STUDIUL PRIVIND EFECTUL NANOARGILEI ASUPRA CARACTERISTICILOR STRUCTURALE ȘI MORFOLOGICE ALE COMPOZITELOR EPOXIDICE

A STUDY OF EFFECT OF NANOCLAY ON THE STRUCTURAL AND MORPHOLOGICAL BEHAVIOR OF EPOXY COMPOSITES

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Composite materials are being widely employed in numerous modern applications. Fabrication of new composite materials has been holding the consideration of scientists worldwide and attempts are being made to improve the applicability of these materials. In perspective of this advancement in the research field, the present work attempts to concentrate the impact of nanoclay content on the structural and morphological behavior of epoxy composites. Epoxy materials were reinforced with various particulate portions of chosen nanoclay and the specimens were investigated. The structural examination of the polymer composite with X-ray diffraction showed that the nanoclay was distributed as an intercalated structure in the polymer matrix, and the d-spacing of layers decreased with increasing nanoclay content. SEM images analysis revealed that 2% nanoclay reinforced samples exhibited less number of but more uniform pores compared with 10% nanoclay reinforced samples.

Keywords:*Composite materials, Nanoclay, Scanning electron microscopy, X-ray diffraction.*

1. Introduction

Composite materials offer great promise and attraction because of their peculiar properties that are totally different from those of the constituent materials. They consist of two or more chemically different constituents, namely the polymeric matrix and the reinforcement. The reinforcement normally is stiffer and stronger than the matrix, while the matrix holds the reinforcement in its set place [1, 2]. Growing awareness about the environmental pollution has necessitated the usage of natural fiber as reinforcements in polymer composites [3, 4]. Various reusing and renewable waste materials assets including leaves, wood chips, waste newspaper, waste concrete, reservoir silt, etc., are in effect progressively used in gypsum or polymer matrix because of developing environmental issues from recent years in the constructional and building applications with a view to replacing the traditional expensive building materials like bricks and cement [5]. This subsequently reduces the need for raw materials, waste management/production and a wide range of environmental impacts [6]. Natural fiber reinforced composites have their own advantages and disadvantages compared with the conventional synthetic composites. Poor wetting and weak interfacial bolding that decrease the mechanical and additionally thermal properties of the composites contribute to disadvantages; however, they can be overcome by the change of the fibers through physical/chemical treatment or by joining interfacial added additives/ compatibilizers [7–9]. The interfacial added substances might be nano sized filler (nano silica, nanotubes, nanoclay) or synthetic fiber that can produce hybrid composites through proper material design [10].Epoxy polymers are broadly utilized for the matrices of fiber reinforced composite materials and adhesives. When cured, epoxy polymers are amorphous and highly-cross linked (i.e. thermosetting) polymers. This microstructure brings about numerous valuable properties for structural engineering applications, for example, a high modulus and failure strength, low creep, and great performance at elevated temperatures. However, such epoxy polymers have such a structure, to the point that their property is rendered exceptionally undesirable, that is to state, they are generally weak materials, with a poor resistance to crack start and development.

The transition from micro particles to nanoparticles gives dramatic modifications in physical properties. Nanoscale substances have a large surface area for a given quantity. Because many critical chemical and physical interactions are governed by surfaces and surface properties, nanostructured materials will have considerably extraordinary properties from a larger-dimensional material of the same composition. Within the case

