Zn-Ion Coated Structural SiO$_2$ Filled LDPE: Effects of Epoxy Resin Encapsulation

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Abstract: In the present work, a low-density polyethylene (LDPE) composite, filled with Zn-ion coated structural silica encapsulated with the diglycidyl ether of bisphenol-A (DGEBA), was synthesized using the conventional melt-blending technique in a sigma internal mixer. The catalytic activity of the Zn-ions (originating from the structural silica) towards the oxirane group (diglycidyl ether of bisphenol-A (DGEBA): encapsulating agent) was assessed by infrared spectroscopy. Two composites, each with a filler content of 2.5 wt% were developed. The first one was obtained by melt blending the Zn-ion coated structural silica with LDPE in a co-rotating sigma internal mixer. The second one was obtained by melt blending the same LDPE, but with DGEBA encapsulated Zn-ion coated structural silica. Epoxy resin encapsulation of the Zn-ion coated structural silica resulted in its having good interfacial adhesion and a homogeneous dispersion in the polymer matrix. Furthermore, the encapsulation of epoxy resin over the Zn-ion coated structural silica showed improvements in both the mechanical and thermal properties, viz. a 33% increase in the elastic modulus and a rise in the onset degradation temperature from 355 to 371 °C, in comparison to the Zn-ion coated structural silica.

Keywords: structural silica, encapsulation, thermal stability, elastic modulus.

Introduction

The academic and industrial interest in polymer nanocomposites is steadily increasing because of the more diversified opportunity in terms of selectivity that these materials provide. In general, composite materials are formed when at least two distinctly dissimilar materials are mixed to form a monolith. The overall properties of a composite material are determined not only by the parent components but also by the composite morphology and interfacial properties. A nanocomposite is formed when phase mixing occurs on a nanometer length scale. Nanocomposites usually exhibits improved performance properties compared to conventional composites, owing to their unique phase morphology and improved interfacial properties.[1]

The preparation of composite material by melt blending the polymeric matrix and the filler is a straightforward procedure but is less efficient when the reinforcing filler is in nanoscale due to agglomeration of nanoparticles. In order to overcome this limitation, a first strategy has been proposed that is based on the filler encapsulation by a polymer coating.[2] A second approach relies upon the chemical modification of the filler surface by functional silanes and titanate esters, which are able to promote adhesion to the polymer matrix.[3-8] Moreover, the high cost of the functional silane compounds also limits their applicability in mass production.

Epoxy resins are used in high performance coatings, adhesives, reinforced plastics, and potting and encapsulating compounds. The resins are highly reactive towards reactive mineral surfaces through their oxirane and hydroxyl groups by suitable catalyst through Lewis acid base interactions and hydrogen bonding through the hydroxyl functionality. Zn-ion activity towards the polymerization of oxirane groups is a well documented property.[9] The present study, therefore, focuses on the activity of Zn-ion present on the surface of structural silica towards the oxirane group of DGEBA to form a chemical network over Zn-ion coated structural silica.

Experimental

Materials. The thermoplastic low density polyethylene

(LDPE, M_w, 90,000) was obtained from IPCL, India. Zn-ion coated structural silica with particle size in the range of 25-30 nm was developed at department of chemistry, IIT Kharagpur, India, using a sol-gel method. The particles are spherical in shape and amorphous in nature. The epoxy resin was liquid diglycidyl ether of bisphenol–A (DGEBA) type (Ciba Geigy, Araldite LY 556) with an equivalent weight per epoxide group of 195±5, used as received.

Das *et al.*[10] while reporting Zn-ion coated structural nano-silica as vulcanizing agent for styrene butadiene elastomer proposed a tentative model structure of Zn-ion and oxygen network over nanosilica.

