

## OPTICAL PLASTICS FROM ACRYLATES & CINNAMATES; INCORPORATION OF BARIUM FOR IMPROVED PROPERTIES

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### ABSTRACT

An attempt has been made to transform a basic material like acrylic acid into a highly valuable optical plastic. Three methodologies have been adopted in order to prepare barium-containing nanocomposites using acrylic acid and cinnamic acid. Barium hydroxide was found to be the most suitable compound to be incorporated in acrylic acid matrix to produce optical plastic of desired properties.

Gamma radiation has been used as a novel technology for polymerization. In order to achieve the mechanical as well as other related properties, certain monomers were also used along with the cross-linkers. The nanocomposites obtained have successfully resulted in better optical properties than the conventional material, i.e., high refractive index of 1.53-1.56.

Evaluation of the nanocomposites has been carried out with respect to key optical properties such as refractive index, Abbe number, transmittance, etc. Thermal stability and physico-mechanical properties have been studied and compared with the conventional optical plastic material. The interactions between barium hydroxide and acrylic acid have been studied by UV-Visible spectroscopy and infrared spectroscopy. Overall, this paper emphasizes on the development of high refractive index barium-containing nanocomposites for optical applications.

**Keywords:** *Optical plastics, acrylates, cinnamates, barium-containing optical plastics, nanoparticles, gamma irradiation, thermal stability, refractive index.*

### 1. INTRODUCTION

Acrylic acid and cinnamic acid are an important class of compounds which form the building blocks for the production of some of the commonly used industrial and consumer products. Acrylic acid and acrylates are essential ingredients in paints, coatings, textiles, adhesives, plastics and other applications. The unique attributes of the structure of acrylic acid are due to the fact that it is a molecule of small size having a carboxylic acid for derivatization and a double bond for linkages of monomers.

One of the most well known applications of acrylates is in the optical industry where polyacrylates such as polymethyl methacrylates, phenyl ethyl acrylate, phenyl ethyl methacrylate are some of the acrylates used for optical applications and are obtained by the esterification of acrylic acid with alcohols having varying alkyl chain length. This means that one can design the polyalkyl acrylates by varying the alcohol structure. A large range of polyacrylates have already been in use for various applications. Here, it must be noted that the whole range has yet to be developed.

Cinnamic acid has been widely studied because of its very specific structure. The carboxylic acid group is separated from the aromatic ring by a double bond and causes conjugation between the C=C bond and the  $\pi$ -electron system. It has two different donor sites to form bonds with the metal ions: the double bond between the carbon atoms and the oxygen atoms of the carboxylic acid group [1-3]. Cinnamic acid has two different donor sites for forming bonds with metal ions: the double bond between the carbon atoms and the oxygen atoms of the carboxylic acid group [4]. Cinnamic acid and cinnamates are used in flavours and pharmaceutical industries [5].

### 2. EXPERIMENTAL

#### 2.1 Materials

For the preparation of barium-containing nanocomposites, barium compound used for the experimental work was Barium hydroxide octahydrate [Ba(OH)<sub>2</sub>·8H<sub>2</sub>O] of 99.9% purity having a melting point of 86 °C, procured from Qualigens, India.

Acrylic acid having a boiling point of 141°C was procured from s.d.Fine Chemicals, India was used as a dispersing media for the preparation of acrylate nanocomposites.

Cinnamic acid, a carboxylic acid having a melting point of 133 °C was procured from LOBA Chemie, India and was used for the experimental studies to prepare metal containing nanocomposites. The carboxylic acid was of laboratory grade and used as such for the studies without any further processing or treatment.

The co-monomer used for polymerization of barium containing compositions was styrene having a boiling point of 142-146 °C and purity of > 99%. Styrene was procured from G.S. Chemical Testing Lab & Allied Industries and was used as such without any further purification.

## 2.2 Methodology

Preparation of barium-containing nanocomposites was carried out by adopting three methodologies.

- (i) Preparation of barium acrylate nanocomposites: A three-necked round bottom (RB) flask fitted with (i) thermometer, (ii) stirrer and (iii) funnel was used for the synthesis of barium containing compositions. Acrylic acid was taken in a three-necked R.B flask to which the addition of barium hydroxide was done under continuous stirring at room temperature. The reaction mixture was stirred continuously using an overhead stirrer for the nanodispersion of barium hydroxide in the monomer. After the dispersion of barium hydroxide in acrylic acid, styrene was added for polymerization and the nanocomposites so obtained were evaluated for various properties.
- (ii) Preparation of barium cinnamate nanocomposites: A three-necked round bottom (RB) flask fitted with (i) thermometer, (ii) stirrer and (iii) funnel was used for the synthesis of barium containing compositions. Cinnamic acid was taken in a three-necked R.B flask and melted. To the melted cinnamic acid, addition of barium hydroxide was done under continuous stirring at 140°C-145°C. The reaction mixture was stirred continuously using an overhead stirrer for the preparation of barium cinnamate. After the preparation of barium cinnamate, styrene was added for polymerization to form barium-containing nanocomposites.
- (iii) Preparation of barium cinnamate-barium acrylate nanocomposites: A three-necked round bottom (RB) flask fitted with (i) thermometer, (ii) stirrer and (iii) funnel was used for the synthesis of barium cinnamate-barium acrylate compositions. Barium cinnamate (prepared in above step) was added to barium acrylate (as described above) gradually. The reaction mixture was stirred continuously using an overhead stirrer for the preparation of barium cinnamate-barium acrylate compositions. After the dispersion, styrene was added for polymerization to form barium-containing nanocomposites.
- (iv) Preparation of cinnamic acid-acrylic acid polymers: A three-necked round bottom (RB) flask fitted with (i) thermometer, (ii) stirrer and (iii) funnel was used for the synthesis of cinnamic acid-acrylic acid compositions. Cinnamic acid was added to acrylic acid under continuous stirring using an overhead stirrer. After the dispersion, styrene was added for polymerization to form a reference polymeric material.

## 2.3 Characterization

- a) Refractive index and Abbe number  
Refractive index and Abbe number [6] was determined by using Atago Abbe refractometer DRM 4 at wavelengths 589.2 nm, 486.10 nm and 656.3 nm.
- b) UV-Visible Spectroscopy  
The UV-Visible spectroscopy of the cast lenses in the UV-Visible region of 200nm to 800 nm was determined on the UV-Visible spectrophotometer (Model UV-1700) procured from Shimadzu [7].
- c) Thermal Analysis  
For TGA, DTA and DTG studies, model 2960 of TA Instruments, USA was used. TGA was used to study the thermal stability of barium dispersed compositions and barium containing nanocomposites. The TGA studies were carried out in nitrogen atmosphere with operating temperature ranging from room temperature to 700 °C.
- d) Vicat Softening Temperature  
Vicat softening temperature was determined to find out the working temperature of the sample by ASTM D-1525 [8].
- e) Impact strength  
Impact strength was determined using impact tester fabricated as per FDA 21 CFR 801.410 [9], where a steel ball weighing 16.2 g was dropped from a height of 127 cm upon the horizontal upper surface of the lens. Lenses which did not crack or break were taken to be impact resistant.
- f) Shore-D hardness  
Shore-D hardness of the acrylic polymers were measured using the Durometer of Hiroshima Instruments, Japan as per ASTM D-2240 [10]. The hardness value was determined by the penetration of the indenter of the Durometer into the sample.

## g) Infrared Spectroscopy

Metal containing acrylate compositions were studied under infrared radiation to understand the structural changes taking place between the functional groups and metals. The results could be manifested on the basis of the characteristic of the bond formed. The FTIR Spectrophotometer FTIR-ATR BOMEM (FTLA 2000) in transmittance mode from 4000–400  $\text{cm}^{-1}$  was used.

## h) Cross-link density

Cross-link density is used to determine the extent of cross-linking in a polymer. It is determined by ASTM D-2765 [11]. Chloroform was used as a solvent for extraction studies. In this method, swell ratio and extract percentage was evaluated to determine the percentage of cross-link density as given in Equation 1-2.

$$\text{Extract \%} = C / D \times 100$$

(Equation 1)

Where, C=weight (in grams) of solvent entrapped in gel  
D=weight (in grams) of original sample

$$\text{Cross link density (\%)} = 100 - \text{Extract \%}$$

(Equation 2)

## i) Particle Size Analysis

Particle size and particle size distribution were analyzed by Particle Size analyzer nano-sizer by Metrohm Inc.

## j) Acid value

Acid value is determined by directly titrating the material in an alcoholic medium with aqueous sodium or potassium hydroxide solution as per IS 548 (Part I):1964 [12]. Acid value is determined by Equation 3.

$$\text{Acid value} = (56.1 \times V \times N) / W$$

(Equation 3)

Where V = Volume of standard KOH or NaOH used (in ml)  
N = Normality of standard KOH or NaOH prepared  
W = Weight of the sample (in grams)

### 3. RESULTS & DISCUSSION

Results of various studies performed during the preparation of barium- containing nanocomposites are presented in this section. Observations for various parameters at different stages of the study are discussed.

#### 3.1 Preparation of Barium Acrylate Nanocomposites

##### 3.1.1 Dispersion of Barium Hydroxide in Acrylic Acid

The first step involved the synthesis of barium hydroxide-acrylic acid composition. Addition of barium hydroxide to acrylic acid was done gradually. Barium hydroxide was added at ambient temperature to acrylic acid taken in a round bottom flask, gradually under constant stirring and compositions were prepared with varying content (0%-20% by weight) of barium hydroxide. The effect of addition of barium hydroxide to acrylic acid was monitored by studying the effect of barium hydroxide on the refractive index of acrylic acid after each addition. The results of refractive index of addition of barium hydroxide in acrylic acid are tabulated in Table 1.

