

The Effect of Nano Filler Material on The Polymer Based Nano Composites – A Review

Vishadeep Singh¹, Manjeet Singh¹, J S Saini²

¹Mechanical Engineering Department, Lovely Professional University, Punjab, India

²Mechanical Engineering Department, Thapar University, Patiala, Punjab, India.

Abstract: Nano composite are being used in most of the applications nowadays. The addition of nano particles to the composites has been reviewed in this paper. The various methods, the processing techniques and their effects on the various properties like physical properties, mechanical properties, glass transition temperature were studied. When the different nano particles are added their shape and volume percentage of these nano particles effect these properties which are reviewed in this paper. This review will help to serve as a reference for future research work.

Keywords: Polymer nano composite, Filler material, Properties.

1. Introduction

The traditional material in majority of the engineering applications are being replaced by the composite materials. The composite material is formed when two or more materials mixed at macroscopic level. It mainly consist of the reinforcement phase and matrix phase. The reinforcement phase can be the continuous or discontinuous fibers, also the reinforcement phase can be in the form of particles. The properties of the composite are mainly controlled by the length, shape, orientation and material of the reinforcement phase. The matrix phase also plays the major role in the strength of the composite. The mechanical properties of the matrix phase is low as compared with reinforcement phase but still it is used because it acts mainly as the binder. In the composite material when the load is applied it directly acts at the matrix phase and then this load is transferred to the fibers through fiber-matrix interface. The study of this matrix phase or resins which are used as binder is of utmost importance. The different materials, there properties, there behaviour are studied in this paper. Also the effect of the nanoparticles when added to these resins, how the properties are changed has been studied in this paper.

2. Effect of filler material on nano composites

Liu *et al* [1] studied a new altered method for the formation of hybrid composites. They used epoxy resin and silica to form the composite. To form the resin phenolic novolac curing agent was mixed with cresol novolac epoxy and processed with the sol-gel reaction of tetraethoxysilane. Due to its low thermal expansion, excellent thermal stability and high-reaching glass transition temperatures it was used to construct epoxy molding compounds. As per observation, silica had higher degree of condensation with more pieces of siloxane bridges were $p > 80\%$ measured by Si NMR. The major usage of epoxy resin is as an outer cover for electric circuits and devices. PF-silica and cresol novolac epoxy along with 500ppm of triphenylphosphine were mixed to analyze curing cycles from DSC tracing of reactions performed at different temperatures ranging from 160-220°C.

Maet *al.*[2] studied about the phenolic resin Nano composite and the impact of elastomeric nanoparticles (which includes nitrile butadiene and carboxylic nitrile butadiene rubbers) on the behavior of phenolic resin. PR-nanoparticles has been modified with 5 wt% of elastomeric nanoparticles which brought about up gradation in impact strength, flexural strength and heat resistance. Irradiation process has been used to manufacture these elastomeric nanoparticles which are exceptional ultra-fine full vulcanized powdered rubbers, so it increased the toughness in phenolic composite. As per scanning electron microscope images there were number of minute cracks formed on the fracture surface, by introducing elastomeric nanoparticles, as it got evenly diffused in phenolic matrix having approximate diameter of 100nm. Due to the toughening effect the size of dispersal phase was smaller as compared to conventional rubbers. These cracks can deplete impact energy and enhance the impact characteristics of phenolic composites. As per different analysis, presence of appropriate interface between nanoparticles and phenolic is the major reason for great thermal property.

Huanget *al.*[3] studied about the cryogenic tensile properties and thermal expansion coefficient of SiO₂/epoxy Nano composites which was prepared via sol-gel process using epoxy and tetraethylorthosilicate. It was also compared with tensile properties at room temperature. The cracked surfaces of samples were inspected with SEM pictures. Tensile strength observed at low degrees was much higher as compared to raised temperature. By adding silica nanoparticles, the failure strain was marginally boosted and the composite strength also increased significantly. This happened because matrix strength and adhesive strength at interface was much higher at low degrees. On the other hand, at room temperature, it certainly improved. Also the average thermal expansion from 298K to 77K was apparently cut down as aimed by cryogenic application but glass transition temperature has been increased by introducing silica nanoparticles. At the given cryogenic temperature the matrix became brittle and cracks could be easily seen in it.