Epoxy Resin Encapsulation on Zn-Ion Coated Structural Silica. The reaction of Zn-ion coated structural silica particles with diglycidyl ether of bisphenol-A (DGEBA), encapsulating agent was carried out as follows. Zn-ion coated structural silica particles were suspended in methyl isobutyl ketone solvent. To this Zn-ion coated structural silica particle solution, epoxy resin was added. The weight ratio of Zn-ion coated structural silica and epoxy resin was taken as 40:60. The suspension was introduced into a three neck round bottomed flask equipped with mechanical stirrer, water condenser and a thermometer. The reaction was carried out at 130-140 °C for 2 h, then solvent was removed with a rotary evaporator and the product was dried in vacuum oven for 1 h. The dried sample was used for spectroscopy analysis. Fourier transform infrared spectroscopy experiments were done on Zn-ion coated structural silica and DGEBA encapsulated Zn-ion coated structural silica using a NEXUS 870 FTIR (Thermo Nicolet) in humidity less atmosphere at room temperature.

Nanocomposite Preparation. Two separate compoundings-first, LDPE polymer with Zn-ion coated structural silica and second, LDPE polymer with DGEBA encapsulated Zn-ion coated structural silica were performed in a co-rotating sigma internal mixer at 150 °C and 100 rpm, for 15 min. Formulations for the compoundings are given in Table I. Polymer sheets of the composites, thus, obtained were compression molded at 150 °C under 1 ton pressure for 10 min. The molded sheets were allowed to cool under the same pressure at ambient temperature.

Characterization. Morphological: Scanning electron microscope (JEOL JSM-5800 SEM) was used to evaluate the morphological properties of the fillers (Zn-ion coated structural silica and epoxy encapsulated Zn-ion coated structural silica) as well as the composites formed by melt blending. SEM images pertaining to these have been included towards the end of this paper and a brief discussion based on these has been presented later in the text.

Mechanical: Dumbbell shaped testing samples were cut from the molded sheets and were used for tensile testing at least 24 h after molding. Tensile testing was repeated for at least four samples at an extension speed of 5 mm/min with an initial gaze length of 35 mm using a universal tensile testing machine, Hounsfield HS 10 KS model at room temperature.

Thermal: Thermogravimetric analysis (TGA) was carried out using a TGA V50 IA Dupont 2100 thermogravimetric analyzer instrument in presence of dry air with a heating rate of 10 °C/min from room temperature to 700 °C.

Results and Discussion

Effect of Epoxy Resin Encapsulation on Zn-Ion Coated Structural Silica. Since the present study aims to evaluate the effect of DGEBA encapsulation over Zn-ion coated structural silica on the mechanical properties of LDPE composites, this requires apriori knowledge of variation in the chemical structure of the Zn-ion coated structural silica particles. Figure 1 shows the FTIR spectra of Zn-ion coated structural silica and DGEBA encapsulated Zn-ion coated structural silica.

In comparison to the spectrum of Zn-ion coated structural silica (as received) stretching vibration bands can be observed at 1168 cm⁻¹, 1234 cm⁻¹ (Si-O-C), 827 cm⁻¹, 2938 cm⁻¹ (1, 4

Table I. Compounding Formulations of LDPE Composites

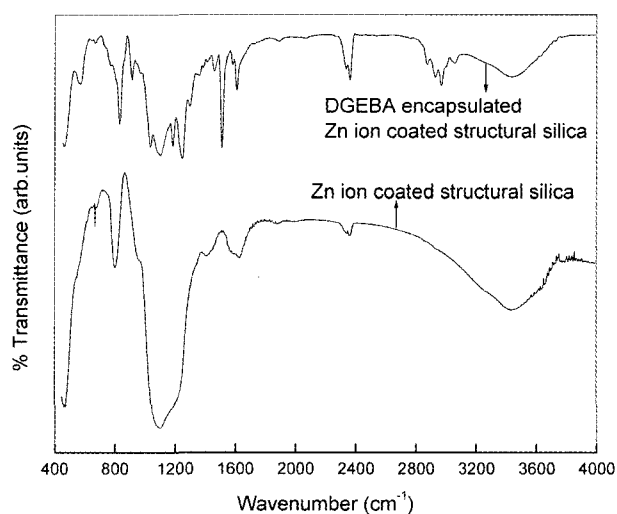| Sample	Feeding Compositions (wt%)		
	LDPE	Zn-ion Coated Structural Silica	DGEBA Encapsulated Zn-ion Coated Structural Silica
LDPEZNS-0	100	0	0
LDPEZNS-1	100	2.5	0
LDPEZNS-2	100	0	2.5