Table 1: Effect of addition of barium hydroxide on the refractive index of acrylic acid. The maximum amount of barium hydroxide that could be dispersed in acrylic acid is 16% which leads to 0.8 % increase in refractive index of acrylic acid. The increase in refractive index confirms the formation of barium hydroxide-acrylic acid composition by the reaction between acrylic acid and barium hydroxide.

S. No.	Amount (% by wt)	Refractive index
1.	0.0	1.424
2.	4.0	1.431
3.	8.0	1.433
4.	12.0	1.433
5.	16.0	1.436
6.	18.0	1.436
7.	20.0	--

The formation of barium hydroxide-acrylic acid composition results in an increase in refractive index of acrylic acid from 1.424 to 1.431 in the case of 4 % addition of barium hydroxide. Further addition upto 8 % and then upto 12 % barium hydroxide to acrylic acid leads to a refractive index of 1.433 and 1.436 in the case of addition of 16 % barium hydroxide to acrylic acid. Dispersion of barium hydroxide beyond 16% in acrylic acid leads to no change in refractive index as can be seen from Table 1. Beyond 16%, refractive index of barium acrylate composition remains constant. This shows that 16% is the optimum concentration of barium hydroxide to bring about maximum improvement in the refractive index of acrylic acid. Here it may be noted that the addition of barium hydroxide beyond 16% resulted into a hazy dispersion indicating that for optical applications, the incorporation of barium hydroxide will have to be restricted to 16% by weight.

Refractive index is a property which is dependent upon the molar refractivity of the bonds constituting the compound. The change in refractive index of acrylic acid is a confirmation of the fact that the addition of barium hydroxide to acrylic acid results in the formation of a compound such as barium acrylate with higher intrinsic molar refraction than the reactants. Barium belongs to the sixth group of the periodic table; ionic size of barium is 1.36 Å. This causes the change in refractive index of the acrylic acid when barium is incorporated into it.

To study the thermal behavior of barium hydroxide-acrylic acid compositions, TGA/DTA/DTG analysis were carried out. The differential thermograms obtained from TGA analysis clearly indicate the changes in the thermal behavior of acrylic acid as a result of interactions between acrylic acid and barium hydroxide (Figures 1 to 3).

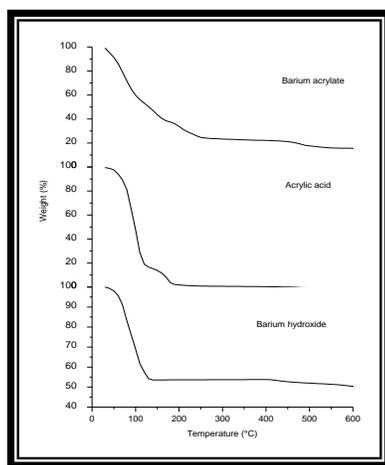


Figure 1: TGA thermograms of barium hydroxide, acrylic acid and barium hydroxide-acrylic acid composition indicate increased thermal stability of acrylic acid due to incorporation of barium

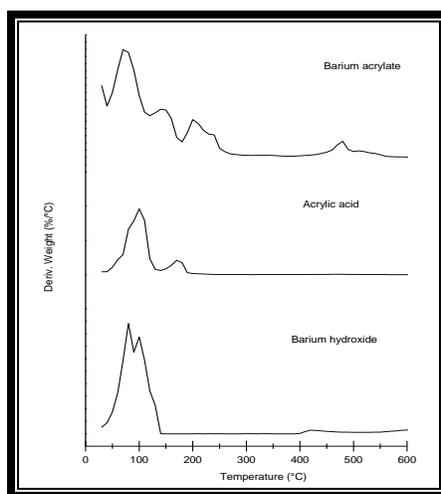


Figure 2: DTG thermograms of barium hydroxide, acrylic acid and barium hydroxide-acrylic acid indicate formation of new peaks

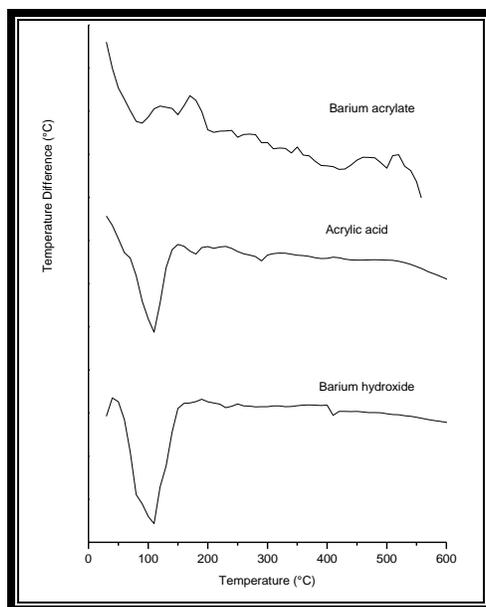


Figure 3: DTA thermograms of barium hydroxide, acrylic acid and barium hydroxide-acrylic acid composition indicate completely different behaviour than acrylic acid and barium hydroxide forming a new compound (barium acrylate)

For better understanding, the TGA results have been further examined as per the weight loss percentage due to thermal decomposition as presented in Table 2.

Table 2: Weight loss (%) due to thermal decomposition of barium hydroxide, acrylic acid and barium hydroxide-acrylic acid

Product	Weight loss (%)					
	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
Barium hydroxide	31.0	46.43	46.3	46.4	48.0	49.7
Acrylic acid	52.2	98.2	100	100	100	100
Barium hydroxide-acrylic acid	40.2	66.1	76.7	77.9	82.3	84.4
Theoretical loss in weight of barium hydroxide-acrylic acid	48.8	89.9	91.4	91.4	91.7	92.0

TGA analysis of barium hydroxide, acrylic acid and barium hydroxide-acrylic acid composition clearly show change in existing components forming new compound.

Weight loss due to decomposition in the case of barium hydroxide-acrylic acid is much less as compared to acrylic acid, simply because of the fact that there is a formation of a strong bond between barium and acrylic acid. Upto 200 °C, theoretical weight loss of acrylic acid and barium hydroxide is 90%. On the other hand, upto 200 °C, weight loss in the case of barium hydroxide-acrylic acid composition is 66%. This indicates that the product obtained after the reaction between acrylic acid and barium hydroxide is not just a mixture but a solution consisting of strong bonds between barium and acrylic acid. The results obtained with acrylic acid matched well with the already reported data. The observed weight loss upto 600 °C in the case of barium hydroxide-acrylic acid composition is much less than the calculated one. Thus, barium hydroxide-acrylic acid exhibits higher stability which is due to the fact that barium is not just mixed in acrylic acid but bonded to it resulting in a new compound (barium acrylate).

The reaction product of barium hydroxide with acrylic acid was analyzed for acid value. Acrylic acid has a pH value of less than 1 and an acid number of 626 which is indicative of the acidic character of acrylic acid. Acid value was determined to study the interactions between the acid and metal salt. The acid value is taken as an indication of the presence of free acrylic acid and the results are tabulated in Table 3.

As can be seen from Table 3, acid value of acrylic acid decreases with increase in the dispersion of barium hydroxide. From the data, it is evident that the reaction takes place involving barium and acrylic acid.

Table 3: Effect of addition of barium hydroxide on the acid value of acrylic acid. As the amount of barium hydroxide increases, the acid value decreases.

S.No.	Barium hydroxide (% by wt)	Acid number	pH
1	0.0	626	< 1
2	4.0	596	1.53
3	8.0	542	1.79
4	12.0	502	1.96
5	16.0	477	2.12

In order to understand the interactions taking place between barium hydroxide and acrylic acid, UV-Visible spectroscopy was performed from 200-800 nm on the compositions of barium hydroxide-acrylic acid in ethanol as a solvent (Figure 4 a-e).

The maximum absorption peak ( $\lambda_{\max}$ ) of acrylic acid was observed at 210 nm. As can be seen from Figure 4, there is no change in the  $\lambda_{\max}$  value of acrylic acid with increase in the amount of barium hydroxide dispersed in acrylic acid. This confirms that the vinyl group of acrylic acid remains intact and hence the only site for the reaction of barium hydroxide is the carboxylic acid group.

IR analysis was carried out to study the reaction occurring between acrylic acid and barium hydroxide. The IR spectrum is presented in Figure 5. As can be seen from the IR spectrum, acrylic acid exhibits a characteristic band at  $3100\text{ cm}^{-1}$  ascribed to C-H group of -C=C-H group and C=O stretch at  $1725\text{ cm}^{-1}$ . C=C stretching due to the presence of vinyl group appears at  $1640\text{ cm}^{-1}$  [13]. Barium hydroxide on the other hand shows a broad band due to the presence of -OH at  $3600\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$ . IR spectrum of barium acrylate shows the presence of bands due to C=O and C=C. This indicates that during the reaction of barium hydroxide with acrylic acid, reaction is not taking place at the vinyl group. Absence of O-H band and presence of C=O band in the case of barium acrylate shows that the addition of barium hydroxide takes place at the carboxylic group of acrylic acid forming an acrylate. Presence of a sharp peak at  $1555\text{ cm}^{-1}$  is due to the presence of -COO<sup>-</sup> group.

Particle sizes of the compositions were evaluated on Particle size analyzer. The results are tabulated in Table 4.

Table 4: Particle size analysis of barium acrylate compositions indicates that the dispersion of barium hydroxide takes place in the nanoscale dimension.