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of particles and fibers, the surface area per unit volume is inversely proportional to the material's diameter, thus, the smaller the diameter, the more the surface area per unit volume [11]. Polymer nanocomposite is a new class of materials in which resin is commonly tailored via inorganic nanoparticles to show enhanced mechanical, thermal and fire resistance properties [12, 13]. Such enhancement in the properties of nanocomposites happens primarily because of their unique phase morphology and improved interfacial properties [14]. The kinds of nanomaterials which might be most broadly used for this purpose encompass: nanotubes, nanoclays, silica particles and electro-spun polymeric nanofibers. Individual platelet thicknesses are simply one nanometer. One gram of powdered fabric can have billions of nanoparticles with a surface area of many square meters [15]. Organo treated montmorillonite clay is broadly used as nanofiller in the polymer because of its superior compatibility with natural matrix, specific surface area, aspect ratio and nano dispersible characteristics. Nanoclay will increase strength, stiffness and heat resistance however decreases moisture absorption, flammability and permeability to fuel and water. This in turn can result in sizable weight loss that is of apparent importance in aerospace and marine applications [16]. In polymer nanocomposites (PCNs), montmorillonite based totally layered silicate clay is usually used as reinforcement in polymer matrix [17]. Its crystal lattice consists of two-dimensional layers wherein a crucial octahedral sheet of alumina or magnesia is fused into outside silica tetrahedron through the end, so that the oxygen ions of the octahedral sheet additionally belong to tetrahedral sheets[18]. Nanocomposites have come to be regarded as the most promising, attractive, indispensable and encouraging approaches in the field of advanced engineering applications and they have a bright future. They can be tailored by including nano scale fillers in the polymer matrix to meet the developing demands of the particular properties in the versatile and practical applications [19, 20].Nanocomposites have unique mechanical, thermal, optical, electrical, magnetic and barrier properties compared with pure polymer [21] and they are different from even traditional/conventional composites, for example, glass fiber reinforced composites [22]. The hybrid nanocomposites have brought about revolution in the field of material science which can give the most hi-tech advanced composite materials. The addition of nano particles seems to work wonders in effecting remarkable developments in the thermal, physical, mechanical and thermomechanical properties due to perfect dispersion, a high aspect ratio and effective polymer filler interaction [23]. This study focuses on investigating the effect of structural and morphological behavior of epoxy composites.

2. Materials and methods

2.1. Epoxy resin

The strips were made by having different composition of Cloisite 30B varying from 2 % to 10 % along with epoxy and the hardener. After curing the strips 4 specimens were taken for each combination and the tests were conducted. In this study, a commercially available epoxy resin (include grade) was procured and used as the polymer matrix. Aliphatic amine (HY-951) was used as the hardener for epoxy resin. The Nano composite powder Cloisite 30B with a particle size (<13 nano meter) was obtained from Southern Clay Products, Inc.

2.2. Cloisite 30B

Cloisite 30B is a natural montmorillonite modified with a quaternary ammonium salt and it is designed to be used as an additive for plastics and rubbers to improve various physical properties such as reinforcement, CLTE, synergistic flame retardant and barrier. Cloisite 30B consists of organically modified nano meter scale layered magnesium aluminium silicate platelets. The silicate platelets that the additives are derived from are 1 nanometer thick and 70 to 150 nanometers across. The platelets are surface modified with an organic chemistry technique and it allows exhaustive dispersion into and provides miscibility with the thermoplastic systems for which they have been designed to improve. While enhancing the flexural and tensile modules, the CLTE has lowered when the additives have been proved to reinforce thermoplastics. By incorporating the nano particles into the structure of the surface char formation and flame retardance of the thermoplastic systems have also been found to be improving.

2.3. Preparation of composite sheets

Weighed amounts of epoxy resin and Cloisite 30B powder were mixed in varying proportions and then the hardener, aliphatic amine (HY-951) in the ratio10:1 to the epoxy was added to initiate the reaction. The mixture was then poured into the mould. Different sheets of epoxy resin reinforced with varying amounts of Cloisite 30B filler i. e., 2, 4, 6, 8, and 10 wt.-% of resin were prepared and tested. Filler amount was limited to 10% in the composite sheet because as the filler concentration increased to 10%, gelation occurred rapidly and the mixture became thick losing fluidity. The curing time was maintained for 24hrs.

3. Characterization techniques

3.1. XRD Analysis

The analysis of crystal structure is of great importance in the description of materials; such an analysis is typically performed by employing X-ray diffraction techniques (Other techniques include electron diffraction method and neutron diffraction method). The basic information that can be obtained from such diffraction patterns is the d_{hkl} spacing, the crystal lattice type, lattice parameters and crystalline phases present in materials, the structural properties of these phases and atomic arrangements of crystalline materials.

3.2. SEM Analysis

The fracture surfaces of the flexural and impacted samples were examined using scanning electron microscopy (SEM) to understand the deformation and failure behaviors at various magnifications. SEM was carried out using Hitachi S-3400N which operated at an acceleration voltage of 120 kV. For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface.

