Optical Properties of Modified Epoxy Resin with Various Oxime Derivatives in the UV-ViS Spectral Region

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ABSTRACT: Optical absorbance measurements have been performed on the epoxy resin and the composites prepared by its modification with two different oxime derivatives (benzaldoxime and 2-furaldoxime) in the wavelength interval of 190–680 nm by unpolarized light. Using the experimental absorbance data, dielectric constant and refractive index dispersion have been determined by means of standard oscillator fit procedure. Moreover, based on the dispersion analysis, direct and indirect band gap energies of the samples have been calculated. It is found that direct band energy for epoxy is nearly 3.49 eV, while its value for the oxime derivatives has been increased up to the 4.15 eV. Another important result to be pointed out is that the absorbance for the 2-furaldoxime doped resin has been greatly increased in a respectively, narrow interval ($\sim$ 30 nm wide) in the UV region, while in the case for the benzaldoxime doped sample, a decreasing has been observed in the absorbance at the same region. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1490–1495, 2011

Key words: resin; optical properties; refractive index; UV-VIS spectroscopy

INTRODUCTION

Epoxy resin and its composites have many distinctive mechanical, electrical and optical properties. Because of their remarkable resistivities to water, acidic media, and alkalides, and also their strong bonding abilities to various materials, they have a wide range of application area extending from optoelectronics to the space technology.[1] The thermal stability of pure resin is relatively low and therefore it has to be improved. In practice this is achieved by using various modifiers. Because of their strong adhesive properties, several modifiers can be easily doped to the resin, including a variety of materials changing from metal particles[2] to glass.[3] Use of these various dopant materials allows preparation of various epoxy composites suitable for many different applications while enhancing the thermal stability of the resin. It is possible to produce many different epoxy-composites having greatly distinguished electrical and optical properties by doping it with various materials. The average refractive index of the conventional epoxy resin lies in the range of 1.50–1.56, but using different modifiers, resins with higher refractive index can be produced.[4,5] These epoxy-composites with improved optical properties have been widely used in manufacturing of various optical devices such as lenses and optical fibers.[6–9]

Optical studies performed on the epoxy have attracted a great attention because of the technological demands arising in the design and fabrication of optical devices. Spectroscopic properties of epoxy-based composites have been widely investigated.[10–15] Epoxy resin and the composites prepared from it are very sensitive to UV light due to the atom groups forming the chemical structure of materials. In this study, we investigated the optical properties of pure epoxy resin and the composites prepared by its modification with oxime derivatives in the UV-VIS region. For this purpose, first, we have measured the absorption spectra of samples and then determined the real and imaginary parts of dielectric constant of the sample and also refractive index by means of standard oscillator fit procedure. Finally, on the basis of the dispersion analysis, we calculated direct and indirect band energies of the samples.

EXPERIMENTAL

Materials

Triethylene tetramine (TETA) was purchased from Merck (Darmstadt, Germany). The epoxy resin used in this study was pure bisphenol A- diglycidyl ether (DGEBA) with an epoxy group percentage of 18.65 as
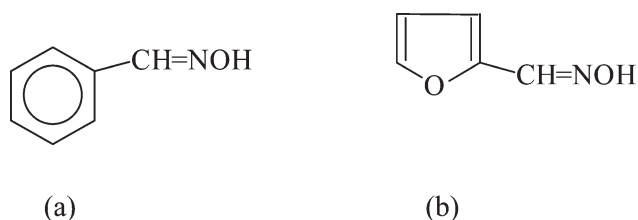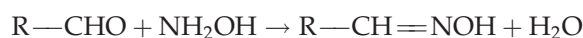
Figure 1 Synthesized aldoximes. (a) benzaldoxime (S_1), (b) furaldoxime (S_2).

measured by acid titration and was supplied by Chemical Factory Sumgait (Azerbaijan). We have carried out optical absorbance measurements on the pure epoxy resin (ER) and two different epoxy derivatives labeled by S_1 (benzaldoxime) and S_2 (2-furaldoxime) in the wavelength range of 190–700 nm using a Jasco Model V-570 type UV/VIS/NIR spectrophotometer.