S.No.	Barium hydroxide (% by wt)	Particle size (nm)
1	0.0	< 0.8
2	4.0	< 0.8
3	8.0	< 0.8
4	12.0	< 0.8
5	16.0	< 0.8

The results of the particle size analysis show that the dispersed particles of barium hydroxide are in the range much lower than nanometer size and that is why no particles could be observed in the particle size analyzer (nanosizer). The dispersion in this scale is responsible for overall improvement of the properties of acrylic acid. The clarity and transparency of the compositions of the barium hydroxide-acrylic acid also suggests the same.

### 3.1.2 Cast Polymerization of barium acrylate compositions

The attempt was made to polymerize the composition of acrylic acid and barium hydroxide containing 16% by weight of barium hydroxide to obtain the optical lenses. It was observed that on polymerization, the material turned into a solid product with full of foam and hence, it could not be considered suitable for making lenses. In order to convert the composition of barium hydroxide and acrylic acid into optical products, therefore, further work was done for the incorporation of styrene as a co-monomer for the purpose of obtaining lenses.

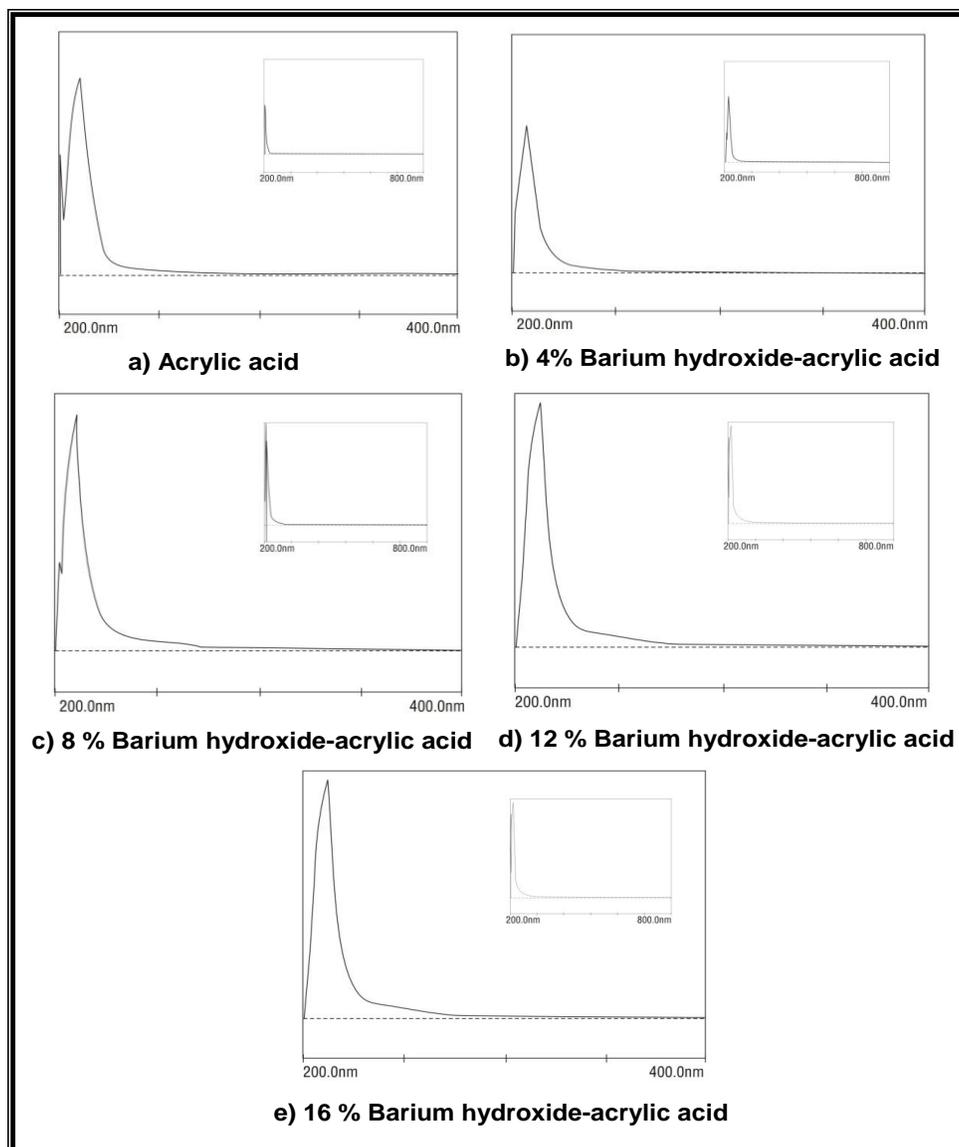


Figure 4 (a-e): UV-Visible spectra of acrylic acid and barium hydroxide-acrylic acid composition (varying concentrations). The  $\lambda_{max}$  value of acrylic acid does not change with the dispersion of barium hydroxide and hence it can be said that the reaction between barium hydroxide and acrylic acid is taking place at the carboxylic acid group of acrylic acid.

On addition of styrene, how the final product changed in its form and appearance can be seen in Table 5. It may be noted here that with the incorporation of styrene, the composition of barium hydroxide and acrylic acid could be transformed into clear and transparent lenses on polymerization. The amount of styrene needed for this purpose was found to be 150% by weight. The composites consisting of barium hydroxide, acrylic acid and styrene were made and then characterized for various essential parameters of optical plastics. It must be mentioned here that styrene alone does not get polymerized at gamma irradiation doses from 10 kGy to 30 kGy.

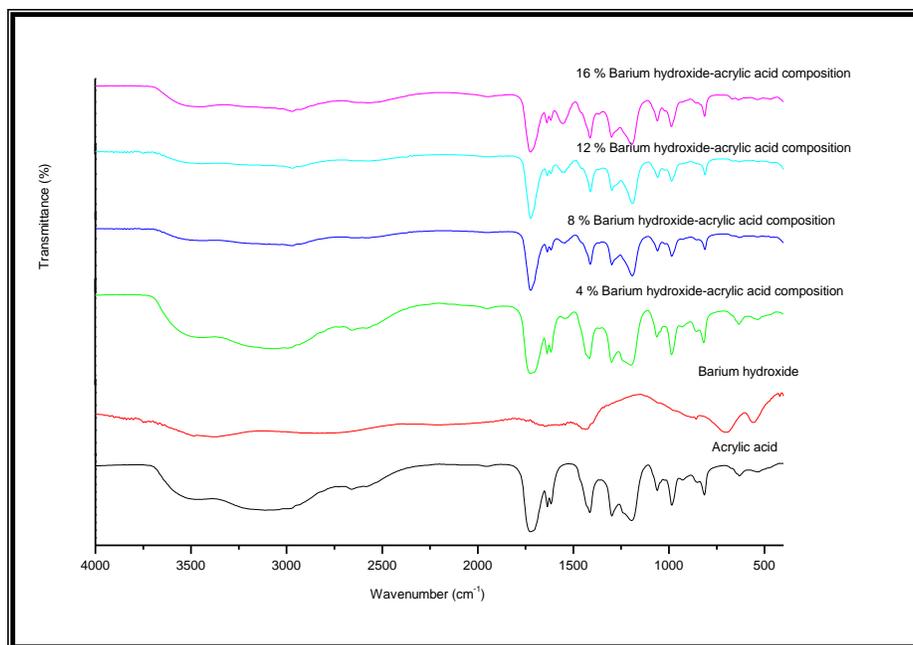


Figure 5: IR analysis of acrylic acid, barium hydroxide and barium hydroxide-acrylic acid composition. Absence of band pertaining to carboxylic acid and presence of band pertaining to ester group confirms the formation of new compound as barium acrylate after the reaction between barium hydroxide and acrylic acid

From the results presented in Table 5, it may be seen that in the absence of styrene, the nanocomposite obtained was foamy and opaque with shore-D hardness of 40. With 30% to 90% styrene (by weight of barium acrylate), the nanocomposite obtained was soft and sticky which could not be released from the molds. With 150% styrene (by weight of barium acrylate), the shore-D hardness achieved was between 90 and the nanocomposites were easily released from the mold. Clear and transparent nanocomposites suitable for optical applications were obtained. This indicates that 150% styrene (by weight of barium acrylate) was sufficient for polymerization. The appearance of polymers with and without styrene is depicted in Figure 6.

Table 5: Results of effect of styrene on polymerization indicating that 150% (by weight of barium acrylate) of styrene is required for polymerization of barium acrylate. The nanocomposites obtained were hard and transparent which were easily released from the molds.

S. No.	Styrene (% by weight)	Shore-D Hardness	Transmittance (%)	Appearance, etc.
1.	0	40	*	Foamy and opaque, Brittle
2.	30	*	*	Sticky could not be released
3.	60	*	*	Sticky could not be released
4.	90	*	*	Sticky, could not be released
5.	120	90	77	Hazy at the surface, hard
6.	150	90	90	Clear, transparent, easily released

\*: Shore-D hardness and Transmittance could not be determined as the nanocomposites were foamy or sticky in nature

It can be very clearly seen that the presence of styrene as a co-monomer for polymerization of barium acrylate compositions is very important to obtain clear, transparent and hard nanocomposites.

In the case of polymerization of acrylic acid, the beta carbon atom, polarized by the carbonyl group, behaves as an electrophile. This favors the addition of nucleophile and active hydrogen compounds to the vinyl group. Moreover, the carbon-carbon double bond undergoes radical-initiated addition reactions, Diels-Alder reactions with dienes and polymerization reactions [14-17].