Kaynak and Tasan[4] studied the effects of production parameters of nano composites. The layers were produced when clay was mixed with resol resin. They studied the effects of mixing methods, for how long the components are mixed, what is the effect of temperature, different resins, modification in clay and clay amount curing method were analysed. All these parameters were analysed using morphological study of the samples. The two main processes involved for curing were heat cure route and acid cure route. Preserved Cloisite Na⁺ and altered Rheospan clays were used. Two main origin for these clays were USA and Turkey. Different clay quantities were introduced one after the other ranging from 0.5% to 10%. As per the observation of different tests like SEM, TEM, XRD and other mechanical analysis it led to better structure when it was blend with ethylene glycol and acidic curing agent. The altered clays with approximate 1.5%wt in phenolic matrix brought better mechanical performance, structure and exfoliation.

Su *et al.* [5] studied about mechanical and tribological characteristics of carbon fabric composites consist of various nanoparticles like SiO₂, TiO₂ and CaCo₃. The method used for manufacturing is dip-coating which included phenolic resin too. The friction and damage performances of carbon fabric based polymer composites falling over AISI-104 steel on pin on disc structure was examined on a Xuanwu-III great temperature friction and depreciation tester. Scanning electron microscope and energy dispersive x-ray analysers were used to

analyse the arrangement of worn-out area of carbon fabric in both the condition of filled and unfilled along with the transfer films on steel pins. The elemental plane distribution on the transfer films were also studied. The nanoparticles were observed to improve the mechanical attributes and wear and tear resistance of the carbon fabric. Nano-calcium carbonate as the filler was adequate and efficient to increase the wear resistance however silicon dioxide in increasing the friction reducing capability. Nano grainy as the contents devoted to raise the bonding strength between carbon fabrics and adhesive resin.

Chen *et al.* [6] studied the effects of dispersion process on tribological characteristics by synthesizing carbon nanotube reinforced epoxy resin nanocomposites. The carbon nanotubes were preprocessed in 3 ways i.e. pretreatment, stimulating in HNO_3 and stimulation in HNO_3 along with coupling agent. The twin asymmetric centrifuge, sonication and hand mixing were various methods used for dispersing and blending the materials. DSC used for study of curing behavior and DMA for the study of thermo mechanical attributes. Ball-on-prism test was conducted to examine the tribological properties under which composites were slide against austenitic stainless steel. For untreated carbon nanotubes, the wear resistance seemed to be improved with the increasing force put into dispersion. There were positive effects of sonication and even much better wen incorporated with dual asymmetric centrifuge. A pretreatment with nitric acid and saline coupling agent improved the wear resistance however preprocessed carbon nanotubes required to be dispersed without ultrasound as it seems dangerous for pretreated carbon nanotubes.

Suet *al.*[7]have discussed about the tribological and mechanical properties of the composite which was prepared from the Nomex fabric. The properties were analysed for the composite which was in pure form and when the nanoparticles were added to the composite. The SiO_2 nanoparticles and polyfluo 150 wax (PFW) was added to the composite. To prepare the composite phenolic resin was used. The adhesion and tensile strength of the composites were analysed and found that the properties improvedwhen PFW and SiO_2 was added, as compared with the pure composite. The composite with PFW exhibits the lowest wear rate and friction coefficient. The morphological study of the composites has been done using SEM images of the samples prepared from composites. It was found from these SEM images that fiber pull outs are observed in unfilled composite as well as cuts in the matrix material.

