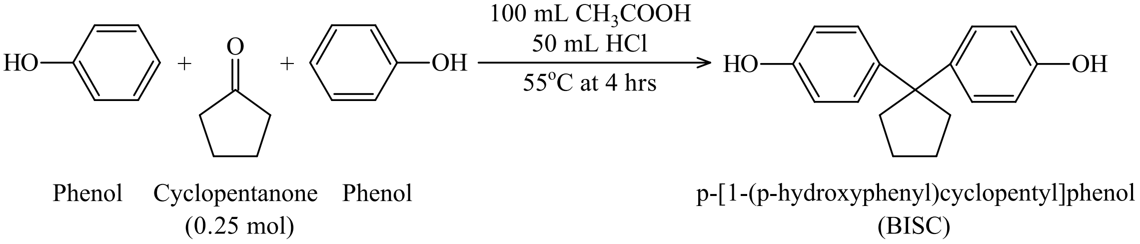
Benzene, ethanol, isopropanol, epichlorohydrin, potassium hydroxide (KOH), sodium hydroxide (NaOH), 1,4-dioxane, triethylamine, chloroform ($CHCl_3$), acetone, cyclopentanone, phenol, benzene, tetrahydrofuran (THF), N, N'-dimethyl formamide (DMF) and N, N'-dimethyl sulphoxide (DMSO), sulphuric acid ($H_2 SO_4$), hydrochloric acid (HCl), acetic acid (CH_3COOH) were purchased from SRL and used without further purification. The diluent, tri(ethyleneglycol)dimethacrylate (TEGDMA) and the photoinitiator, 1-hydroxycyclohexylphenyl ketone (HCPK) were purchased from Aldrich (USA) and used without further purification.

Methods and measurement

^{1}H NMR and ^{13}C NMR spectra of samples were taken in $CDCl_3$ on Bruker DPX-300 MHz spectrometer. The internal reference used was tetramethylsilane (TMS). FTIR spectra of the prepolymer and photocrosslinked samples were recorded on Perkin-Elmer spectrum one (4000-400 cm^{-1}) spectrometer, using KBr pellets. The photocurable formulation containing a prepolymer, a diluent and a photoinitiator were irradiated under medium pressure mercury vapour lamp with intensity of $125W/cm^2$. To study, the effect of the photoinitiator, HCPK concentration (%), different formulations were prepared by mixing the prepolymer, BISCEDA (75%), diluent, TEGDMA (25%) and different concentration of the HCPK, 0.25%, 0.50%, 0.75%, 1.00% and 1.25% separately. The percent double bond conversions (%) were determined by FTIR Spectroscopy. The gel content (%) and swelling studies were carried out using the solvent, DMF. The swelling coefficient (Q), crosslink density (υ) and molecular weight between crosslinks (M_c) were calculated. The shore hardness of the photocrosslinked polymers were determined by A Type-JIS K-6301 hardness (Germany) tester.

Synthesis of p-[1-(p-hydroxyphenyl) cyclopentyl] phenol (BISC)

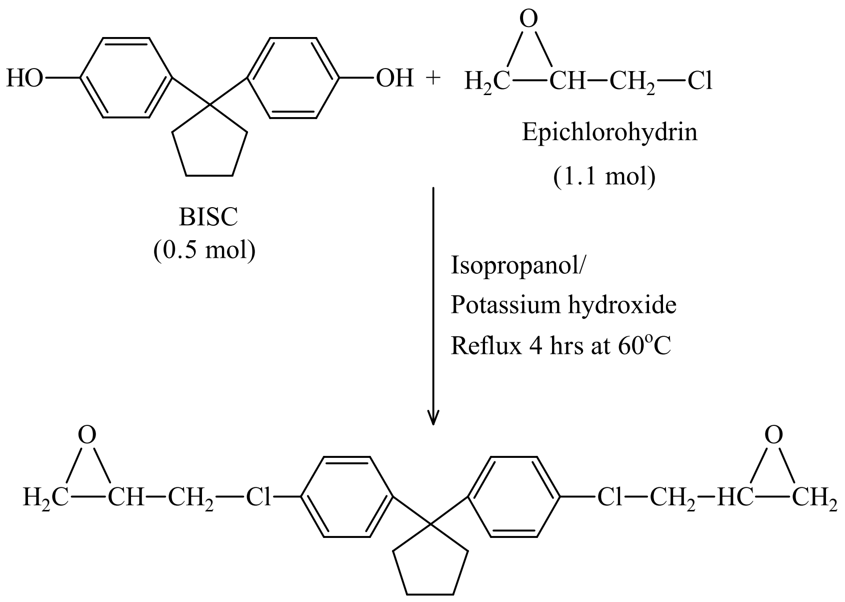
A solution of cyclopentanone (0.25 mol) and phenol (0.5 mol) in 150 mL solution containing H_2SO_4 (50 mL**)** dissolved in CH_3COOH (100 mL) was taken in five necked round bottom flask equipped with a condenser, mechanical stirrer with heating mantle, funnel and thermometer. The mixture was heated at 55°C for 4 hrs, pink colour product was removed, added 50 mL of boiled water and 2 N potassium hydroxide (10 mL) solution. The resin product was filtered, precipitate was obtained, washed with acetone and dried at 40°C. The white colour solid was obtained, recrystallized from benzene and ethanol-water system. Yield: 85~87%. The synthesis of BISC is shown in **Scheme 1**.