Figure 1. FT-IR spectra of Zn-ion coated structural silica and DGEBA encapsulated Zn-ion coated structural silica.
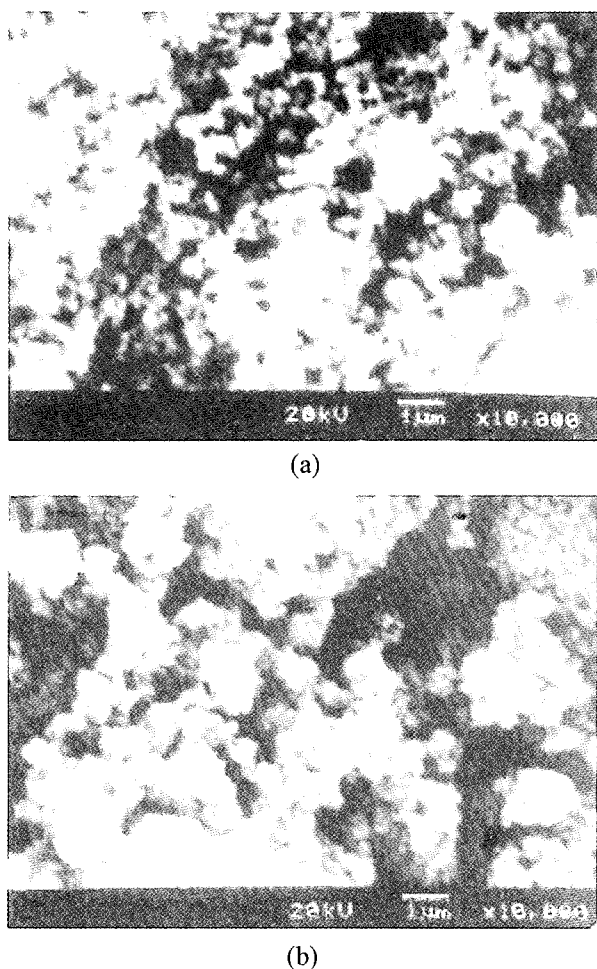
(a)

(b)

Figure 2. SEM images of Zn-ion coated structural silica (a) and DGEBA encapsulated Zn-ion coated structural silica (b).

substituted benzene ring), 1589 cm^{-1} (COO⁻M⁺), in case of DGEBA encapsulated Zn-ion coated structural silica. This proves, as expected, Zn-ion activity towards the oxirane group of DGEBA to form chemical network over Zn-ion coated structural silica.

Figure 2 shows the SEM images of Zn-ion coated structural silica (a) and, DGEBA encapsulated Zn-ion coated structural silica (b), respectively. A chain like branched structure of the agglomerated Zn-ion coated structural silica particles can be observed [Figure 2(a)]. When the particles are encapsulated with DGEBA, the sizes of the agglomerates become larger and the edges are no longer discernible [Figure 2(b)]. Such a change demonstrates the role of encapsulation. Based on FTIR assessment and SEM morphological study we proposed a tentative model structure of DGEBA encapsulation over Zn-ion coated structural silica, and, shown in Scheme I.

As observed from the Scheme I, the structure of Zn-ion coated structural silica filler was established by the previous work.[10] When we are encapsulating this Zn-ion coated structural silica filler, the coordinating complex through Zn-ion and oxygen of the epoxy takes place as shown in the Scheme I. The FTIR analysis (as earlier) explained this type of coordinate complex. This type of encapsulation improves the filler-matrix interactions and thus improving the mechanical properties (which has been discussed in later stage).