Synthesis of aldoximes

Furyl (2-furaldoxime) and aryl (benzaldoxime) aldoximes were prepared by the reaction of hydroxylamine with aldehydes. To a vigorously stirred $1M$ solution of aldehyde in toluene an equal volume of $2M$ hydroxylamine solution was added at 0°C. Hydroxylamine solution was adjusted to pH 7.0 with NaOH before mixing. After 2 h, the reaction product was extracted into toluene, dried over anhydrous Na_2SO_4, and evaporated in vacuum. The reaction scheme of synthesis of the aldoximes is:

$$R\!-\!CHO + NH_2OH \rightarrow R\!-\!CH\!=\!NOH + H_2O$$

Syntesized aldoxsimes have been shown in Figure 1.

Determination of epoxy group

To determine the percentage of the epoxy groups in DGEBA (Fig. 2), the epoxy group in the sample was cleaved with an excess of HCl and then the remaining HCl was back titrated with $0.1N$ KOH.[16]

Modification of epoxide resin

Aldoximes were used as modifier. As hardener agent, TETA was employed. The reactant compositions were mixed in a 85 : 15 wt % ratio of epoxy resin to each aldoxime at room temperature and 10.0 wt % of TETA was added. The mixture was stirred until a homogeneous solution is obtained, then it was poured into steel molds and was cured first at 80°C for 2 h, then at 100°C for 1 h, and finally at 120°C for 1 h. The composite samples were shaped into discs of 14.5 mm ($\pm$%1 mm) diameter and 1 mm ($\pm$%1 mm) thickness.

RESULTS AND DISCUSSIONS

The absorption spectra of the three samples were plotted in Figure 3. The absorbance values for S_2 sample have been found to be extremely large in comparison to the other samples. Also, it is important to notice that, the spectra corresponding to the epoxy and S_2 have maxima approximately at the same wavelength of 280 nm. Considering the general behavior of the absorbance spectra, it is clearly seen that, apart from a wavelength interval of 240–300 nm, all three spectra show nearly similar smooth structure.

It is well known that benzene has a characteristic absorption band at 256 nm, resulting from the π - π^* transitions.[17] This absorption peak has been clearly seen in the UV spectrum of S_1 sample in the figure. On the other hand, 2-furaldoxime has double C=N bonds, and therefore a strong absorption peak has been observed nearly at 280 nm due to n - π^* transitions in the UV absorption spectrum of S_2. This value is quite close to the result given by Fakhfakh et al.[18] for furfural, as 274 nm.

The absorption coefficient α for a sample can be determined from the absorbance spectra by means of the following formula:

$$\alpha = 2.303 \, A/d \qquad (1)$$

where A is absorbance and d is thickness of the sample. In Figure 4, we have plotted the variation of absorption coefficient α with the photon energy for pure epoxy resin and also for two different composites S_1 and S_2. On the other hand, the extinction coefficient k is related to the absorption coefficient by the following well-known expression:

$$k = \alpha\lambda/4\pi \qquad (2)$$

In this study, we have performed firstly an oscillator fit procedure to determine the refractive index and dielectric constant. For this purpose, we have
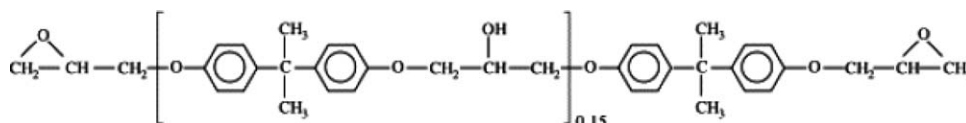