4. Results and Discussion

4.1. Structural analysis

The morphological structure of Cloisite30B/epoxy Nanocomposite samples was examined with the assistance of the XRD patterns. It is outstanding that intercalated Nanocomposite is shown by reflections in the low angle region [24]. Generally, the formation of an ordered intercalated system with alternating polymer/silicate layers is indicated by the intense reflections within the range of 0-10° (2θ). In the completely delaminated hybrids, silicate layers with a thickness of about 1 nm can be seen to be relatively homogeneously dispersed in the polymer matrix. The clay dispersion processes, in this study, were studied by X-ray diffraction (XRD). Figure 1 shows the XRD patterns of the nanoclay. The distance between silicate platelets was calculated by using Bragg's law and it was compared with the basal plane distance of Cloisite 30B so that the occurrence of intercalation or exfoliation could be ascertained:

$$2d \sin \theta = \lambda n \qquad (1)$$

Where d is the distance between the crystallographic planes, θ is the half-angle of diffraction, n is an integer, and λ is the wavelength of the X-ray radiation.

The $2\theta = 4.75°$ peak is related to pure clay with d_{001} = 1.82 Å. In the sample with 2% nanoclay, the peak shifted to a lower angle ($2\theta = 2.10°$; d_{001} = 4.30 Å), which implied the formation of intercalation morphology. The peak related to 4% nanoclay appeared at $2\theta = 2.20°$; d_{001} = 4.08 Å. The peak related to 6% nanoclay appeared at $2\theta = 2.20°$; d_{001} = 4.08 Å. The peak related to 8% nanoclay appeared at $2\theta = 2.23°$; d_{001} = 3.88 Å. The peak related to 10% nanoclay appeared at $2\theta = 2.30°$; d_{001} = 3.80 Å. These data showed that the order of intercalation was higher at 2 wt.% nanoclay than at 10 wt.% nanoclay concentration.

Consequently, the accomplishment of an intercalated structure in these nanocomposites could be attributed to better scattering of the nanoclay all through the reprocessed high density polyethylene. This bears clear proof of finish dispersion of the nanoclay in the epoxy matrix. Further, a comparison of the relative forces for all nanoclay rates, prompted to the conclusion that nanoclay dispersion may be in both intercalation and shedding modes relying upon the nanoclay percentage for each. The d-spacing values and the vanishing of the crest at 4.75 in all nanocomposites clearly demonstrated the entire dispersion of the clay into epoxy matrix showing an intercalation mode in all clay percentages. Likewise, a vital perception could likewise be made by looking at d -spacing for every clay percentage. As the wt% of clay increased from 2 wt% to 10 wt%, there was a noticeable increase in 2θ and consequently an obvious decrease in d-spacing values.

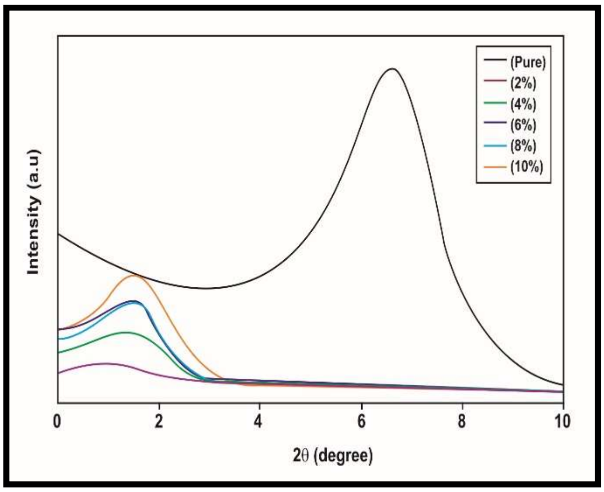

Fig.1 - X-ray diffraction patterns of Cloisite 30B with epoxy/ nanocomposites containing pure, 2, 4, 6, 8 and 10 wt% nanoclay contents.

4.2 Scanning electron microscopy

The pictures acquired from the SEM revealed that proper distribution and consistency existed between the filler and the matrix. The made voids implied a weak association connection area between the fibers and the matrix. It implied that the fibers were confined from the surface of the matrix due to the stress and pressure caused by the powerless ties they had with the matrix. The shape and points of interest of the morphology could be comprehended from the pictures of the SEM recorded at higher amplifications.