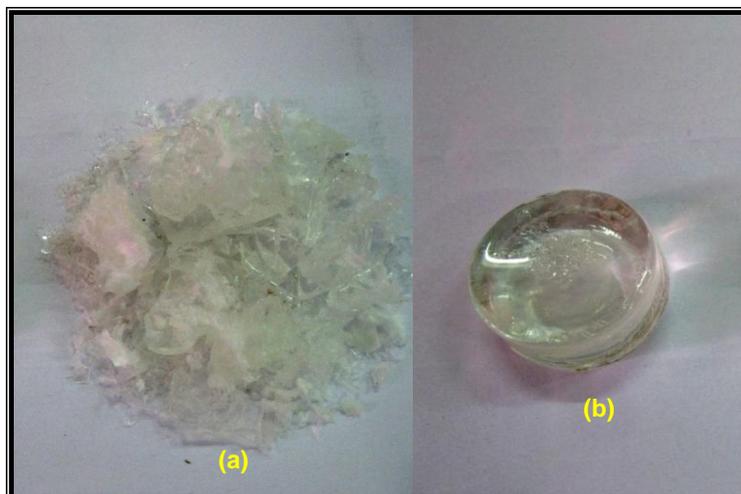


Figure 6: Barium acrylate nanocomposites a) without styrene and b) with styrene indicating that addition of styrene as co-monomer is essential for obtaining clear and transparent nanocomposites.

The results of the effect of gamma irradiation on polymerization of barium acrylate-styrene nanocomposites are presented in Table 6. Polymerization of barium acrylate-styrene compositions was carried out at various doses of 10 kGy, 15 kGy, 20 kGy, 25 kGy and 30 kGy.

Table 6: Effect of gamma irradiation on the polymerization of barium acrylate-styrene composition. 20 kGy was found to be the optimum dose for barium acrylate-styrene nanocomposites.

S.No.	Dose (kGy)	Shore-D Hardness	Cross-link density (%)	Appearance
1	10	*	72	Soft, sticky, unpolymerized liquid at the surface
2	15	*	84	Transparent, sticky at the surface
3	20	90	95	Transparent, hard and easily released
4	25	90	95	Transparent, hard and easily released
5	30	90	96	Transparent, hard and easily released

\*: Shore-D hardness could not be measured due to sticky nature of nanocomposites

As seen from the results in Table 6, barium acrylate-styrene compositions when subjected to a dose of 10 kGy-15 kGy, soft and sticky nanocomposites were obtained. At doses of 20 kGy and higher, transparent and hard nanocomposites with a shore-D hardness of 90 and cross-link density of 95% were obtained. It can be seen that as the dose of irradiation increases further, the shore-D hardness of samples does not change. The suitable dose for polymerization by gamma radiation was optimized as 20 kGy for barium acrylate-styrene compositions. It may be noted here that compositions without styrene at all the irradiation doses of 10-30 kGy led to the formation of brittle and foamy polymer.

Having cast polymerized the lenses using various compositions of acrylic acid and barium hydroxide plus styrene, the lenses were evaluated for various parameters. The results are discussed in the following section.

Refractive index and Abbe number of the nanocomposites were determined on the Abbe refractometer. The results are presented in Figures 7-8.

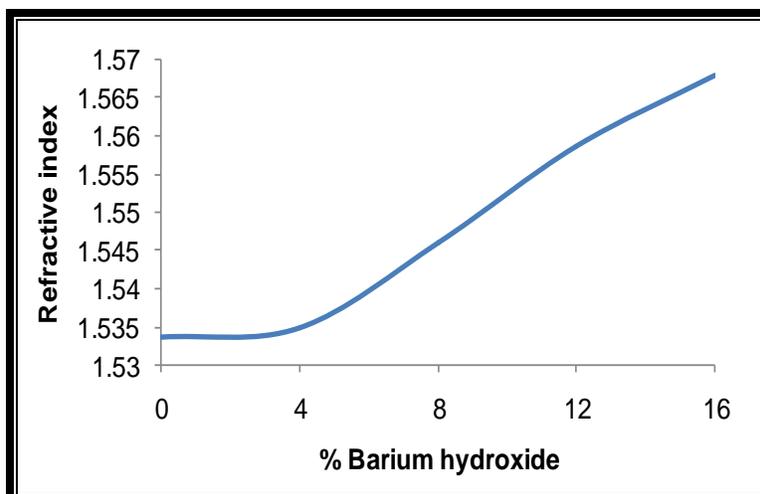


Figure 7: Effect of barium hydroxide on refractive index of acrylic acid. The refractive index increases as the percentage of barium hydroxide is increased

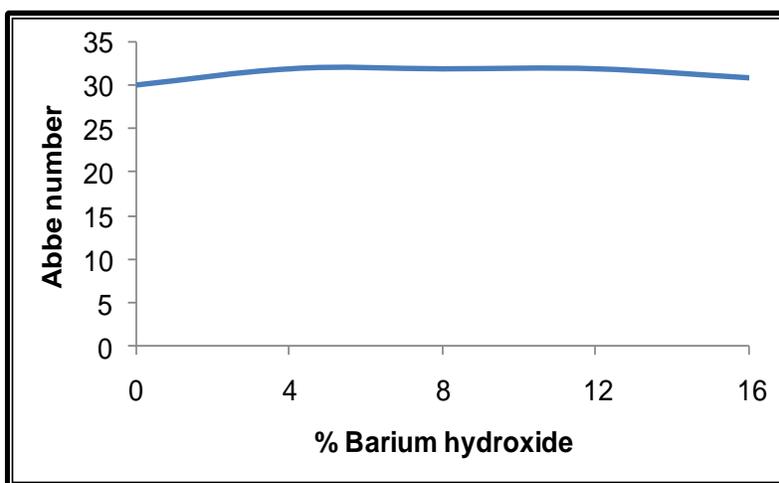


Figure 8: Effect of barium hydroxide on Abbe number of barium acrylate. No significant changes in Abbe number was observed as the percentage of barium hydroxide was increased. Abbe number lies in the well desired limit for optical applications.

As can be seen from the figures, polyacrylate-styrene polymer has a refractive index of 1.5336 and Abbe number of 30. A refractive index of 1.5348 and an Abbe number of 32 was obtained for barium acrylate-styrene nanocomposites with 4 % dispersion of barium hydroxide in acrylic acid. A refractive index of 1.5459 and an Abbe number of 32 was obtained with 8 % of barium hydroxide and a refractive index of 1.5587 and Abbe number of 32 was obtained with 12% of barium hydroxide. The refractive index further increases to 1.5681 and Abbe number of 31 with the dispersion of 16% barium hydroxide. It is found to be better than commercially available polyacrylates i.e. Polymethyl methacrylate, a commercial grade of acrylate polymer for various optical applications, which has a refractive index of 1.491.

Thermal analysis of barium acrylate-styrene nanocomposites by TGA/ DTG was studied. Thermal studies (Figure 9 –10) of the acrylate nanocomposites indicate the formation of a highly cross-linked, thermally stable structure. The weight loss of the nanocomposites was recorded at various temperatures, which is given in Table 7. The heat stability of the barium containing nanocomposite systems is found to be much higher than the polyacrylates due to the formation of a cross-linked structure.

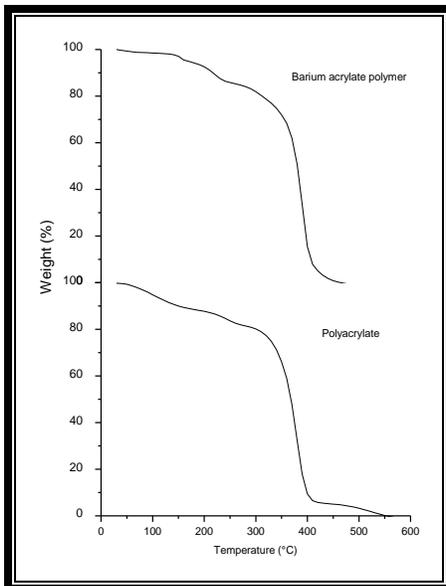


Figure 9: TGA thermograms of polyacrylate and cast polymerized barium acrylate-styrene nanocomposite indicate stability due to addition of barium and formation of nanoparticles of barium.

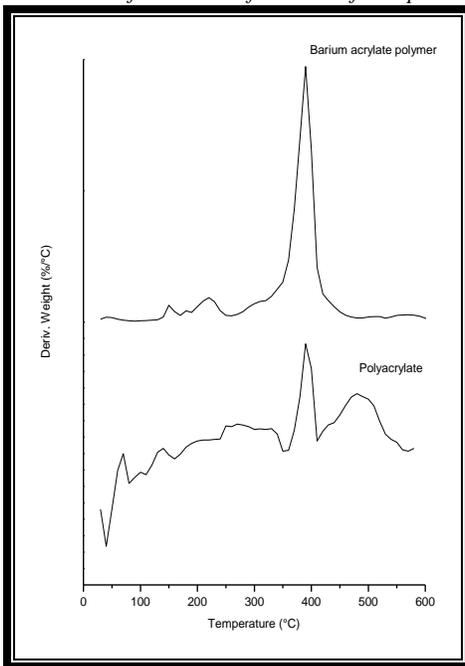


Figure 10: DTG thermograms of acrylic acid-styrene polymer and barium acrylate-styrene nanocomposite indicate stability due to addition of barium and formation of nanoparticles of barium.