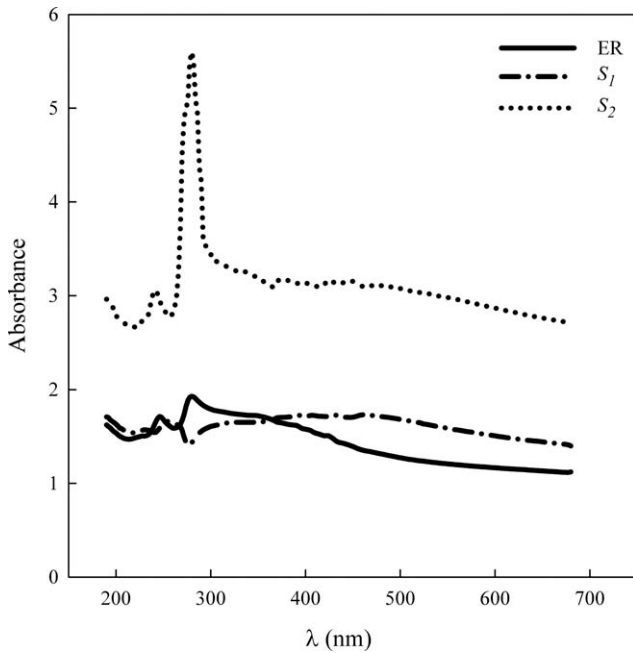**Figure 2** Chemical structure of DGEBA.

Figure 3 The optical absorption spectra of pure epoxy resin (ER) and two composites (S_1 and S_2).

considered the following expressions for the refractive index n and extinction coefficient k:

$$k(\omega) = \frac{\varepsilon''(\omega)}{\sqrt{2\varepsilon'(\omega) + 2\sqrt{\varepsilon'^2(\omega) + \varepsilon''^2(\omega)}}} \quad (3)$$

$$n(\omega) = \frac{1}{2}\sqrt{2\varepsilon'(\omega) + 2\sqrt{\varepsilon'^2(\omega) + \varepsilon''^2(\omega)}} \quad (4)$$

where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are real and imaginary parts of the dielectric constant, respectively.

In the spectral range involving the lattice vibrations, the complex dielectric constant of a solid is represented as a sum of classical oscillators such as:

$$\tilde{\varepsilon}(\omega) = \varepsilon_\infty + \sum_{i=1}^{N}\left(\frac{S_i}{1 - (\omega^2/\omega_i^2) - iF_i(\omega/\omega_i)}\right) \quad (5)$$

where S_i, ω_i and F_i are oscillator strength, oscillator frequency, and bandwidth of the i_{th} oscillator respectively,.[19] ε_∞ is the contribution to the dielectric constant due to high frequencies, especially from electronic transitions, and is called the "high frequency dielectric constant."

Thus, the real and imaginary parts of the complex dielectric constant can be given, respectively, by:

$$\varepsilon'(\omega) = n^2(\omega) - k^2(\omega)$$
$$= \varepsilon_\infty + \sum_{i=1}^{N}\left(\frac{S_i(1 - (\omega^2/\omega_i^2))}{(1 - (\omega^2/\omega_i^2))^2 + F_i^2(\omega/\omega_i)^2}\right) \quad (6)$$

$$\varepsilon''(\omega) = 2n(\omega)k(\omega)$$
$$= \sum_{i=1}^{N}\left(\frac{S_iF_i\omega/\omega_i}{(1 - (\omega^2/\omega_i^2))^2 + F_i^2(\omega/\omega_i)^2}\right) \quad (7)$$