The morphological distribution of the samples could analyzed by means of a scanning electron microscope and Figures2 (a-f) show the morphological characterization of samples of various wt % of nanoclay (0-10wt%) Cloisite 30B with epoxy resin. The nanoclay particles were seen to be distributed evenly in the specimens. Figure.2 (a) shows the SEM micrograph that

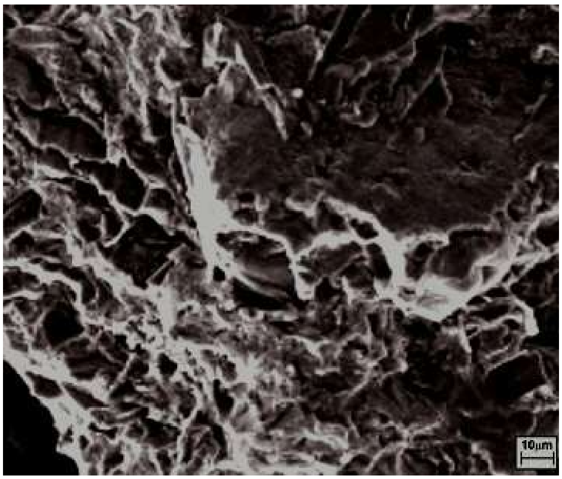

Fig 2 (a) - SEM Image of the composites of 0wt% nanoclay.

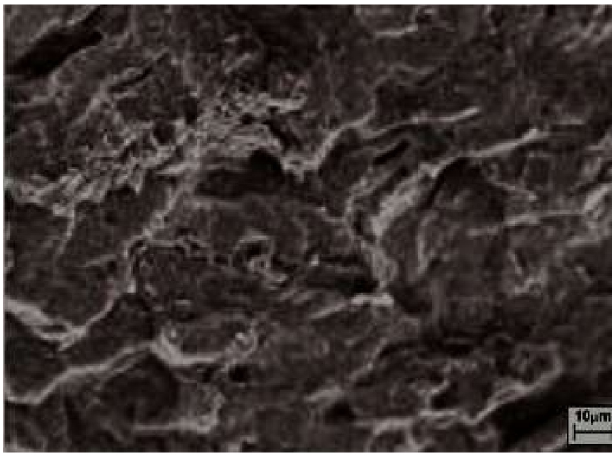

Fig 2 (b) - SEM Image of the composites of 2wt% nanoclay.

Fig 2 (c) - SEM Image of the composites of 4wt% nanoclay.

Fig 2 (d) - SEM Image of the composites of 6wt% nanoclay.

Fig 2 (e) - SEM Image of the composites of 8wt% nanoclay.

Fig 2 (f) - SEM Image of the composites of 10wt% nanoclay.

reveals the fractured surface of the Cloisite 30B/epoxy nanocomposite with nano surface treatment.

The obtained micrographs confirmed the results of mechanical and physical tests on the composites. The created voids implied a weak bond zone dividing the fibers from the matrix. It meant that the nano particles could not adhere to the surface of the matrix because of the stress and pressure effectuated by the weak bonds they had with the matrix. The nanoclay is a good absorbent of the coupling agent and in the event of using a larger amount of the nanoclay (10 wt %), any further addition of it will increase the absorption of the coupling agent, too. The mechanical and the physical properties of the composites and their microstructure seemed to be closely correlated. As has already been stated, the nanoclay is a good absorbent of the coupling agent and any further addition of the nanoclay will increase the number of pores, thereby reducing the tensile/bending strength upon using 10 wt% nanoclay in the composite.

5. Conclusion

The present work is an attempt to synthesize advanced nanocomposite material for aerospace and structural applications. Special attention was directed towards the reinforcing efficiency of nanoclay particles on the polymer composites. To analyze the XRD, SEM was performed on the test specimens. An investigation of the structural and morphological characteristics of an epoxy strip reinforced with Cloisite 30B nanoclay was carried out. The specimens obtained by reinforcing epoxy materials with different particulate fractions of chosen nanoclay were investigated. The content of the reinforcing material, namely the nanoclay, was varied from 0 to 10 wt.-% by weight of total matrix in the matrices. The creation of an intercalated structure in the composite material became apparent from the morphological studies of the nanocomposite with the use of the XRD spectra. It was observed that the order of the intercalation for samples containing 2 wt.% nanoclay was higher than that containing 10 wt.% nanoclay. Another notable observation was that the d-spacing of layers decreased with increasing nanoclay content. Scanning Electron Microscopy (SEM) revealed that 2 wt% nanoclay samples exhibited less number of but more uniform pores compared with 10 wt% nanoclay samples.

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