Table 7: Weight loss due to thermal decomposition of acrylic acid-styrene polymer and barium acrylate-styrene nanocomposite indicates higher thermal stability of barium acrylate-styrene nanocomposite due to formation of nanoparticles of barium

Product	Weight loss (%)					
	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
Acrylic acid-styrene polymer	5.2	12.3	19.9	90.6	96.7	100
Barium acrylate-styrene nanocomposite	2.7	7.4	18.1	72.0	89.8	93.1

The transmittance of the samples as determined by UV-Visible spectroscopy was found to be 90%. The nanocomposites were found to be impact resistant as per FDA regulations.

The hardness of the lenses was checked by determining the shore-D hardness by Shore-D Durometer and scratch resistance power of the nanocomposite. Shore-D hardness of the nanocomposites was found to be 90. Pencil hardness and scratch resistance of barium acrylate-styrene nanocomposites was found to be higher than PMMA. PMMA has a scratch resistance of “C” grade and a pencil hardness of 4H while barium acrylate-styrene nanocomposites have scratch resistance of “B” and pencil hardness of 6H. Barium acrylate-styrene nanocomposites are superior in hardness to PMMA due to the dispersion of metal atoms.

For barium acrylate-styrene nanocomposites, specific gravity of 1.19 was obtained. The specific gravity of PMMA is 1.26. This suggests that metal-containing nanocomposites are much lighter in weight as compared to the conventional optical material used. This is an achievement where low weight polymers are required especially for high diopter lenses.

The Vicat softening temperature of 120 °C for barium acrylate-styrene nanocomposites indicate that the working temperature of barium acrylate-styrene nanocomposites is much higher than PMMA which has a working temperature of 109 °C. This clearly indicates that barium acrylate-styrene nanocomposites can be used for applications where high temperatures are required.

### 3.2 Preparation of Barium Cinnamate Nanocomposites

#### 3.2.1 Dispersion of barium hydroxide in cinnamic acid

Barium cinnamate was synthesized by the reaction of barium hydroxide and cinnamic acid. The molar ratios of barium hydroxide and cinnamic acid were varied where the synthesis of barium cinnamate was carried out by adding barium hydroxide to cinnamic acid in different molar ratios of barium hydroxide: cinnamic acid i.e. 0.2:2, 0.4:2, 0.6:2, 0.8:2 and 1:2. It was observed that 0.2:2 (Ba/0.2/CA/2) and 0.4:2 (Ba/0.4/CA/2) molar ratios were successful for the preparation of a homogeneous compound while beyond a molar ratio 0.4: 2, phase separation takes place (Table 8).

Table 8: Addition of different amounts of barium hydroxide to cinnamic acid. Addition of upto 0.4 moles of barium hydroxide in 2 moles cinnamic acid led to the formation of homogeneous compound. Beyond 0.4 moles, phase separation takes place

S.No.	Ba (OH) <sub>2</sub> (moles)	Cinnamic acid (moles)	Observations
1.	0.2	2	Homogeneous compound
2.	0.4	2	Homogeneous compound
3.	0.6	2	Phase separation
4.	0.8	2	Phase separation
5.	1.0	2	Phase separation

The reaction between barium hydroxide and cinnamic acid was established by evaluating barium hydroxide-cinnamic acid composition for various parameters such as acid value, barium content (%), structure elucidation and thermal analysis. Barium content and barium oxide content present in the composition was evaluated by ICP-OES and the results are tabulated in Table 9.

Table 9: Results of barium (% by weight) and barium oxide (% by weight) in barium cinnamate. As expected, the percentage content of barium increases with increase in the addition of barium hydroxide.

Sample	Ba (%)	BaO (%)	Acid value
Barium hydroxide octahydrate	45.8	48.6	0
Cinnamic acid	0.0	0.0	368
Ba/0.2/CA/2	6.4	7.42	264
Ba/0.4/CA/2	13.5	15.7	150

It can be seen from Table 9 that with increasing molar ratios of barium hydroxide : cinnamic acid, the amount of barium (%) in the resulting product increases. Similarly, amount of barium oxide in the compositions increases by increasing the percentage of barium hydroxide added from Ba/0.2/CA/2 to Ba/0.4/CA/2. As barium reacts with cinnamic acid, percentage of barium present in the compound increases. Table 9 shows various percentages of barium that has reacted with cinnamic acid. The results show that 13.5 % of barium could be incorporated successfully to form barium hydroxide-cinnamic acid composition as can be seen from Table 9.

To confirm the reaction between cinnamic acid and barium hydroxide, acid value of the product was determined. The results of acid value are tabulated in Table 9. At the initial point of the reaction, acid value of cinnamic acid was determined to be 368. As can be seen from Table 9, acid value decreases to 264 when 0.2 moles of barium hydroxide is added to 2 moles of cinnamic acid. The acid value further decreases to 150 when 0.4 moles of barium hydroxide is added to 2 moles of cinnamic acid. The decrease in acid value is a clue to the reaction taking place between barium hydroxide and cinnamic acid resulting in the formation of barium cinnamate.

The reaction taking place between barium hydroxide and cinnamic acid was further understood by crystallographic studies. X-ray diffraction pattern was studied for barium hydroxide, cinnamic acid and barium hydroxide-cinnamic acid composition from Figure 11.

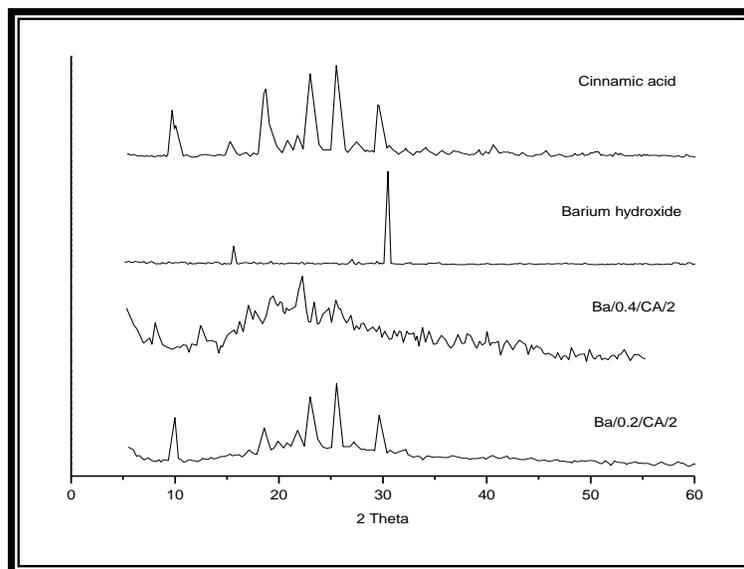


Figure 11: XRD pattern of barium hydroxide, cinnamic acid and barium hydroxide-cinnamic acid. The peaks barium hydroxide and cinnamic acid are absent in the case of higher amount of barium hydroxide indicating complete reaction between barium hydroxide and cinnamic acid

As can be seen from the XRD pattern, the peaks pertaining to cinnamic acid at  $2\theta$  value 9.73, 18.76, 23.00 and 25.4 and barium hydroxide at  $2\theta$  values of 15.6 and 30.4 are completely absent in Ba/0.4/CA/2. This indicates the completion of the reaction between cinnamic acid and barium hydroxide to form a new compound i.e. barium cinnamate. The XRD pattern is also a confirmation of the amorphous nature of barium cinnamate, as no sharp peaks due to crystalline nature is observed.

The thermal stability of barium cinnamate was analyzed by DSC and TGA. The thermograms are presented as Figure 12 for DSC analysis and Figure 13 for TGA analysis

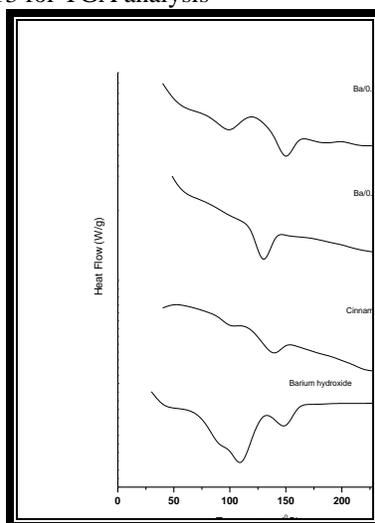


Figure 12: DSC thermograms of barium hydroxide, cinnamic acid and the reaction product barium cinnamate. The endothermic peaks in barium hydroxide are absent in barium cinnamate indicating the reaction to take place between the two starting materials. The endothermic peak due to cinnamic acid is absent in the case where higher content of barium hydroxide is incorporated, indicating the complete reaction of cinnamic acid with barium hydroxide to form barium cinnamate.

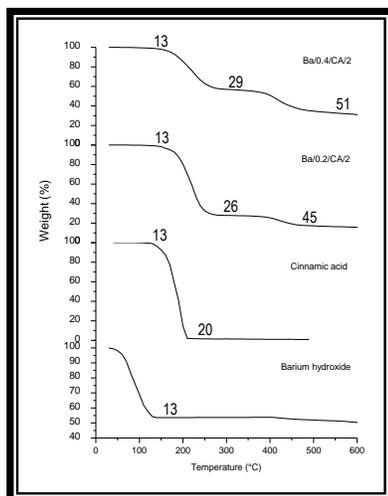


Figure 13: TGA thermogram of barium hydroxide, cinnamic acid and barium cinnamate. The thermograms indicate higher stability of barium cinnamate as compared to cinnamic acid due to the presence of barium in it.

The DSC curve of cinnamic acid shows a sharp endothermic peak at 135.2 °C corresponding to the melting event, characteristic of a pure substance. The onset temperature of the melting peak is 133.5 °C and  $\Delta H$  fusion is 142.7 J/g. The DSC curve of barium hydroxide shows two sharp endothermic peaks at 84.6 °C, corresponding to the melting event and 114.4 °C due to loss of water molecules. The onset temperature of the melting peak is 81.6 °C and  $\Delta H$  fusion is 241.4 J/g.

