Indian Journal of Science and Technology, *Vol 9(4), DOI: 10.17485/ijst/2016/v9i4/81100, January 2016*

ISSN (Print) : 0974-6846
ISSN (Online) : 0974-5645

A Review on Polymer Nanocomposites: Synthesis, Characterization and Mechanical Properties

Shivraj Puggal*, Novepreet Dhall, Navjeet Singh and Manpreet Singh Litt

Department of Mechanical Engineering, Lovely Professional University, Phagwara - 144411, Punjab, India; Shivraj.16125@lpu.co.in, novepreet.16022@ipu.co.in; navjeet.16991@ipu.co.in; manpreet.16017@ipu.co.in

Abstract

Polymer nanocomposites are being used in packaging, sports equipment, automobile sector and bio-medical applications due to their exceptional property combinations and distinctive design feasibility. So keeping these property enhancements polymer nanocomposites has received greater attention in both academic and industrial areas. This paper reviews the various methods for dispersion of nanofillers, their coating on fibres and corresponding properties improvement. Unlike composites these enhancements in properties can be achieved without increase in density as very small amount 1–5% of nanoparticles are loaded. Study reveals that incorporation of different nanoreinforcements such as layered silicate clays, carbon nanotubes, nanofibres and silica nanoparticlenanocomposites into elastomers possess high surface to volume ratio of the reinforcing phase, high aspect ratio and intercalation/exfoliation characteristics which causes properties up gradation such as modulus, strength, durability, toughness and barrier to gases when compared to traditional materials. In addition to property enhancements they are environmental- friendly also. Although they provide great benefits but still manufacturing them in terms of quantity and quality will be one of the biggest challenges.

Keywords: Diffraction and Mechanical Properties, Nanocomposites, Polymer Composites, Scanning Electron Microscope, X-Ray

1. Introduction

Epoxy being highly cross linked posses many excellent properties mainly high stiffness and strength, creep and chemical resistance in addition to appropriate performance at elevated temperatures. However, like most of the thermoset plastics, epoxy is intrinsically brittle, due to which poor resistance to crack growth is offered. On the addition of second phase of polymeric particles, such as rubbers and thermoplastics to epoxy overcomes this undesirable property but this further result in loss of modulus, glass transition temperature, solvent resistance and stiffness. Another method to reduce brittleness is to add fibres as reinforcement in epoxy matrix and both retain their physical and chemical properties. The properties obtained by combination cannot be achieved by either of the component alone. Epoxy resin is used in both laminating and molding techniques to make fibre reinforcement with good mechanical strength, chemical resistance and electrical insulating properties[1].

The properties of polymers composites depend upon various parameters like shape, properties and extent of constituents as well as interfacial interactions between matrix and dispersed phase. Further advancements in the properties can be accomplished by alternating the properties of the filler, the adhesion between matrix and filler and especially the aspect ratio of the filler. The aspect ratio of the filler is very important and crucial for many properties in composite such as electrical, mechanical and thermal properties. So the nanofillers like platelet clays, carbon nanotubes and nanofibres with high aspect ratio and its nanoscale dispersion within polymer matrix are proving to be the mainstay to structural materials as they improve the polymer properties at very low filler

*Author for correspondence

volume fractions. The use of low filler volume fraction in Polymer matrix composites retains low density as well as macroscopic homogeneity in final nanocomposite. So the nanocomposite becomes very popular and researchers are continuously trying to improve fabrications methods for producing them with effective properties.

In nanocomposite any one of the components having minimum size of one dimension in the nanometer units (<100 nm). The nano composites are also found in nature such as carbohydrates; fats, and proteins. Those are instances of nanocomposites, formed by meshing more than one phase just as particles, layers or fibres, where to a certain extent one of the phases is having its size in nanometer range. The first practical application for nanocomposites was performed in Japan by Toyota Central Research Laboratories by using nylon-montmorillonate clay nanocomposite for timing belt cover of Toyota Camry[2]. This showed that on addition of 4.2% clay increases the strength by 50% also doubled the modulus moreover the heat distortion temperature also raised by 80ºc of nylon-6. After this nanoclay has provided Potential benefits which include increased mechanical strength, decreased gas permeability, superior flame-resistance, and even enhanced transparency when dispersed nanoclay plates suppress polymer crystallization.