Effect of Epoxy Resin Encapsulation on Zn-Ion Coated Structural Silica on Morphology of Composites. Figure 3 shows the surface morphology of control (LDPEZNS-0) and composite samples, filled with Zn-ion coated structural silica (LDPEZNS-1) and DGEBA encapsulated Zn-ion coated structural silica (LDPEZNS-2), respectively. The morphology was studied on the compression molded poly-
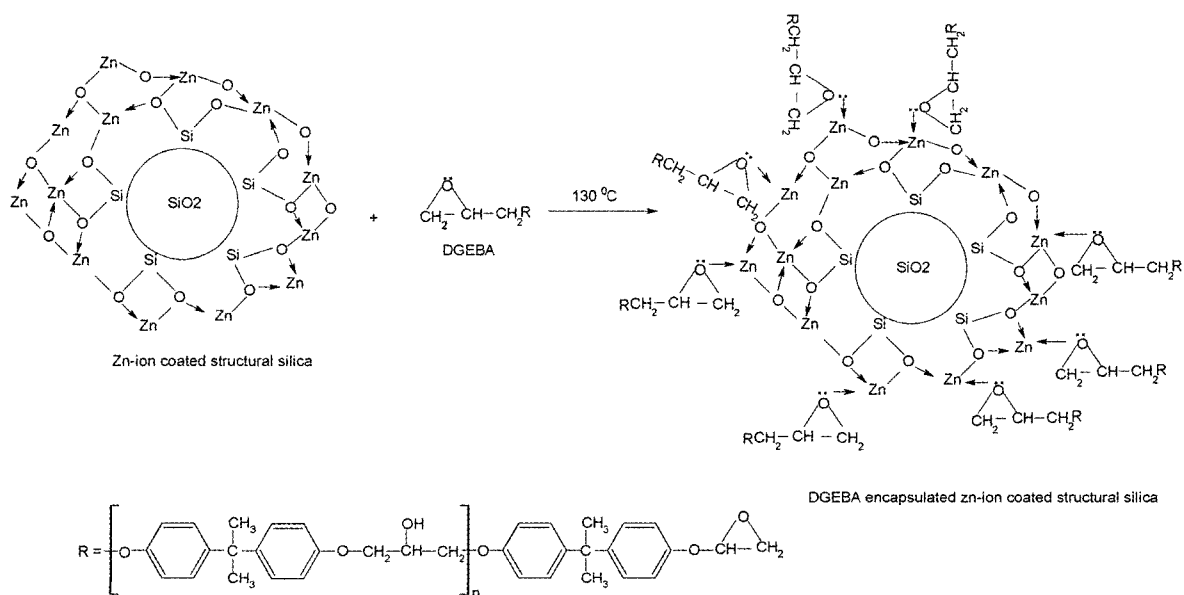
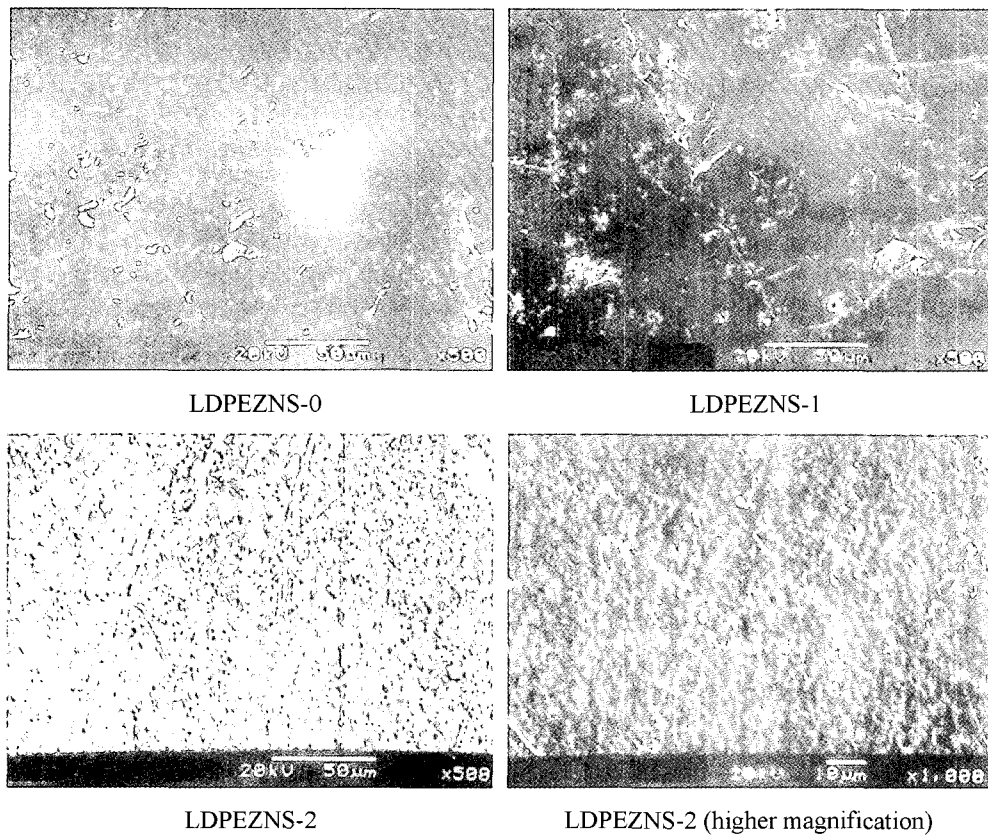**Scheme I.** A tentative model structure of DGEBA encapsulation on Zn-ion coated structural silica.