While, the DSC curve of Ba/0.2/CA/2 shows a sharp endothermic peak at 130.2 °C, ascribed to the melting point of cinnamic acid, the DSC curve of Ba/0.4/CA/2, on the other hand shows a sharp endothermic peak at 98.66 °C, which is ascribed to the loss of moisture. A sharp peak at 153.0°C is ascribed to the melting of the compound. The onset temperature of the melting peak is 147.7 °C and  $\Delta H$  fusion is 18.12J/g. It is evident from the DSC analysis that cinnamic acid is left unreacted in the case of Ba/0.2/CA/2 and complete reaction between barium hydroxide and cinnamic acid takes place at molar ratio 0.4:2 (barium hydroxide:cinnamic acid) to form barium cinnamate.

As can be seen from the table (Table 10), the thermal stability of barium cinnamates lie between that of barium hydroxide and cinnamic acid. Barium cinnamate with more amounts of barium exhibit lower weight loss and hence higher thermal stability as compared to the one having less amount of barium. Weight loss in the case of barium cinnamate takes place very gradually. Initial weight loss upto 100 °C is more in the case of barium hydroxide due to the loss of water of crystallization. This is not present in the case of barium cinnamates as weight loss upto 100 °C is negligible. Also for barium cinnamate which has less amount of barium or more amount of organic cinnamic acid (in the case of Ba/0.2/CA/2), decomposes fast as compared to the other.

The thermograms obtained from TGA analysis clearly indicate the changes in the thermal behavior of barium cinnamate as a result of interactions between barium hydroxide and cinnamic acid.

Table 10: Weight loss (%) due to decomposition of barium hydroxide, cinnamic acid and barium cinnamate

Product	Weight loss (%)					
	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
Barium hydroxide	31.0	46.4	46.3	46.4	48.0	49.7
Cinnamic acid	0	98.3	100	100	100	100
Ba/0.2/CA/2	0.2	19.5	72.1	74.5	82.8	84.2
Ba/0.4/CA/2	0.5	14.5	43	49	65.3	68.9

The thermal stability of barium cinnamates lie between that of barium hydroxide and cinnamic acid. Barium cinnamate with more amount of barium exhibits higher thermal stability as compared to the one having less amount of barium. Weight loss in the case of barium cinnamate takes place very gradually. Initial weight loss upto 100 °C is more in the case of barium hydroxide due to the loss of water of crystallization. The same is not observed in the case of barium cinnamate where weight loss upto 100 °C is negligible. Barium cinnamate which has less amount of barium decomposes faster than the one with more amount of barium, confirming the higher thermal stability of Ba/0.4/CA/12.

### 3.2.2 Cast Polymerization of barium cinnamate compositions

An attempt was made to polymerize barium cinnamate compositions to obtain the optical lenses. The compositions were subjected to various doses of gamma irradiation from 10 kGy to 30 kGy. Visual observations indicated that there is no change in the appearance of the compositions before and after irradiation. Further confirmation was obtained by DSC analysis of the compositions before and after irradiation. The melting point of 152 °C was obtained for both. Thus, this clearly indicates that barium cinnamate as such does not undergo polymerization.

To facilitate the polymerization of barium cinnamate, effect of co-monomer such as styrene on its polymerization was studied. It was observed that barium cinnamate does not form homogeneous composition with styrene at any concentration. Thus, it was not possible to co-polymerize barium cinnamate.

### 3.3 Preparation of barium cinnamate-barium acrylate nanocomposites

#### 3.3.1 Synthesis of barium cinnamate and barium acrylate

Barium cinnamate and barium acrylate were synthesized as described previously in the above sections.

#### 3.3.2 Dispersion of barium cinnamate in barium acrylate

Barium cinnamate was dispersed in barium acrylate (16 %) in different percentages (by weight) to study the effect of incorporation of barium cinnamate on properties of barium acrylate. Transparent and clear compositions were obtained by the dispersion of upto 12% by weight of barium cinnamate in barium acrylate. Beyond 12% by weight, barium cinnamate was found to settle down to the bottom of the composition.

Barium cinnamate-barium acrylate compositions were evaluated for various properties such as refractive index, transmittance, thermal stability, etc.

The results of the effect of dispersion of barium cinnamate on the refractive index of barium acrylate is given in Table 11. As the percentage of barium cinnamate in barium acrylate increases, refractive index increases. A maximum refractive index of 1.457 is obtained in the case of dispersion of 12% by weight of BA/0.2/CA/2 in barium acrylate. On the other hand, a refractive index of 1.464 is obtained by the dispersion of 12% by weight of Ba/0.4/CA/2 in barium acrylate. This shows that there is formation of new bonds between barium cinnamate and barium acrylate taking place which is responsible for the improvement in refractive index of barium acrylate.

Table 11: Effect of dispersion of barium cinnamate on refractive index of barium acrylate. Refractive index increases with increase in the concentration of barium cinnamate in barium acrylate.

S. No.	Barium cinnamate (%)	Refractive index		Transmittance (%)
		Ba/0.2/CA/2	Ba/0.4/CA/2	
1.	0	1.436	1.436	94
2.	2	1.443	1.442	94
3.	4	1.447	1.445	94
4.	6	1.448	1.447	94
5.	8	1.451	1.454	94
6.	10	1.454	1.458	94
7.	12	1.457	1.464	94

Thermal stability of barium cinnamate-barium acrylate compositions was evaluated through TGA analysis. The thermogram is presented in Figure 14.

The thermal stability of the compositions containing barium cinnamate is found to be comparable to barium acrylate indicating that the presence of barium affects the overall stability of the composition. Values of weight loss, both observed and calculated are presented in Table 12.

Table 12: Weight loss of barium cinnamate, barium acrylate and barium cinnamate-barium acrylate composition due to thermal decomposition

Product	Weight loss (%)					
	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
Barium cinnamate (Ba/0.4/CA/2)	0.5	14.5	43	49	65.3	68.9
Barium-acrylate	40.2	66.1	76.7	77.9	82.3	84.4
Barium cinnamate- barium	39.5	70.4	79.1	80.1	85.8	87.4

acrylate composition						
Theoretical loss in weight in Barium cinnamate- barium acrylate composition	35.3	59.9	72.7	74.5	80.2	82.6

**3.3.3 Cast Polymerization of Barium cinnamate-barium acrylate compositions**

Barium cinnamate-barium acrylate compositions were subjected to gamma irradiation for polymerization using styrene as a co-monomer. The effect of addition of amount of styrene and gamma irradiation at doses 10-30 kGy, were studied. The dose of gamma irradiation required for complete polymerization was optimized and the effect of styrene on polymerization was studied by varying percentages of styrene (by weight of barium acrylate-barium cinnamate).

The results of the effect of styrene (percentage by weight of barium cinnamate-barium acrylate) on the polymerization of barium cinnamate-barium acrylate composition by gamma irradiation are presented in Table 13.

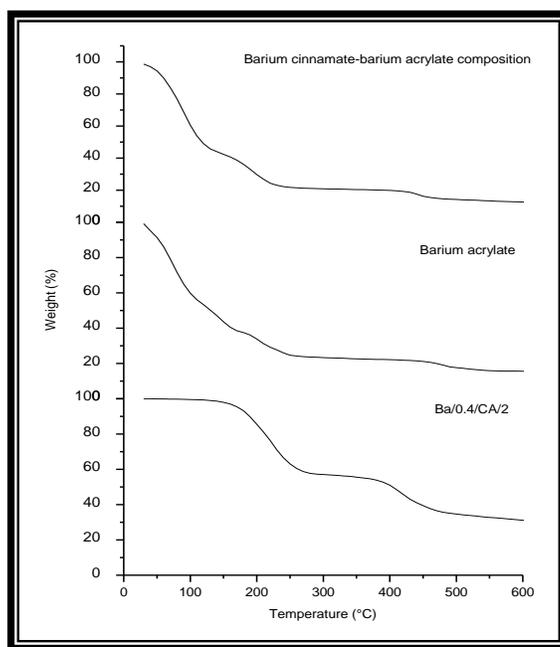


Figure 14: TGA thermograms of barium cinnamate, barium acrylate and barium cinnamate-barium acrylate composition. The thermograms show that the barium cinnamate-barium acrylate composition is stable at high temperatures

Table 13: Effect of styrene on polymerization of barium cinnamate-barium acrylate compositions indicating that 150% (by weight of barium cinnamate-barium acrylate) of styrene is optimum amount required to obtain clear, transparent and hard nanocomposites which are easily released from the mold

S. No.	Styrene (% by weight of barium cinnamate-barium acrylate)	Shore-D Hardness	Transmittance (%)	Appearance, etc.
1.	0	40	*	Foamy and opaque, Brittle
2.	30	*	*	Sticky could not be released
3.	60	*	*	Sticky could not be released
4.	90	*	*	Sticky, could not be

				released
5.	120	90	77	Hazy at the surface, hard
6.	150	90	90	Clear, transparent, easily released

\*: Shore-D hardness and transmittance could not be determined due to the incomplete polymerization of the sample.

As can be seen from Table 13, polymerization with 30% to 90% styrene (by weight of barium cinnamate-barium acrylate), soft, sticky and brittle polymer was obtained due to insufficient amounts of styrene for polymerization. The polymer could not be released from the mold, which limits the processing characteristics of the polymer. At 120% addition of styrene (% by weight of barium acrylate-barium cinnamate), hazy polymer was obtained. Further, at 150% addition of styrene (% by weight of barium acrylate-barium cinnamate), hard, transparent and clear polymers which were easily released from the mold were obtained. This indicates that 150% (by weight) of styrene is sufficient for polymerization of barium cinnamate-barium acrylate compositions.