2. Fabrication of Nanocomposites

2.1 Methods for Dispersion of Nanofillers in Matrix Phase

Many researchers have used different nanofillers such as like clay platelet, metallic, nanotubes and halloysite with different preparation methods. The nano scale fillers have received increasing attentions due to properties improvement of the matrix in which they are distributed. There are several reasons for using clay such as availability, cost and high aspect ratio. Most commonly used fillers are montmorillonite, copper oxide, silica nanoparticles and nanodioamonds. The property enhancement of nanocomposites mainly depends upon the scattering of nano size particles in the matrix. The intercalation and exfoliation is always desirable to confirm the formation of nanocomposites. Many researchers have used various different techniques for the uniform dispersion of nano particles.

Rajmohan[3] used Cooper oxide (CuO) nano particles and Polyester resin for nanocomposites. Firstly, ultrasonic bath sonicator was used for mixing nano fillers for 2 hours and followed by mixing using rotary shaker for additional 5 hours to ensure homogeneous mixing of CuO nano particles into epoxy resin without their accumulation. Sharma[4] first heated the virgin epoxy for 30 minutes at 60º in an oil bath to make it less viscous so that nanoclay can be dispersed uniformly. The clay was added to epoxy and mechanical stirrer was used for mixing with continuous heating for 2 hours. Afterwards mechanical blending of the epoxy solution, same blend was ultrasonicated for 2 hours. Aymerich et al.[5] used shear mixing at 3500 rpm for 1 hour to get good dispersion of nanoclays by breaking of nanoclays clusters. Resin overheating caused due to shear mixing, was controlled by cooling epoxy solution in an external bath. Jumahat et al.[6] utilized pure resin Epikote and nanosilica, firstly solution was mechanically mixed with maintaining 80º C in oil bath for continuous 2 hours. Secondly, to remove the entrapped air from modified solution degasification was carried out in vacuum oven at 80º C and then finally incorporated with the appropriate amounts of hardener and accelerator. Jumahata et al.[7] initially dried the nanomer I.28 nanoclay at 60º C for 24 hours under vacuum and then Epikote 828 was preheated in a vacuum oven to lower the viscosity of the resin. Nanoclay in a defined amount was blended with Epikote 828 and mechanically agitated at 400 rpm with continuous heating in oil bath. Eventually, the mixture was degassed to remove the entrapped air. Azzam[8] used clay samples from Delta of Egypt and polymer in liquid state. The samples of soils were first oven-dried at 120º C, then graded, pulverized and sieved through 1.2 mm strainer. To prepare the polypropylene–clay composites, physical mixing was adopted using Kitchen stand blender with a total mixing time of 5–10 min.

2.2 Coating of Matrix Phase on Fibres

After modifying the matrix phase the mixture is applied on the glass/carbon fibres using various methods. One of the simplest methods used is hand layup[3, 4] for making nanocomposites. Modified mixture is applied to the fibre sheet using brush/steel scraper and laminas were left under ambient temperature for curing. This method produces voids which in turn have negative effects on mechanical properties. Vacuum assisted resin infusion molding can also be used for fabricating composite[5, 6, 7]. In this process infusion occurs due to pressure difference between the atmosphere and the vacuum. Large components can be fabricated; Cored structures can be produced in one operation. Dobrzanski[9] used injection molding process for preparation of Polymer nanocomposites reinforced with montmorillonite (MMT). Injection moulding is a quick process to manufacture high quality of large number of parts. Rattikarn[10] used twin screw extruder for the mixing of polymer and silica at the screw speed 60 rpm. The extrudate were cut and dried at 50º c for 12 hours to prevent from moisture. Manoharan[11] prepared Polypropylene/Montmorillonite (PP/MMT) nanocomposites by using twin-screw extruder at the screw speed 150rpm and maintain the temperature difference of barrel in twin screw extruder were 160, 170 and 180oC between feed zones to die zone, followed by granulation in a pelletizer and drying. He also incorporated the polypropylene grafted maleic anhydride (PP-g-mA) as compatibilizer used for better dispersion of nanoclay in the polymer matrix.

3. Characterization Techniques

Various powerful techniques are available for studying the degree of intercalation/exfoliation and their corresponding effect on the nanocomposite properties. However, one needs to be very careful with the interpretation of the results. Lack of sensitivity of the analysis and limits of the equipment can lead to wrong conclusions about the nanocomposite structure.