Scheme 1: The synthesis of BISC

Synthesis of 2-oxiranyl-[p-(1-{p-[(2-oxiranyl)methoxy] phenyl} cyclopentyl) phenoxy] methane (DGEBISC)

A 250 mL of isopropanol was added to a mixture of 0.5 mol of BISC and 1.1 mol of epichlorohydrin in 500 mL five necked round bottom flask equipped with a condenser, mechanical stirrer with heating mantle, funnel and thermometer. The mixture was heated at 60°C for 15 minutes, 10 mL of 1.25 mol of potassium hydroxide was slowly added to the mixture and refluxed for 4 hours. The separated solid was filtered, washed with warm water and dried at room temperature, recrystallization from ethanol to give white crystals. Yield: 90~92%. The synthesis of the DGEBISC is shown in **Scheme 2**.

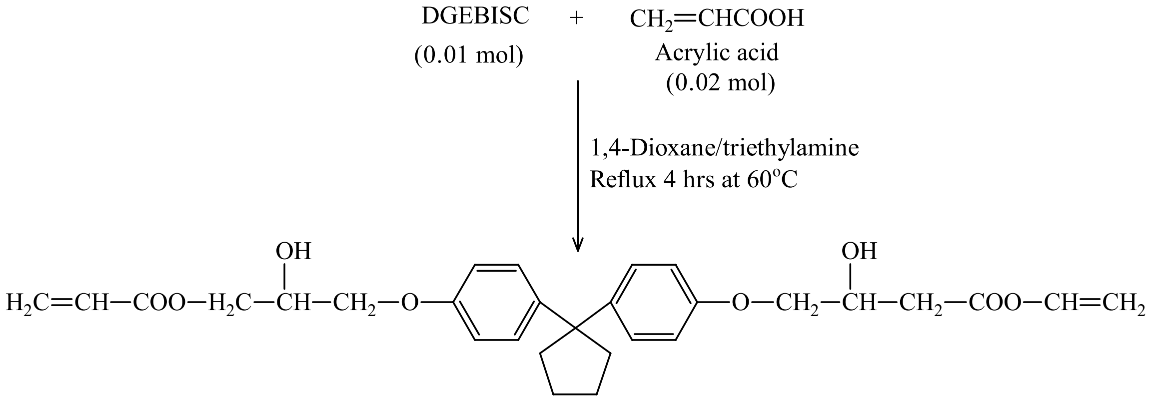


2-Oxiranyl-[p-(1-{p-[(2-oxiranyl)methoxy]phenyl}cyclopentyl)phenoxy]methane
(DEGBISC)

Scheme 2: The synthesis of DGEBISC

Synthesis of 2-hydroxy-3-[p-(1-{2-hydroxy-3-(isoprophenylcarbonyloxypropoxy] phenyl} cyclopentyl) phenoxy] propylacrylate (BISCEDA)

A 500 mL five necked round bottom flask equipped with a condenser, mechanical stirrer with heating mantle, funnel and thermometer, 100 mL of 1,4-dioxane was added with the mixture containing 0.01 mol DEGBISC, 0.02 mol of acrylic acid, a catalyst, 2 mL triethyl amine slowly added and then refluxed at 55°C for 6 hours to get acid value < 10. The resin, BISCEDA was obtained and it is soluble in common organic solvents such as, chloroform and acetone. This indicates that the resin may be linear or branched chain compound. Yield: 91~94%. The synthesis of the prepolymer, BISCEDA is shown in **Scheme 3**.