If these equations are substituted into eq. (3), an analytical expression can be obtained for the extinction coefficient k in terms of the oscillator parameters. Next, this equation can be used in the fitting procedure of k data obtained from the experimental results by eq. (2). In Table I, the values of oscillator parameters, which is obtained by the fitting procedure, have been given for epoxy and its composites. After oscillator parameters have been determined, these parameters in turn can be used to calculate the real and imaginary parts of dielectric constant by eqs. (6) and (7), and hence the refractive index n by eq. (4). The variations of the real and imaginary part of dielectric constant so obtained with the wavelenght are plotted in Figure 5. As shown by this figure, there is a decreasing trend in the $\varepsilon''(\omega)$ spectrum with wavelength in the whole measurement range, except a narrow wave length interval between $\sim$ 239–296 nm. In this narrow region, all graphs show stronger structures. The curves for ER and S_2 demonstrate a peak, while the curve for S_1 shows a dip approximately at the 276 nm. This dip in $\varepsilon''(\omega)$ spectrum for S_1 corresponds to the significant decreasing of absorbance of this sample in this wavelength region, as seen from Figure 3. On the other hand, S_2 sample shows a sharp peak at 280 nm.

The refractive index n values obtained from the oscillator fit procedure for samples have not been plotted, since the variation of n with energy show
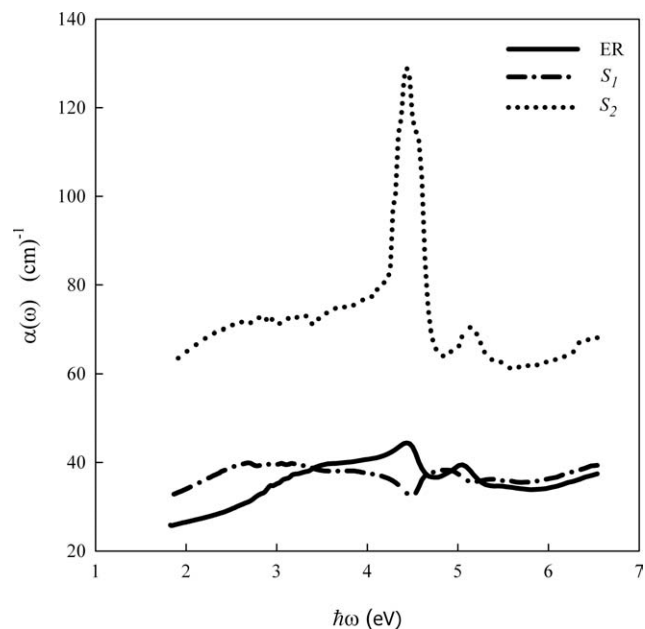

Figure 4 The variation of absorbtion coefficient α with photon energy $\hbar\omega$ for pure epoxy resin (ER) and two composites (S_1 and S_2).

TABLE I
Values of Oscillator Fitting Parameters for Pure Epoxy
and Two Composites

	ER	S_1	S_2
ε_∞	2,3716	2,4964	2,3593
S1	2,126e-4	4,508e-4	6,901e-4
S2	4,804e-6	7,976e-7	9,302e-7
S3	3,123e-4	4,808e-5	3,565e-5
S4	2,732e-6	4,258e-6	4,233e-5
S5	3,348e-6	3,679e-6	3,534e-5
S6	4,433e-5	7,491e-5	2,672e-4
S7	4,664e-6	1,682e-5	4,328e-6
S8	7,156e-2	1,401e-1	9,780e-2
S9	1,751e-7	3,513e-7	4,513e-7
w1	1,4581	1,7781	1,72231
w2	3,1035	4,6850	7,932e-7
w3	2,7562	3,2991	4,4381
w4	4,4531	5,3692	3,8980
w5	5,0480	4,8921	3,3613
w6	3,6821	2,6142	2,6513
w7	4,2470	4,0025	5,1474
w8	156,14	468,50	288,81
w9	5,5713	4,2502	6,5703
F1	1,0722	1,0071	0,90541
F2	0,2255	0,0315	51,0431
F3	1,5241	0,3874	0,07121
F4	0,0546	0,1542	0,26700
F5	0,0777	0,0780	0,36571
F6	0,4616	0,4913	0,66251
F7	0,1361	0,2433	0,06306
F8	0,0432	0,0870	0,13117
F9	0,0919	0,0419	0,02193

very small dispersion and remain nearly constant in the whole energy range. Therefore, we have calculated average values for the refractive indices of the samples and listed in Table II. On the other hand, the extinction coefficient k values for the samples have been found to be very small (on the order of 10^{-4}). Thus, the real part of the dielectric constant will show very similar behavior to the refractive index, as can be foreseen from eq. (6).