Polymerization of barium cinnamate-barium acrylate-styrene compositions was carried out at various doses from 10 kGy-30 kGy. Results of polymerization are shown in Table 14. The results of the polymerization vary with the molar ratio of barium cinnamate added i.e. Ba/0.2/CA/2 and Ba/0.4/CA/2.

Table 14: Results of effect of gamma irradiation on the polymerization of barium cinnamate-barium acrylate nanocomposites. The styrene content for all the cases is kept at 150% (by weight of barium cinnamate-barium acrylate compositions)

Dose	Barium Cinnamate				
	Ba/0.2/CA/2			Ba/0.4/CA/2	
	2%	4%, 6%, 8%	10%, 12%	2%	4%, 6%, 8%, 10%, 12%
10	Viscous Liquid	Viscous Liquid	Viscous Liquid	Viscous liquid	Viscous liquid
15	Foamy	Foamy	Foamy	Sticky	Sticky
20	Foamy	Transp., clear	Foamy	Foamy	Transp., clear and hard
25	Foamy	Transp., clear	Foamy	Foamy	Transp., clear and hard
30	Foamy	Transp., clear	Foamy	Foamy	Transp., clear and hard

As seen from the results in Table 14, it is clear that compositions at 10-15 kGy doses are viscous liquid to sticky in nature. Beyond 15 kGy, transparent, hard and clear nanocomposites are obtained for compositions containing 4-8% Ba/0.2/CA/2 while in the case of Ba/0.4/CA/2 maximum percentage of barium cinnamate that could be dispersed in barium acrylate is 12%. This clearly indicates that with varying percentages of barium, different interactions take place resulting in the nanocomposite.

Refractive index and Abbe number of the nanocomposites were determined on the Abbe refractometer. The results are tabulated in Table 15.

Table 15: Refractive index and Abbe number of barium-cinnamate-barium acrylate nanocomposites

S. No.	Barium Cinnamate (%)	Refractive index		Abbe number	
		Ba/0.2/CA/2	Ba/0.4/CA/2	Ba/0.2/CA/2	Ba/0.4/CA/2
1.	0	1.5681	31	1.5681	31
2.	2	N.D	N.D	N.D	N.D
3.	4	1.5655	33.4	N.D	N.D
4.	6	1.5608	34.6	1.5538	31.5
5.	8	1.5623	32.8	1.5669	34.6
6.	10	N.D	N.D	1.5641	32.3
7.	12	N.D	N.D	1.5629	31.0

N.D: Not determined

As can be seen from Table 15, addition of barium cinnamate to barium acrylate does not bring much change in the optical properties of the final complex nanocomposite. The refractive index of barium cinnamate-barium acrylate nanocomposites lie in the range of 1.5538-1.5669 and Abbe number in the range of 31-35.

It is clearly visible from Table 16 that barium cinnamate-barium acrylate-styrene nanocomposite is thermally stable as compared to polyacrylate as such. This is due to the fact that the presence of barium in the nanocomposite builds a strong network resulting in high thermal stability of the final product.

Table 16: Weight loss due to thermal decomposition of acrylic acid-styrene polymer and barium cinnamate-acrylate-styrene nanocomposite

Product	Weight loss (%)					
	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
Acrylic acid-styrene polymer	5.2	12.3	19.9	90.6	96.7	100
Barium cinnamate barium-acrylate-styrene nanocomposite	1.5	1.4	15.1	73.3	90.1	94.4

The transmittance of the samples as determined by UV-Visible spectroscopy was found to be 90%. The lenses were found to be impact resistant as per FDA regulations.

Machinability of the nanocomposites was checked by subjecting the samples to grinding. No odour was observed during the machining and the samples were easily machined into various shapes. The hardness of the lenses was checked by determining the shore-D hardness and scratch resistance. Shore-D hardness of the nanocomposites was found to be 94. In the case of barium cinnamate-barium acrylate-styrene nanocomposite, specific gravity of 1.19 was obtained. This would help in designing of light-weight optical devices.

The Vicat softening temperature of 123 °C for barium cinnamate-barium acrylate-styrene nanocomposite indicates that the working temperature is much higher than PMMA which has a working temperature of 109 °C. This brings scope for the barium nanocomposites to be used in extreme conditions.

### 3.4 Preparation of cinnamic acid-acrylic acid polymers

#### 3.4.1 Synthesis of cinnamic acid-acrylic acid composition

Synthesis of cinnamic acid-acrylic acid composition was done by gradual addition of cinnamic acid to acrylic acid in a round bottom flask at ambient temperature. Cinnamic acid was added to acrylic acid in varying percentages under vigorous stirring. The observations related to the dispersion of cinnamic acid to acrylic acid are tabulated in Table 17. For understanding the changes taking place during the reaction of acrylic acid and cinnamic acid, cinnamic acid-acrylic acid compositions were evaluated for refractive index.

Table 17: Effect of dispersion of cinnamic acid on clarity and refractive index of acrylic acid. Cinnamic acid is soluble upto a concentration of 13% (by weight). Beyond 13%, cinnamic acid could not be dispersed in acrylic acid. Maximum refractive index achieved by the dispersion of cinnamic acid in acrylic acid is 1.448.

S. No.	Cinnamic acid (%)	Observations	Refractive index
1.	0	Transparent, clear solution	1.424
2.	2	Transparent, clear solution	1.431
3.	4	Transparent, clear solution	1.435
4.	6	Transparent, clear solution	1.438
5.	8	Transparent, clear solution	1.441
6.	10	Transparent, clear solution	1.442
7.	12	Transparent, clear solution	1.445
8.	13	Transparent, clear solution	1.448
9.	14	Could not be dispersed	*

\*: Refractive index could not be determined as cinnamic acid was not homogeneously dispersed

It was being observed that upto 13% (by weight) addition of cinnamic acid to acrylic acid resulted in clear and transparent solutions. Beyond 13%, cinnamic acid could not be dispersed in acrylic acid. It can be seen from the results presented in Table 17 that the addition of cinnamic acid to acrylic acid brings an improvement in the refractive index of acrylic acid. The refractive index of acrylic acid increases from 1.424 to 1.448 by the dispersion of 13% (by weight) of cinnamic acid to acrylic acid. Here, it may be noted that the aromatic ring of cinnamic acid which is characterized by a high intrinsic molar refraction (26.14) is responsible for bringing an improvement in the refractive index of acrylic acid.

Acid value of cinnamic acid-acrylic acid compositions was determined and is presented in Table 18.

Table 18: Acid value of cinnamic acid-acrylic acid compositions indicate that the acid value do not change significantly due to acidic character of both the components

S. No.	Cinnamic acid (%)	Acid value
1.	0	626
2.	2	616

3.	4	608
4.	6	596
5.	8	582
6.	10	575
7.	12	568
8.	13	560

As can be seen from Table 18, there is a decrease in the acid value of acrylic acid as cinnamic acid is added to it. Acrylic acid has an acid value of 626. Cinnamic acid being acidic possess an acid value of 368. On addition of 2% cinnamic acid to acrylic acid, the acid value of acrylic acid decreases to 616, 608 with 4% addition of cinnamic acid, 596 with 6% addition, 582 with 8% addition of cinnamic acid, 575 with 10% addition, 568 with 12% addition and 560 with 13% addition of cinnamic acid to acrylic acid. It is clear that the acid value does not change much as both the components are acidic in nature.

The results of weight loss due to thermal decomposition of acrylic acid, cinnamic acid and cinnamic acid-acrylic acid compositions are given in Table 19.

Table 19: Weight loss due to thermal decomposition of acrylic acid, cinnamic acid and cinnamic acid-acrylic acid composition

Product	Weight loss (%)					
	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
Acrylic acid	52.2	98.2	100	100	100	100
Cinnamic acid	0	98.5	100	100	100	100
Cinnamic acid- acrylic acid composition	61.2	100	100	100	100	100
Theoretical loss in weight of Cinnamic acid- acrylic acid composition	45.4	98.2	100	100	100	100

As can be seen from Table 19, the thermal decomposition behaviour of cinnamic acid-acrylic acid composition is similar to the individual raw materials used to prepare it. The weight loss (%) is on the same lines as expected and calculated theoretically.

### 3.4.2 Cast Polymerization of cinnamic acid-acrylic acid compositions

Cinnamic acid-acrylic acid compositions were subjected to different doses of gamma irradiation for polymerization. Styrene was used as a co-monomer for polymerization. The effect of addition of styrene and gamma irradiation dose on polymerization of acrylic acid-cinnamic acid compositions was studied. The polymers were evaluated for various properties based on which optimization of process parameters was carried out.

The effect of amount of styrene (% by weight of cinnamic acid-acrylic acid composition) on the polymerization of cinnamic acid-acrylic acid composition by gamma irradiation was studied and the results are presented in Table 20.