2-Hydroxy-3-[p-(1-{2-hydroxy-3-(isoprophenylcarbonyloxy]propoxy]phenyl}phenoxy]propyl acrylate (BISCEDA)

Scheme 3: The synthesis of the prepolymer, BISCEDA

Formulation of UV curable coating

An UV curable formulations of consisting of prepolymer, BISCEDA, diluent, TEGDMA and photoinitiator, HCPK were shown in Table 1. In each formulation, chemicals were mixed well at room temperature for 15 min and then formulated solution was coated on a glass sheet on 20 mm thickness by using bar coater and irradiating under ultraviolet light source of 365 nm at various concentration of HCPK and at different time intervals.

Table 1: Formulation of UV curable coating

Component	Various formulations				
BISCEDA (%)	75	75	75	75	75
TEGDMA (%)	25	25	25	25	25
HCPK (%)	0.25	0.50	0.75	1.0	1.25

RESULTS AND DISCUSSION

The structures of the compounds, BISC, DGEBISC and BISCEDA were confirmed by ^{1}H NMR, ^{13}C NMR and FTIR spectroscopy.

p-[1-(p-hydroxyphenyl) cyclopentyl] phenol

FTIR (KBr, cm^{-1}): 3415 (O-H str), 3042 (Ar-C=C-H str), 2946 (C-H asym str), 2861 (C-H sym str), 1621 (Ar-C=C str), 1450 (C-H def), 1225 (C-O str) and 1180 (Ar-C-H def). ^{1}H NMR (CDCl$_3$, TMS, 300 MHz) (δ/ppm): 1.16 (t, 4H, β-CH$_2$ cyclic), 2.18 (t, 4H, α-CH$_2$ cyclic), 5.22 (s, 2H, Ar-OH), 6.70-7.12 (d, 4H, Ar-H) and 7.41-7.72 (d, 4H, Ar-H). ^{13}C NMR (CDCl$_3$, TMS, 300 MHz) (δ/ppm): 25.33 (β-CH$_2$ cyclic), 39.74 (Ar$_2$-C), 41.54 (α-CH$_2$ cyclic) and 112.29, 126.93, 142.49, 155.13 (Ar-C).

2-Oxiranyl-[p-(1-{p-[(2-oxiranyl)methoxy]phenyl} cyclopentyl) phenoxy] methane

FTIR (KBr, cm^{-1}): 3413 (O-H str), 3041 (Ar-C=C-H str), 2944 (C-H asym str), 2860 (C-H sym str), 1639 (-C-H cyclic epoxy str), 1619 (Ar-C=C str), 1449 (C-H def), 1238 (epoxy half ring str), 1223 (C-O str), 1178 (Ar-C-H str), 1150 (-O-CH$_2$ str) and 827 (epoxy whole ring str). ^{1}H NMR **(**CDCl$_3$, TMS, 300 MHz) (δ /ppm): 1.15 (t, 4H, β-CH$_2$ cyclic), 2.21 (dd. 4H, Ar-O-CH$_2$), 2.17 (t, 4H, α-CH$_2$ cyclic), 2.71 (dt, 4H, CH$_2$-O), 3.71 (m, 2H,-CH-O-), 6.68-7.10 (d, 4H, Ar-H) and 7.38-7.69 (d, 4H, Ar-H). ^{13}C NMR (CDCl$_3$, TMS, 300 MHz) (δ/ppm): 25.30 (β-CH$_2$ cyclic), 39.72 (Ar$_2$-C-), 41.52 (α-CH$_2$ cyclic), 63.52 (Ar-O-CH$_2$), 66.36 (-CH-O), 71.58, (-CH$_2$-O-) and 112.27, **1**26.91, 142.48, 155.10 (Ar-C).

2-Hydroxy-3-[p-(1-{2-hydroxy-3-(isoprophenylcarbonyloxypropoxy] phenyl} cyclopentyl) phenoxy] propyldiacrylate