It is very important to determine the absorption edge in the understanding of optical properties of the materials. By inspection of the absorption edge, valuable information can be obtained about the absorption mechanisms occurring within the materials and also about the direct and indirect band energies. The position of the absorption edge can be determined by extrapolating the linear part of the absorption coefficient versus photon energy graph on to the energy axis.

As well known, the direct band energy E_{gd} of a sample is related to the absorption coefficient by:

$$\alpha\hbar\omega = C(\hbar\omega - E_{gd})^{1/2} \quad (8)$$

where $\hbar\omega$ is the incident photon energy and C is a constant depending on the sample. If a plot of $(\alpha\omega)^2$ versus photon energy $\hbar\omega$ is plotted, a linear region is obtained. The interception of the extrapolation of this linear part to the energy axis gives E_{gd} direct

band energy. In Figure 6, we have plotted $(\alpha\hbar\omega)^2$ versus photon energy for three samples. In figure, upper insert belongs to the sample S_1 and the lower insert to S_2. For only visual reasons, the axes of figures have been chosen to represent only the vicinity of linear part, but the extrapolation procedure has been performed using the whole scale. Similarly, if indirect transitions were present in the material, the indirect band energy E_{gid} of the sample can be given in terms of absorption coefficient as:

$$\alpha\hbar\omega = A(\hbar\omega - E_{gid} + E_p)^2 + B(\hbar\omega - E_{gid} - E_p)^2 \quad (9)$$
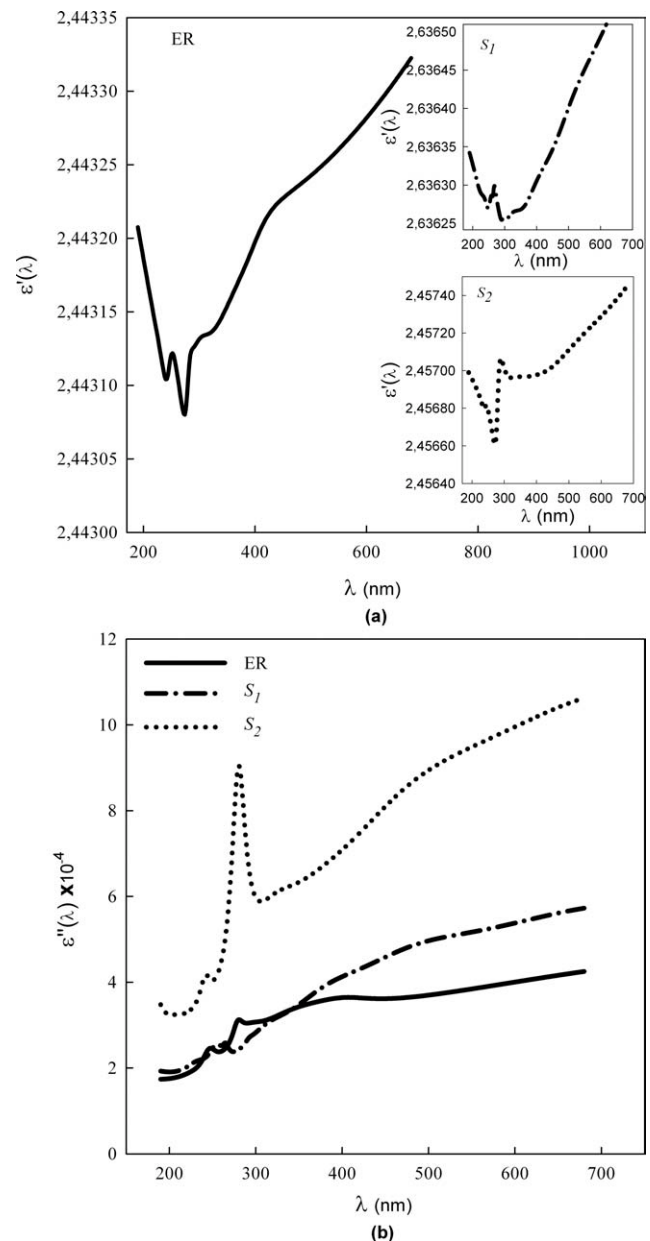