3.1 X-Ray Diffraction (XRD)

X-ray diffraction was used to scrutinize the changes that occur to the clay due to the intercalation and/or exfoliation of the polymer into the clay galleries. XRD is a good way to investigate the spacing between the clay layers due to its easiness and availability. XRD analysis shows a peak for clays and organoclays reason being their regular layered structures. This peak conform platelet separation or d-spacing in clay structure.

With increase in d- spacing XRD peak also shifted to lower diffraction angles (2θ). Intercalation indicates that the polymer has entered the space between the clay platelets but stacking is still there. B. Sharma[4] finds increase in d-spacing values from 18.26854 to 38.05891 stipulated that polymer was able to enter the interlayer spacing between platelets and eventually getting an intercalated structure. The absence of absence of intensity peaks stated exfoliation. Chow[12] detected complete disappearance of the characterization peak of OMMT in epoxy/glass fibre/OMMT. This indicates that the silicate platelets in the epoxy matrix were exfoliated.

3.2 Transmission Electron Microscopy (TEM)

XRD is very sensitive at low angles 2θ, which is the critical area for determining the interlayer spacing. Therefore, the absence of peaks does not mean that exfoliation is completely achieved but that they are intercalated due to large spacing. TEM provides a most direct way to examine the states of clay exfoliation as this technique can image materials on the nanometer scale. The states of clay exfoliation, such as whether the clay is intercalated or exfoliated, can be observed directly. Wetzel[13] used TEM technique to visualize the dispersion quality of nanoparticles. He founded homogeneous distribution of nano particles with some small agglomerates in the matrix. TEM micrographs in Figure 1 conforms the uniform distribution of nanosilica in Epikote 828[6]. There was no agglomeration of the SiO2 nanoparticles even at high volume fraction.

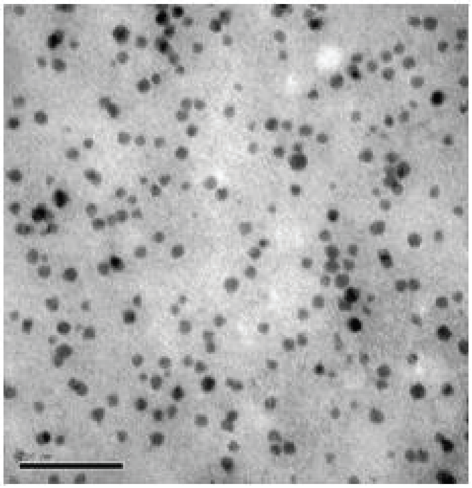

Figure 1. TEM micrographs showing a homogeneous dispersion of 5 wt %[6].

3.3 Scanning Electron Microscopy (SEM)

SEM uses focused beam of electrons which produces images of a sample by scanning it. The polishing of surface is done to make it conductive. The polished specimen was used to contemplate clay dispersion at different magnification. Figure 2 shows the SEM micrograph of nano filled GFRP composites resulting in homogeneous distribution of the reinforcement in the matrix[3].

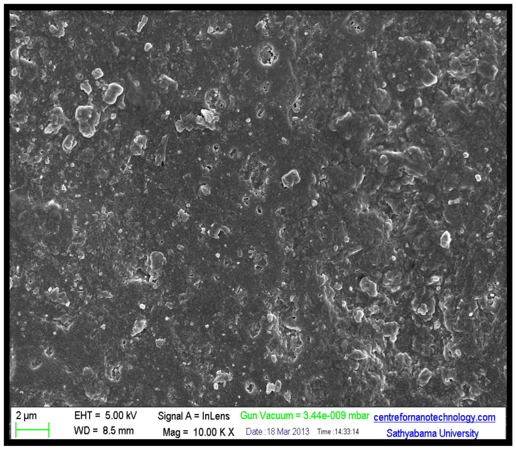

Figure 2. SEM Micrographs[3].

4. Properties Enhancements

The aim for the addition of nanofillers to the polymers is to improve the polymer properties and to produce the polymer nanocomposites with desired properties. Because of the low price, availability, high aspect ratio as well as desirable nanostructure and interfacial interactions, clays can provide dramatic and adjustable improved properties at very lower loadings which help to the more remaining of polymer original useful properties. In this section the various improved properties of polymer nanocomposites are discussed.