FTIR (KBr, cm^{-1}): 3412 (O-H), 3040 (Ar-C=C-H str), 2943 (C-H asym str), 2856 (C-H sym str), 2926 (C-H str), 1752 (C=O str), 1653 (-C=C- str), 1617 (Ar-C=C str), 1462 (-C=C-H bend str), 1447 (C-H def), 1361 (-C=C-H rock str), 1221 (C-O str), 1176 (Ar-C-H str), 1148 (-O-CH$_2$ str), 810 (-C=C-H bend str) and 725 (-C=C-C-H rock str). ^{1}H NMR (CDCl$_3$, TMS, 300 MHz) (δ/ppm): 1.14 (t, 4H, β-CH$_2$ cyclic), 2.15 (t, 4H, α-CH$_2$ cyclic), 2.69 (dt, 4H, -CH$_2$–O-), 3.25 (d, 2H, -OH-), 4.03 (m, 4H, Ar-O-CH$_2$), 5.58 (d, 2H, -CH=CH$_2$ trans), 6.11 (d, 2H, CH=CH$_2$ cis), 6.31 (t, 2H, -CH=CH$_2$), 6.65-7.11 (d, 4H, Ar-H) and 7.37-7.67 (d, 4H, Ar-H). ^{13}C NMR (CDCl$_3$, TMS, 300 MHz**)** **(**δ/ppm**)**: 25.28 (β-CH$_2$ cyclic), 39.70 (Ar$_2$-C-), 41.50 (α-CH$_2$ cyclic), 66.32 (-CH-), 68.34 (-CH-O-), 63.50 (Ar-O-CH$_2$-), 126.22 (=CH$_2$), 132.30 (-CH=), 112.25, 126.89, 142.46, 155.08 (Ar-C) and 167.52 (-CO-O-).

Percent double bond conversion

The percent double bond conversion, PDC (%) of the double bonds reacted was calculated from the following equation[10].

$$\text{PDC}(\%) = \left\{1 - \frac{\left(\dfrac{A_{\text{acrylate}}\,C = C}{A_{\text{aromatic}}}\right)\text{Crosslinked polymer}}{\left(\dfrac{A_{\text{acrylate}}\,C = C}{A_{\text{aromatic}}}\right)\text{Prepolymer}}\right\} \times 100 \qquad \ldots(1)$$

The decrease in the intensity of acrylated C=C absorbance ($A_{acrylate}$) at 1635-1660 cm^{-1} was monitored. The phenyl absorbance ($A_{aromatic}$) at 1605-1620 $cm^{-1}$was used as the internal standard. The effect of HCPK concentration (%) on percent double bond conversion is shown in Fig. 1. The percent double bond conversion is increased with increasing the HCPK concentration (%) is due to increasing in number of free radicals produced and involved in photopolymerization.

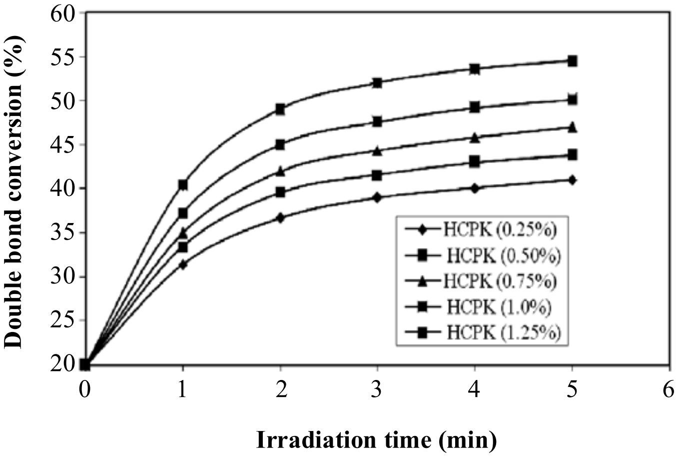


Fig. 1: Effect of HCPK concentration (%) on percent double bond conversion

Rate of polymerization (R_p)

Rate of polymerization (R_p) was calculated using by the following equation[11].

$$R_p = [M_0] \times \left[\frac{(A_{810})t_1 - (A_{810})t_2}{(A_{810})t_0\,(t_2 - t_1)} \right] \quad \ldots(2)$$

where $[M_0]$ is the monomer concentration before irradiation, $(A_{810})t_0$, $(A_{810})t_1$ and $(A_{810})t_2$ represent the absorption due to carbon-carbon double bond before and exposure during t_1 and t_2 time, respectively. The effect of HCPK concentration (%) on rate of polymerization is given in Fig. 2. At 1 min irradiation and 1.25% HCPK concentration, R_p reaches maximum, suddenly decrease and then become constant, this may be due to the percent double bond conversion at 1 min irradiation and 1.25% of HCPK concentration reaches maximum and then increasing irradiation time, percent double bond conversion is almost constant.