LDPEZNS-0 LDPEZNS-1

LDPEZNS-2 LDPEZNS-2 (higher magnification)

Figure 3. SEM surface images of LDPEZNS-0, LDPEZNS-1, and LDPEZNS-2.

Figure 4. SEM surface image of LDPEZNS-1 at higher magnification.

Figure 5. Stress-strain curves of LDPE composites.

mer thin film composites. In the case of LDPEZNS-2, the micrograph, at higher magnification shows homogeneous distribution of micro size and discrete particle in the polymer matrix. This can be attribute to DGEBA encapsulation over Zn-ion coated structural silica forces the filler-matrix interactions to dominate filler-filler interactions. A picture of LDPEZNS-1, in Figure 4, was taken at higher magnification, which shows that the agglomeration of Zn-ion coated
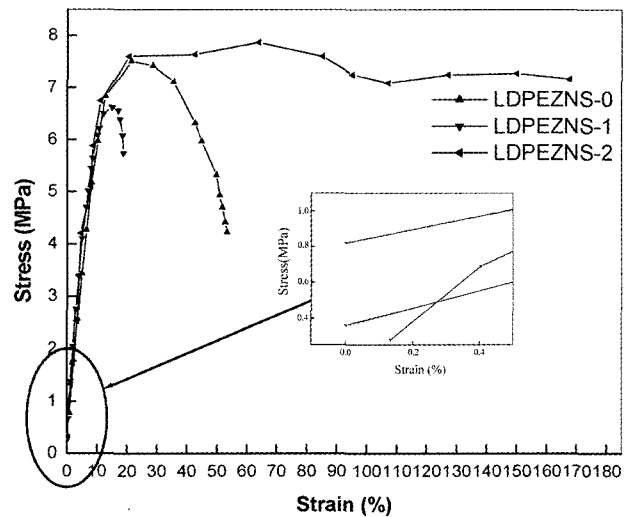
structural silica leads to the formation of micro domains and inhomogeneous distribution in the polymer matrix.

Mechanical Properties and Fracture Morphology. The stress-strain curves of control and composites are shown in Figure 5. The results are listed in Table II. The data can be interpreted in adherence to the earlier works[11,12] as follows.