4.1 Mechanical Properties

Nanocomposites prepared with addition of Cloisite 30 B nanoclay in epoxy and E-glass fibres have shown an increase in the tensile strength, flexure strength and micro hardness[4]. The increase in wt % of nano CuO improves the compressive strength of the glass reinforced fibres composites[5]. The tensile strength increases with addition of clay up to 3 wt% but more addition of clay shows a reduction in the strength[14]. The tensile strength of PP/MMT nanocomposites at both Room Temperature and 77 K reached the maximum at the 5wt. % MMT content, increased by 3.1% and 13.2%, respectively, as compared with those of pure PP sample[11].

Both the elastic modulus and storage modulus got improved on addition of clay particles in virgin epoxy and mainly the value of modulus raised by adding more clay content[15]. The notched impact strength at room temperature increased from 22.33 J/m for the pure PP matrix to 36.53 J/m for the nanocomposite with the 5wt% MMT content[11].

Effect on interlaminar shear strength was also noticed as it decreased from 18.6 MPa to 14.9 MPa, with introduction of nanoclay content up to 4 wt%. In addition to this, maximum value of flexural stiffness was attained 4% loading of nanoclay[16]. Figure 3 shows the pattern for interlaminar shear strength and flexural stiffness by addition of different weight percentage of nanoclay.

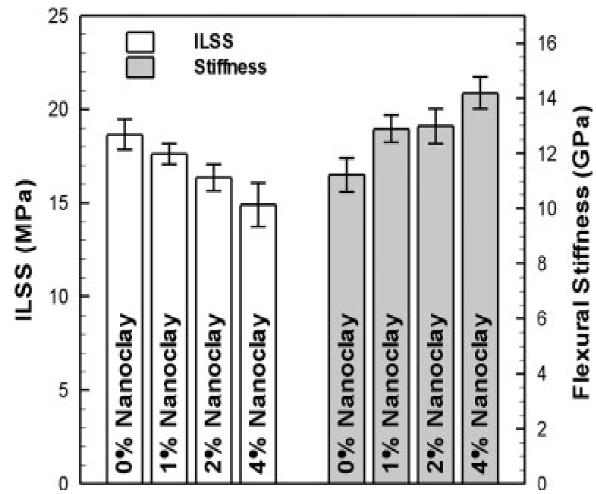

Figure 3. Stiffness and ILSS vs Nanoclay content[16].

Results of durability studies showed better results for the nanocomposites as compared to specimen with virgin epoxy matrix. Nanocomposites resulted in less degradation in tensile and flexural strength when exposed to water and alkaline medium for a period of one month. The curvy path resists water penetration which was caused by the addition of both glass fibre and nanoclay in epoxy[4]. The results of low-velocity impact response indicated a significant improvement in the energy absorption capability with a decrease of the peak impact force due to nanomodification[5]. These Results are very useful for human protection systems, as it needs maximum energy absorption while keeping the impact force lower than a specified level.

4.2 Thermal Properties and Barrier Properties

Due to inherently high Coefficient of Thermal Expansion of plastic materials they are not used in various applications like in automotive parts where thermal stability is important. On scattering clay particles in matrix phase tends to reduce the CTE of pure epoxy and improvement of their thermal stability[17].

Clay being naturally impermeable increases the barriers properties of polymers by offering tortuous path that retards the diffusion of gas molecules through the matrix. On addition of organo montmorillonite to epoxy/glass fibre composite showed improved water resistance properties which are due to tortuous path offered by presence of nanofillers[12]. The incorporation of poly (methyl methacrylate)–graphene oxide (PMMA-GO) nano-fibre mat inside the plain polymer layers presented nearly impermeable barrier to passage of oxygen gas indicating very high suitability in packaging and oxygen sensitive chemical processing applications[18]. The barrier properties largely depend upon aspect ratio of clay scattered in the matrix as well as increasing of exfoliation or dispersion degree.

5. Conclusion and Future Scope

We have discussed various potential benefits of using nanofillers in polymer composites in this review paper. Depending upon the various property enhancements there are several applications of nanocomposites such as timing belt cover of Toyota having polyamide 6 as matrix and exfoliated clay due to improved stiffness. Carbon nanotubes as fillers in epoxy increases strength and stiffness so can be used in tennis rackets and hockey sticks. Polyisobutylene as polymer matrix with small amount of clay produces permeability barriers so can be used for making tennis balls, tyres and soccer balls. Natural rubber mixed with small amount of silver nanoparticles can be used for latex gloves as they are antimicrobial. We also know that sandwich structures having different cores (Honeycomb, foam) that is normally low strength material but its higher thickness provides the sandwich composite with high bending stiffness with overall low density. The use of light core reduces the weight so this weight reduction results in a number of benefits, including increased range, higher payloads and decreased fuel consumption. All have a positive impact on cost as well as a decreased impact on the environment. Many researchers have worked on sandwich structures and summarized that the sandwich structure has better mechanical characteristics compared to its components such as enhanced fatigue resistance, withstands higher loads, possesses greater rigidity and increased the ultimate strength of the composite sandwiches. So we can see whether by replacing composites by nanocomposites in sandwich structures could produce improved properties than the simple sandwich structures.