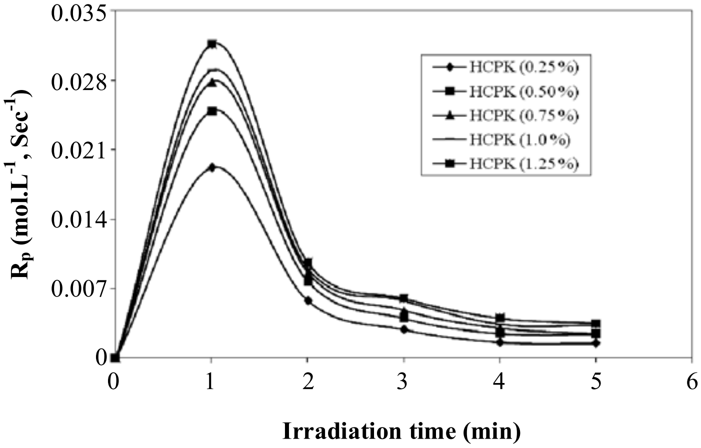


Fig. 2: Effect of HCPK concentration (%) on rate of polymerization (R_p)

Density of photocrosslinked polymer

Density of the photocrosslinked polymers were measured by using the formula.

$$\text{Density} = \left(\frac{a}{a-b}\right) \times d \qquad \ldots(3)$$

where a and b are weight (gm) of photocrosslinked polymer in air and isopropyl alcohol, respectively, d is density of isopropyl alcohol. The density data of the photocrosslinked polymers are given in Table 2. The density of the photocrosslinked polymer increases with increasing irradiation time and HCPK concentration (%) is due to increasing in crosslink density.

Table 2: Effect of HCPK concentration (%) on density of photocrosslinked polymers

HCPK concentration (%)	Density (g/cc)				
	Irradiation time (min)				
	1	2	3	4	5
0.25	0.804	0.827	0.836	0.863	0.897
0.50	0.831	0.876	0.891	0.922	0.964
0.75	0.857	0.905	0.938	0.949	0.991
1.00	0.872	0.953	1.176	1.201	1.256
1.25	0.897	1.079	1.284	1.328	1.413

Swelling study

The crosslink density of the photocrosslinked polymer is defined as the average molecular weight between crosslinks and it is an important parameter of the polymer. The swelling method is used to measure the crosslink density of the photocrosslinked polymer. The molecular weight between crosslinks was calculated from swelling coefficient. The swelling studies were carried out in DMSO at 25 ± 0.05°C. The photocrosslinked polymer (100 mg) was added with DMF (10 mL). After 72 hrs swollen polymer was isolated from DMF and drying at 40°C. The weight of swollen polymer (gm) and initial polymer (gm), swelling coefficient (Q) was calculated using the formula[12].

$$Q = \frac{\text{Weight of the swollen polymer}}{\text{Weight of the polymer}} \times \frac{\text{Density of DMF}}{\text{Density of polymer}} \qquad \ldots(4)$$

The crosslink density (υ) and molecular weight between crosslinks (M_c) were determined by using Flory-Reihner's equation[12].

$$\upsilon = \frac{Vr + xV_r^2 + \ln(1 - Vr)}{d_r V_0 \left(V_r^{\frac{1}{3}} - \frac{V_r}{2} \right)} \qquad \ldots(5)$$

where, υ = crosslink density (effective number of moles of crosslinked units per gram) of crosslinked polymers, $V_r = 1/(1+Q)$, the volume fraction of polymer, d_r = density of polymer, x = polymer-DMF interaction parameter (lattice constant 0.34, for $\delta_s = \delta_p$), V_0 = molar volume of DMF. The solubility parameter of the solvent, DMF (δ_s), which imparts maximum swelling for the polymers, was taken as the solubility parameter of the polymer (δ_p).

$$\text{Molecular weight between crosslinks } (M_c) = \frac{1}{\upsilon} \qquad \ldots(6)$$

The effect of HCPK concentration (%) on Q and ν are given in Table 3. The ν of the photocrosslinked polymers increases with an increasing in irradiation time and HCPK concentration (%) is due to increase in R_p, whereas Q and Mc decrease. 100 mg of the photocrosslinked polymer was added to 75 mL acetone and the mixture was allowed to stand for 72 hrs.