Table II. Mechanical Properties of the Composites

Sample	Stress at Yield (MPa)	Strain at Berak (%)	Stress at Break (MPa)	Modulus (GPa)
LDPEZNS-0	7.51± 0.05	53 ± 2.0	4.23 ± 0.5	0.11 ± 0.03
LDPEZNS-1	6.62 ± 0.03	16 ± 5.4	5.74 ± 0.4	0.15 ± 0.04
LDPEZNS-2	7.60 ± 0.01	167 ± 3.0	7.17 ± 0.6	0.20 ± 0.05

In general, particulate composites have a reduced tensile strength. Moreover, they exhibit less elongation prior to break point. Both these, i.e., reduced tensile strength and reduced elongation can be attributed to weak interfacial adhesion forces among the matrix and the filler. Now, both Zn-ion coated structural silica and DGEBA encapsulated Zn-ion coated structural silica can impart high stiffness of the filler to the matrix polymer. However, the composite, filled with Zn-ion coated structural silica exhibits lower modulus than the composite, filled with DGEBA encapsulated Zn-ion coated structural silica. This can be attributed to poor interfacial adhesion between the Zn-ion coated structural silica and the polymer matrix. The composite, filled with epoxy resin encapsulated Zn-ion coated structural silica has high modulus. Because on filler encapsulation, filler-polymer interactions dominate filler-filler interactions and facilitate filler-matrix compatibility as well as a homogeneous distribution in the matrix and also upon epoxy resin

encapsulation, the density of filler will be lower than that of just Zn-ion coated structural silica. Thus, the volume fraction of epoxy encapsulated filler in the composite (LDPEZNS-2) is larger than that of filler without epoxy encapsulation in the composite (LDPEZNS-1) as the filler content was fixed to be at 2.5 wt%. Thus, the increase of modulus of composite (LDPEZNS-2) than that of composite (LDPEZNS-1) attributed to the increase of volume fraction as well as a better interfacial adhesion. There is a pronounced adhesion between DGEBA encapsulated Zn-ion coated structural silica and polymer matrix due to the presence of micro domains which at lower loadings are freer to move with the matrix and, correspondingly, it becomes easier for the matrix to stretch around them. The viscous drag of small particles with good adhesion to the matrix can produce an apparent strength improvement and greater transference of strain to the matrix, resulting in higher ultimate elongation.[13]

Figure 6, shows the morphology of tensile fractured sam-
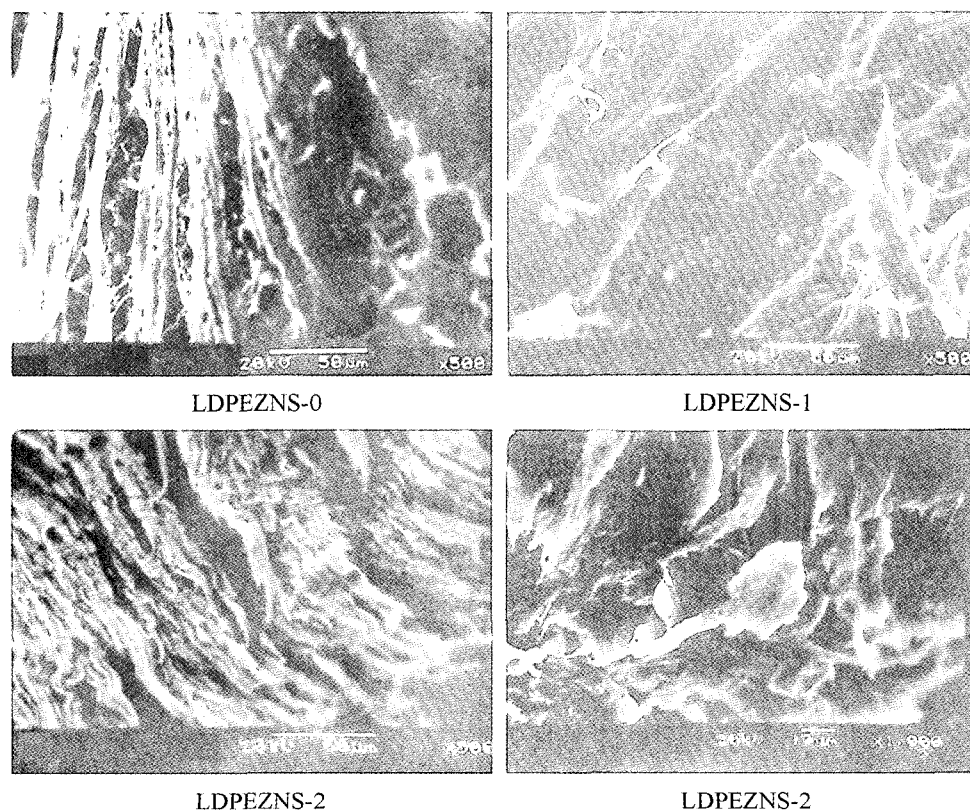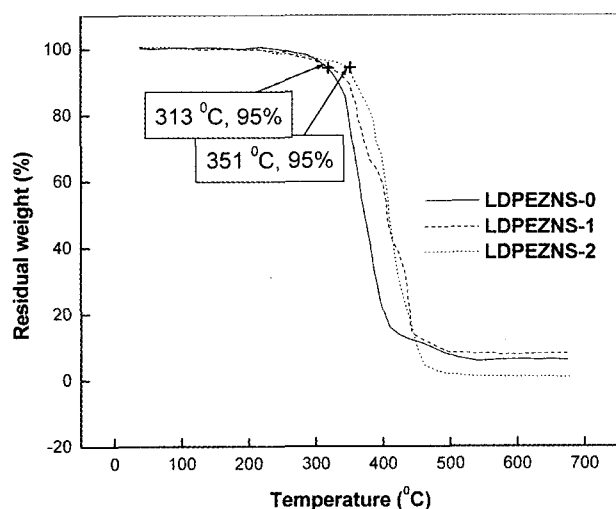