6. References

1. De S, White J. Short fibre-polymer composites. Cambridge, England: Woodhead Publishing Limited; 1996.
2. Usuki A, Kawasumi M, Kojima Y, Okada A, Kurauchi T, Kamigaito O. Swelling behavior of montmorillonite cation exchanged for ω-amino acids by -caprolactam. Journal of Materials Research. 1993;8(06):1174–8.
3. Rajmohan T, Koundinya UK, Arun P, Harish G. Evaluation of mechanical properties of nano filled glass fiber reinforced. IEEE International Conference on Advanced Nanomaterials and Emerging Engineering Technologies, (ICANMEET); 2013 Jul 24–26; Chennai.
4. Sharma B, Mahajan S, Chhibber R, Mehta R. Glass Fiber reinforced polymer-clay nanocomposites: processing, structure and hygrothermal effects on mechanical properties. Procedia Chemistry. 2012;4:39–46.
5. Aymerich F, Via AD, Quaresimin M. Energy absorption capability of nanomodified glass/epoxy laminates. 11th International Conference on the Mechanical Behaviour of Materials, Procedia Engineering; 2011.
6. Jumahat A, Soutis C, Abdullah SA, Kasolang S. Tensile properties of nanosilica/epoxy nanocomposites. International Symposium on Robotics and Intelligent Sensors, Procedia Engineering. 2012;41(2012):1634–40.
7. Jumahat A, Soutis C, Mahmud J, Ahmad N. Compressive properties of nanoclay/epoxy nanocomposites. International Symposium on Robotics and Intelligent Sensors, Procedia Engineering. 2012;41(2012):1607–13.
8. Azzam W. Behavior of modified clay microstructure using polymer nanocomposites technique. Alexandria Engineering Journal. 2014;53(1):143–50.
9. Dobrzanski LA, Bilewicz M, Viana J. Polymer nanocomposites reinforced with montmorillonite. Archives of Materials Science and Engineering. 2012;53(1):5–28.
10. Khankrua R, Pivsa S, Hiroyuki H, Suttiruengwong S. Thermal and mechanical properties of biodegradable polyester/silica nanocomposites. 10th Eco-Energy and Materials Science and Engineering Symposium, Energy Procedia. 2012;34:705–13.
11. Manoharan N, Selvakumar V. Cryogenic mechanical properties of PP/MMT polymer nanocomposites. Indian Journal of Science and Technology. 2014;7(S7):16–23.
12. Chow W. Water absorption of epoxy/glass fiber/organo-montmorillonite nanocomposites. eXPRESS Polymer Letters. 2007;1(2):104–8.

13. Wetzel B, Rosso P, Haupert F, Friedrich K. Epoxy nanocomposites – fracture and toughening mechanisms. Engineering Fracture Mechanics. 2006;73(16):2375–98.
14. Puggal S, Mahajan S, Dhall N. A study on glass fiber reinforced polymer- clay nanocomposites with sandwich structure. International Journal of Research in Engineering and Technology. 2014;3(7):194–8.
15. Yasmin A, Luo J, Abot J, Danial I. Mechanical and thermal behavior of clay/epoxy nanocomposites. Composite Science and Technology. 2006;66(14):2415–22.
16. Aktas L, Altan M. Characterization of nanocomposite laminates fabricated from aqueous dispersion of nanoclay. Polymer Composites. 2010;31(4):620–29.
17. Paul DR, Robeson L. Polymer nanotechnology: Nanocomposites. Polymer. 2008;49(15):3187–204.
18. Upadhyay J, Das R, Rao S, Liu D, Bhattacharyya D. Manufacturing and characterisation of PMMA-Graphene Oxide (GO) nanocomposite sandwich films with electrospun nano-fibre core. Journal of Achievements in Materials and Manufacturing Engineering. 2012;55(2):835–40.