Figure 5 The variation of real part (a) and imaginary part (b) of the dielectric constant with the wavelength for pure epoxy resin (ER) and two composites (S_1 and S_2).

TABLE II
Refractive Indices, Absorption Edges, Direct and Indirect Band Energies and Fitting Parameters For the Pure Epoxy and Two Composites

Sample	n	Absorption edge (eV)	E_{gd} (eV)	E_{gid} (eV)	A_1	a_2 (nm)^2
ER	1,563	3,06	3,45	2,91	0,693	4,483
S_1	1,581	3,53	4,30	3,09	0,611	2,552
S_2	1,567	3,93	4,13	3,62	0,686	7,478

where A and B are again constants depending on the band structure of the material, Ep is the energy of phonon involved in the relevant electronic transitions. Similarly, the graph of $(\alpha\hbar\omega)^{1/2}$ versus photon energy $\hbar\omega$ gives us a linear part as shown in Figure 7, and by extrapolation of this linear curve on to the energy axis yields the indirect band energy E_{gid}.

In Table II, we have listed the absorption edge, direct and indirect band energies of the samples determined as mentioned just above. As seen from table, the absorption edge of epoxy is at a lower energy than those of derivatives. Hence, the direct and indirect band energies of derivatives are found to be larger than that of epoxy resin. On the other hand, the single-term *Sellmeier* dispersion formula,
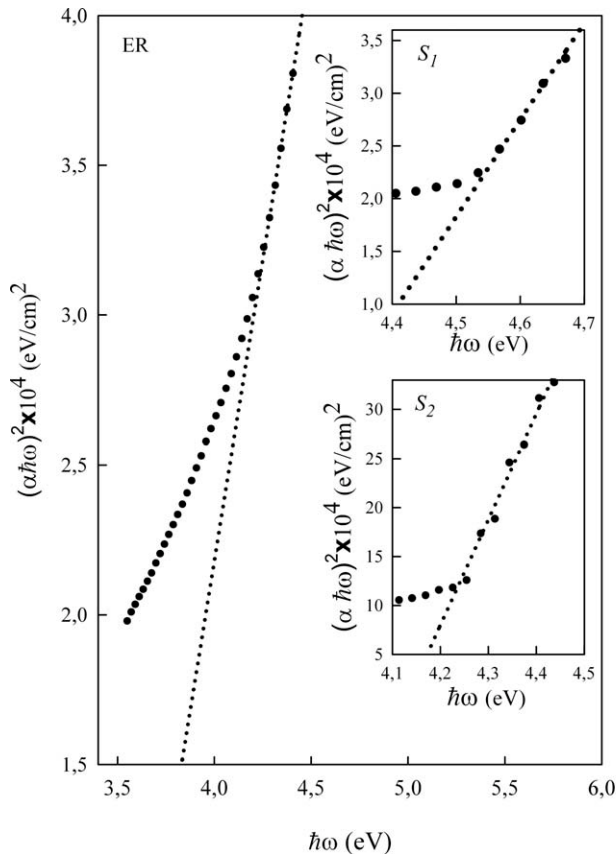