LDPEZNS-0

LDPEZNS-1

LDPEZNS-2

LDPEZNS-2

Figure 6. Tensile fracture surface SEM images of LDPEZNS-0, LDPEZNS-1, and LDPEZNS-2.

Table III. TGA Data of the Composites

Sample	5% wt. Loss in Air Temp.[a] (°C)	On Set of Decomposition Temp.[a] (°C)
LDPEZNS-0	313	344
LDPEZNS-1	313	355
LDPEZNS-2	351	371

[a]Temperature ramp 10 °C/min in air.

Figure 7. TGA traces of LDPE composites.

ples of LDPEZNS-0, LDPEZNS-1, and LDPEZNS-2. Stress whitening zones can be observed in LDPEZNS-1 sample due to larger agglomerated Zn-ion coated structural silica particles and lack of interfacial adhesion. The observed higher shear yielding of matrix in LDPEZNS-2 sample may be due to encapsulation of Zn-ion coated structural silica particles with epoxy resin (DGEBA).

Summary of the thermal characterizations of nanocomposites is listed in Table III. It is observed from the thermograms (Figure 7) that the thermal stability of epoxy resin encapsulated Zn-ion coated structural silica filled composite is increased. This can be attributed to the epoxy resin network cover - over Zn-ion coated structural silica. In addition, the temperature of 5 wt% loss (351 °C) is increased in epoxy resin encapsulated Zn-ion coated structural silica filled composites. Another possible explanation for the improvement of thermal oxidative stability can be attributed to the formation of structural siloxane layer on the surface of the polymer melt in the presence of oxygen, which serves as a barrier to prevent further degradation of the underlying polymer.[14]

Conclusions

The influence of encapsulation on Zn-ion coated struc-

tural silica with epoxy resin has been studied. Epoxy resin encapsulated Zn-ion coated structural silica (LDPEZNS-2) added to LDPE shows a homogeneous dispersion of the filler into the matrix in comparison to particle aggregates of different sizes in case of LDPEZNS-1, i.e., Zn-ion coated structural silica (SEM images). In addition, epoxy resin encapsulated Zn-ion coated structural silica filled LDPE (LDPEZNS-2) is found to have 33% more elastic modulus in comparison to the Zn-ion coated structural silica filled LDPE (LDPEZNS-1) and 80% more elastic modulus in comparison to the pure polymer (LDPEZNS-0). Furthermore, LDPEZNS-2 is observed to be more thermally stable in comparison to the LDPEZNS-1 and the pure polymer (TGA traces).

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