Table 3: Effect of HCPK concentration (%) on Q, υ and M_c

HCPK (%) Irradiation time (min)	Q					$\upsilon \times 10^{-4}$ and ($M_c \times 10^3$)				
	1	2	3	4	5	1	2	3	4	5
0.25	7.46	7.04	6.53	6.12	5.64	1.14 (8.77)	1.21 (8.26)	1.40 (7.14)	1.52 (6.58)	1.68 (5.95)
0.50	5.58	5.18	4.82	4.21	3.74	1.85 (5.41)	2.01 (4.98)	2.46 (4.07)	2.76 (3.62)	3.25 (3.08)
0.75	4.27	3.81	3.53	3.31	2.93	2.78 (3.60)	3.34 (2.99)	3.68 (2.72)	4.08 (2.45)	4.83 (2.07)
1.00	3.63	3.24	2.93	2.56	2.18	3.74 (2.67)	4.20 (2.38)	4.07 (2.46)	5.04 (1.98)	6.33 (1.58)
1.25	2.46	2.02	1.71	1.44	1.13	7.23 (1.38)	8.36 (1.20)	9.28 (1.08)	11.9 (0.84)	16.4 (0.61)

The swollen sample was separated by the Soxhlet extractor and subjected to drying for long time to complete drying. The gel content (%) was determined by using the formula.

$$\text{Gel content (\%)} = \left(\frac{W_a}{W_b}\right) \times 100 \qquad \ldots(7)$$

where, W_a and W_b are weight of original (gm) and extracted sample (gm), respectively. The influence of various concentrations (%) of the photoinitiator, HCPK on the gel content (%) is shown in Fig. 3. The gel content (%) increases with increasing HCPK concentration (%) is due to increasing in extra free radical involved in photocrosslinking reaction.

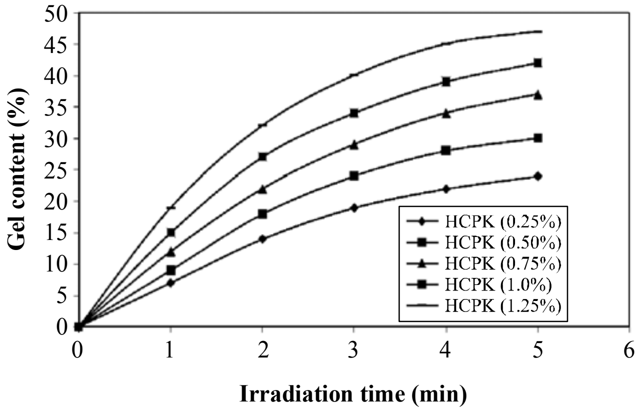


Fig. 3: Effect of HCPK concentration (%) on gel content (%)

Hardness testing

The shore hardness of the photocrosslinked polymer films was determined by A-Type- JIS K-6301 hardness tester. For this study, photocrosslinked polymer thickness of 20 mm was used. The readings were taken at various places on the same photocrosslinked polymer samples by pressing the needle of the hardness tester. The average value was taken for the hardness of the photocrosslinked polymer. The effect of HCPK concentration (%) on hardness is given in Fig. 4. The hardness of the polymers increases with increasing irradiation time and HCPK concentration (%) is due to increasing in crosslink density.

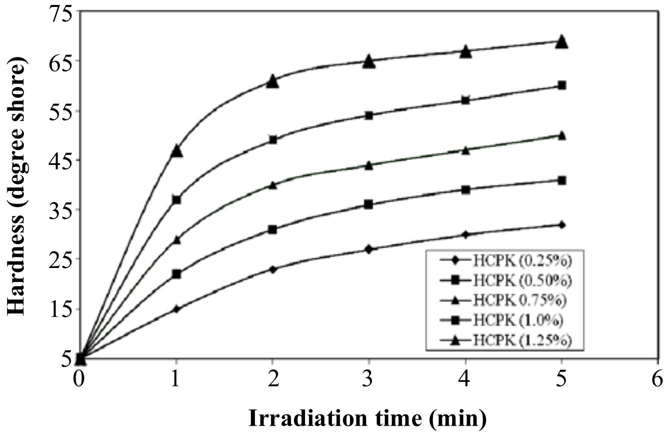


Fig. 4: Effect of HCPK concentration (%) on hardness

CONCLUSION

The acrylated new prepolymer, 2-hydroxy-3-[*p*-(1-{2-hydroxy-3-(isoprophenyl carbonyloxypropoxy] phenylcyclopentyl) phenoxy] propylacrylate (BISCEDA) was synthesized in good yield. The synthesized prepolymer, BISCEDA undergoes photocrosslinked polymerization with the diluent, TEGDMA in the presence of various concentration (%) of the photoinitiator, HCPK to produce three dimensional polymers. The crosslink density of the photocrosslinked polymers was high which showed that, the synthesized prepolymer, BISCEDA was very much resistant to solvent and chemicals. This also revealed that the prepolymer, BISCEDA may be satisfactory to use in coating industry.

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