Figure 7 Variation of $(\alpha\hbar\omega)^{1/2}$ with photon energy $\hbar\omega$ for pure epoxy resin and two composites solid circles are measured points and the dotted lines are obtained from fitting.
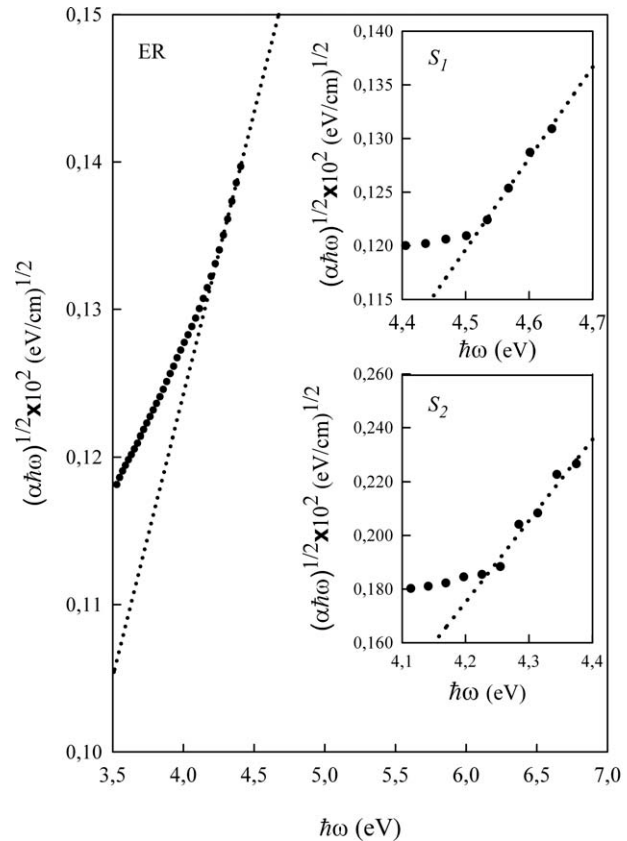
having only two fitting parameters of a_1 and a_2, can be used to represent the refractive index spectrum in the UV region such as:

$$\frac{1}{n^2(\lambda) - 1} = a_1 - \frac{a_2}{\lambda^2} \qquad (10)$$

Therefore, a plot of $1/(n^2(\lambda) - 1)$ versus λ^2 gives us a linear region from which the relevant fitting (dispersion) parameters can be determined by means of a least square fitting procedure. We have carried out the curve fitting for the epoxy and its two derivatives in the wavelength region of $\sim$ 190–260 nm, as seen in Figure 8. The parameters obtained by linear fitting have been given in Table I. These parameters have been found to be in good agreement with those reported in another work.[12]

CONCLUSIONS

We have synthesized two oximes (benzaldoxime and 2-furaldoxime) and then modified epoxy resin with them and finally obtained two new epoxy-based composites. Optical properties of these new composites were studied by analyzing the experimental absorbance data. The refractive indices and the band
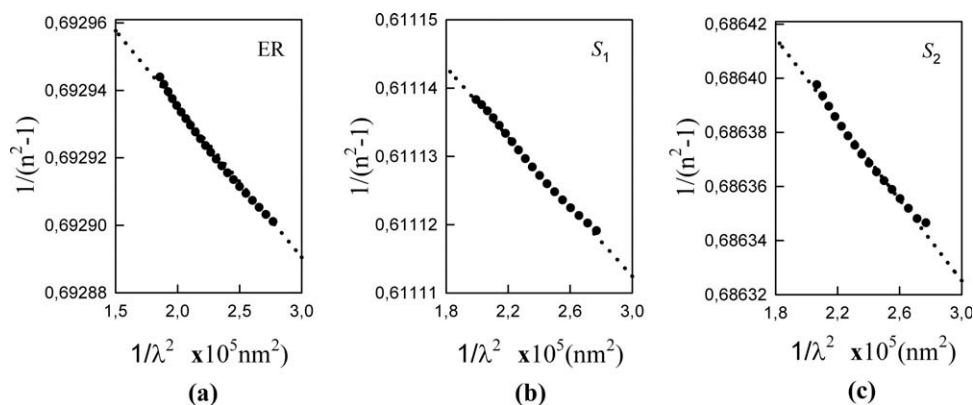

Figure 6 Variation of $(\alpha\hbar\omega)^2$ with photon energy $\hbar\omega$ for pure epoxy resin and two composites. Solid circles are measured points and the dotted lines are obtained from fitting.