Table 20: Effect of styrene on polymerization indicating that 150% of styrene (by weight of cinnamic acid-acrylic acid composition) is sufficient to obtain clear, transparent and hard polymers which are easily released from mold

S. No.	Styrene	Shore-D	Transmittance	Appearance, etc.
1.	0	*	*	Foamy and opaque, Brittle
2.	30	*	*	Sticky could not be released
3.	60	*	*	Sticky could not be released
4.	90	*	*	Sticky, could not be released
5.	120	92	71	Hazy at the surface, hard

6.	150	94	90	Clear, transparent, easily released
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\*: Shore-D hardness and Transmittance could not be determined due to foamy or sticky nature of the polymers

From the results presented in Table 20, it may be seen that polymerization of cinnamic acid-acrylic acid composition by gamma irradiation results in foamy and brittle polymer in the absence of styrene (Figure 35a). In the presence of styrene, clear, transparent and hard polymers suitable for optical applications were obtained (Figure 35b). With the addition of 30%-90% (by weight of cinnamic acid-acrylic acid composition) of styrene, soft and sticky polymers were obtained due to insufficient amounts of styrene. The polymer, being soft and sticky could not be released from the molds, which limits the processing characteristics of the polymer. With 120% addition of styrene (by weight of cinnamic acid-acrylic acid composition), hazy polymer is obtained. With 150% (by weight of cinnamic acid-acrylic acid composition) of styrene, the shore-D hardness increased to 94 and the polymers were easily released from the mold. Transmittance was maximum for 150% (by weight of cinnamic acid-acrylic acid composition) of styrene used. Clear and transparent polymers were obtained.

Thermal analysis of cinnamic acid-acrylic acid polymers was studied by TGA. The TGA studies of the cinnamic acid-acrylic acid-styrene polymer indicate the formation of a highly cross-linked, thermally stable structure as can be seen from Figures 15.

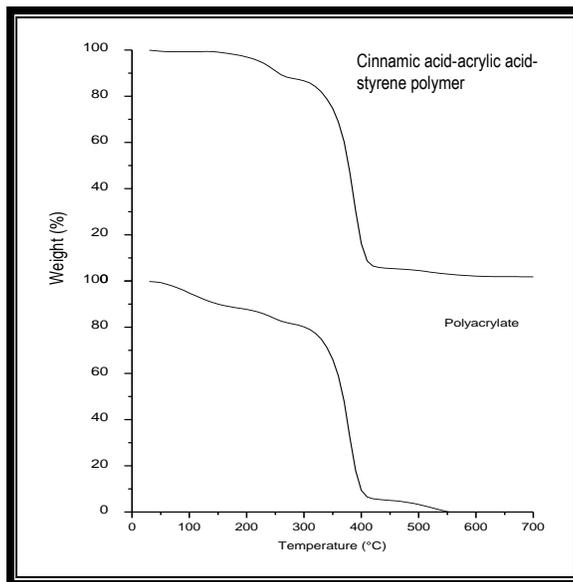


Figure 15: TGA thermograms of cinnamic acid-acrylic acid-styrene polymer indicates higher thermal stability than the polyacrylate

The results of the effect of dose from 10 kGy to 30 kGy of gamma irradiation on the polymerization of cinnamic acid-acrylic acid -styrene compositions are presented in Table 21.

As seen from the results in Table 21, cinnamic acid-acrylic acid-styrene compositions when subjected to a dose of 10 kGy gave a viscous liquid. Dose of 15 kGy gave a sticky polymer which was very soft and difficult to process. A dose of 20 kGy and higher led to transparent and hard polymers with a shore-D hardness of 94. It can be seen that the dose of radiation does not affect the shore-D hardness of samples beyond 20 kGy. The suitable dose for polymerization by gamma irradiation was optimized as 20 kGy for cinnamic acid-acrylic acid-styrene polymers. Refractive index and Abbe number of the polymers were determined on the Abbe refractometer. The results are tabulated in Table 22.

Table 21: Effect of gamma irradiation on the polymerization of cinnamic acid-acrylic acid polymers. 20 kGy was found to be the optimum dose for cinnamic acid-acrylic acid polymer

S.No.	Dose (kGy)	Shore-D Hardness	Cross-link density (%)	Appearance
1	10	*	*	Viscous liquid
2	15	*	84	Transparent, sticky at the surface
3	20	94	95	Transparent, hard and easily released
4	25	94	95	Transparent, hard and easily released
5	30	94	96	Transparent, hard and easily released

\*: Shore-D hardness and cross-link density of the polymers could not be determined due to viscous liquid sticky nature of the polymer

Table 22: Refractive index and Abbe number of cinnamic acid- acrylic acid polymers show that the refractive index of acrylic acid increases as content of cinnamic acid is increased

S.No	Cinnamic acid (% by wt)	Cinnamic acid-acrylic acid polymers	
		Refractive index	Abbe number
1.	0	1.5336	32
2.	2	1.5352	32
3.	4	1.5492	31
4.	6	1.5528	33
5.	8	1.5536	32
6.	10	1.5530	32
7.	12	1.5589	32
8.	13	1.5624	32

As can be seen from Table 22, maximum refractive index of 1.5624 was obtained with 13% (by weight) dispersion of cinnamic acid in polymer with Abbe number of 32. It is found to be better than commercially available polyacrylates i.e. polymethyl methacrylate, a commercial grade of acrylate polymer for various optical applications, which has a refractive index of 1.491.

The weight loss of the polymers was recorded at various temperatures, which is given in Table 23. The heat stability of the polymer system is found to be much higher than that of the acrylic acid-styrene polymer, which is possible only due to the formation of a cross-linked structure.

Table 23: Weight loss due to thermal decomposition of acrylic acid-styrene polymer and cinnamic acid-acrylic acid polymer

Product	Weight loss (%)					
	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
Acrylic acid-styrene polymer	5.2	12.3	19.9	90.6	96.7	100
Acrylic acid-cinnamic acid-styrene polymer	1.2	6.4	16.1	76.4	91.4	95.4

The transmittance of the samples as determined by UV-Visible spectroscopy was found to be 90%. The polymers were found to be impact resistant as per FDA regulations.

Machinability was checked by subjecting the samples to grinding and machining. It was observed that the polymers possessed good machinability characteristics. The hardness of the polymers was checked by determining the shore-D hardness using a shore-D Durometer and scratch resistance. Shore-D hardness of the polymers was found to be 94 for acrylic acid-cinnamic acid polymer. Pencil hardness and scratch resistance of acrylic acid-cinnamic acid polymers was found to be better than PMMA. PMMA has a scratch resistance of grade "C" and a pencil hardness of

4H while cinnamic acid-acrylic acid-styrene polymer have scratch resistance of grade “B” and pencil hardness of 6H. Acrylic acid-cinnamic acid polymer is superior in hardness to PMMA.

In the case of cinnamic acid-acrylic acid-styrene polymer, specific gravity of 1.16 was obtained. The specific gravity of PMMA is 1.26. This indicates that the cinnamic acid-acrylic acid-styrene polymers prepared by gamma irradiation are much lighter as compared to the conventional polymer system.

The Vicat softening temperature of 100 °C for cinnamic acid-acrylic acid polymer indicate that the working temperature of cinnamic acid-acrylic acid polymer is much lower than PMMA which has a working temperature of 109 °C.

#### 4. CONCLUSIONS

In this paper, novel nanocomposites based on acrylates and cinnamates of barium metal have been prepared. The achievements of the present study lies in the modification of an important monomer, acrylic acid, for optical applications, in a novel and cost-effective manner. Three methodologies have been adopted to prepare barium-containing nanocomposites using acrylic acid and cinnamic acid. Barium hydroxide was found to be the most suitable compound for dispersion in acrylic acid.

1. The preparation of barium acrylate nanocomposites resulted in an increase in refractive index from 1.42 to 1.57 and Abbe number from 28 to 31. The optical properties can be tailor-made by varying the content of the metal salt.

The physico-mechanical properties such as specific gravity, hardness, machinability, etc were found to be better than the properties of conventional available polymers.

2. The second approach followed for the preparation of barium-containing nanocomposites pertains to the dispersion of barium in cinnamic acid. A detailed study of the properties of barium cinnamate, an aspect never investigated before has been done successfully. Barium was incorporated upto an extent of 14% to prepare barium cinnamate.

An attempt to polymerize barium cinnamate was carried out. It was observed that barium cinnamate does not get polymerized as such.

3. Third novel approach for preparation of barium-containing nanocomposites was followed by the dispersion of barium cinnamate in barium acrylate. Barium cinnamate-barium acrylate nanocomposites were synthesized using gamma irradiation technology exhibiting better physico-mechanical, thermal and optical properties such as refractive index (found to lie between 1.55 and 1.57) and Abbe number (lies between 31 and 35) than the conventional optical materials used.

The properties obtained while designing barium-containing nanocomposites are given in Table 24. Properties of the conventional available materials are also listed which shows that incorporation of barium leads to an improvement in the properties and thus, overall performance of the optical polymers.

Table 24: Properties of barium containing acrylic nanocomposites which show improved performance as compared to the conventionally available optical materials

S. No.	Property	Barium acrylate-styrene nanocomposite	Barium cinnamate-barium acrylate styrene nanocomposite	cinnamic acid - Acrylic acid styrene polymer	CR-39	PMMA	PTU
1.	Machinability	Good	Good	Good	Good	Good	Good
2.	Specific gravity	1.19	1.19	1.16	1.26	1.26	1.36
3.	Shore-D hardness	90	94	94	87	85	75
4.	Pencil hardness	6H	6H	6H	4H	4H	6H
5.	Vicat softening (°C)	120	123	129	100	109	100
6.	Scratch	B	B	B	C	C	B

	resistance						
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Through these studies, the process technology for making barium acrylate nanocomposites employing in-situ synthesis and dispersion of nanoparticles has been developed. The technology developed for the preparation of barium acrylate nanocomposites for making optical plastics of high refractive index are materials having a high potential for commercialization. The present work has great relevance for the growth of optical plastics industry in India as much as for the society looking for an indigenous product with an affordable cost.

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