Figure 8 The variation of $(1/(n^2 - 1))$ versus λ^{-2} for (a) pure epoxy resin (ER), (b) S_1 and (c) S_2.

energies (direct and indirect) of the samples have been determined. Oxime derivatives have not caused strong changes in the refractive index of the resin, but optical band energies greatly increased by modification. There is an extremely strong absorbance for the 2-furaldoxime doped composites at a narrow wavelength range in the vicinity 280 nm, while for the case of benzaldoxime doped sample, a dip has appeared in the same region arising from the benzene group. At the wavelengths greater than 300 nm, the spectra show a smoothly varying and structureless behavior. In conclusion, the benzaldoxime doped sample can be utilized for the applications in which low absorbance is demanded in the near UV region. On the other hand, the strong absorbance of 2-furaldoxime doped resins would make these materials suitable for devices requiring strong absorptivity in the near UV region.

References

1. Hamerton, I. Encylopedia of Chem Processing; Taylor and Francis: London, 2006; p 911.
2. Tsangaris, G. M.; Kouloumbi, N.; Kyvelidis, S. Mater Chem Phys 1996, 44, 245.
3. Naganuma, T.; Kagawa, Y. Acta Mater 1999, 47, 4321.
4. Cui, Z.; Yang, B.; Shen, J.; Su, X.; Yang, H. Polymer 2001, 42, 10095.
5. Su, W. F.; Fua, Y. C.; Pan, W. P.; Thermochim Acta 2002, 392–393, 385.
6. Palmer, J. P.; US Patent 1984, 4,431,260.
7. Nishimory, S.; Harada, T.; Yamamoto, Y.; Hiromori, N.; Yoshimura, Y.; Muramatsu, K.; Shimada, K. U.S.; Patent 1992, 5,107,327.
8. Chae, K. H.; Gwark, J. C.; Chang, T. Macromol Rapid Comm 2000, 21, 1007.
9. Miao, R.; Kha, L. U. S.; Patent 2006, 7,083,335,B2.
10. Ollier-Dureault, V.; Gosse, B. J Appl Polym Sci 1998, 70, 1221.
11. Brown, J.; Hamerton, I.; Howlin, B. J. J Appl Polym Sci 2000, 75, 201.
12. Iba, H.; Chang, T.; Kagawa, Y. Compos Sci Technol 2002, 62, 2043.
13. Mailhot, B.; Morlat-Thrias, S.; Ouahioune, M.; Gardette, J. L. Macromol Chem Phys 2005, 206, 575.
14. Hino, T.; Taniguchi, S.; Kuramoto, N. J Polym Sci Pol Chem 2006, 44, 718.
15. Raja, V.; Sarma, A. K.; Narasimha Rao, V. R. Mater Lett 2003, 57, 4678.
16. Ahmetli, G.; Cerit, A. J Appl Polym Sci 2007, 104, 2549.
17. Mohan, J. Organic Spectroscopy Principles and Applications; Narosa Publishing Hause: New Delhi, 2001.
18. Fakhfakh, N.; Cognet, P.; Cabassud, M.; Lucchese, Y. Chem Eng Process 2008, 47, 349.
19. Vabrik, R.; Czajlik, I.; Try, G.; Rusznk, I.; Ille, A.; Vig, A. J Appl Polym Sci 1998, 68, 111.