Tai *et al.*[8] studied the properties of single walled carbon nanotubes (SWCNT) which were reinforced with phenolic resin. To prepare the composite chemical vapour deposition method was used. The strength and modulus was analysed for the composite prepared. The modified Halpin Tsai equation was used to compare the theoretical and experimental results. The theoretical and experimental results are approximately same. The tensile strength and young's modulus increases by 20% and 30% respectively with varying percentage of SWCNTs. The morphological study shows that when the volume of SWCNT is low, it bridges the cracks whereas with high loading the penetration of resin with SECNT was inadequate.

Larsen *et al.* [9] investigated the properties of the polymer matrix composites. The main aim of their study is to improve the properties of the epoxy resin while preparing the samples of composites. To improve the properties they added polytetrafluoroethylene (PTFE) micro particles and Copper oxide (CuO) nanoparticles. The samples were prepared from neat composites and composites with nanoparticles. The volume of CuO particles were varied upto 10% whereas the PTFE particles were fixed at 7.5%. The hardness, glass transition

temperature, friction and wear properties were analysed. The morphological study shows that the particles are properly diffused in the resin. For the samples when only the CuO was added the wearing of the sample increases, which shows with addition of CuO strength of the epoxy decreases. Whereas with addition of PTFE and CuO at certain volume percent, will reduce wear and friction.

Tsai *et al.*[10] investigated the improvement of physical properties of the epoxy based nano composite materials which were used to make printed circuit boards. They have prepared the nano composites which were improved by the different clays. The novolac cured epoxy resin composite was prepared by layers. These layers were made up of montmorillonite and nontronite. The modifier and accelerator were added to improve the properties of the nanoclay. The thermal and mechanical properties were analysed by transmission electron microscopy (TEM), dynamic mechanical analysis (DMA), thermo-gravimetric analysis (TGA) and wide-angle X-ray diffraction (WAXD) methods. From the results it was found that the properties are improved when BEN-Benzalkonium Chloride modifier is added to nano composite.

Su *et al.* [11] have studied the tribological behaviour of hybrid composite. This hybrid composite was prepared with glass and PTFE fabric. The phenolic resin was used to bind the fibers and also the effect of addition of TiO₂ nano particles along with the binders were studied. The friction and wear properties were analysed. The morphological study of the samples were done using SEM images. The result shows that 4% of nanoparticles when added to the binder improves the friction and wear properties under dry conditions it is not suitable for wet conditions.

Wang *et al.*[12] studied the thermal stability of the nano composites. Boron and clay were mixed in phenolic resin to prepare the nano composite. These nano composites were prepared in situ polymerization of resol type phenolic resin. The clay with the phenolic resin improves the thermal stability of the composite. The authors studied thermal stability and moisture uptake when boron is added to the nano composite. From the results it is clear that the layers of clay are properly dispersed in the matrix material. The thermal decomposition temperature was increased by 21 – 57 °C with addition of boron whereas 9 – 14% of moisture uptake was also increased with it. To reduce the moisture uptake up to 4 – 6%, the boron containing phenolic resin was prepared by reacting the boric acid.

Tasan and Kaynak[13] investigated the mechanical properties of the resol type polymer layered silicate nano composites. They studied the effects of amount of clay added, modification of clay and curing of clay. The properties were checked by performing flexural test and Charpy test. The result shows that chemically cured composites are stronger. The improvement in flexural strength, flexural strain, impact strength and toughness was approximately 7%, 11%, 16% and 66% respectively.

Bilogurova and Shevtsova[14] studied the properties of the composite when iron and diamond nano sized powders are added to the composite. With the small amount of diamond nano powder when added increases the strength of the composite by approximately two times whereas it decreases the dielectric permittivity so as to increase this property of the composite iron nano powder is added to the composite.

Zhang *et al.* [15] studied the effects of nano silica when added to the carbon fabric reinforced polymer composites. The phenolic resin was used as a matrix material. From the results it was found that when the layer of silica is added to carbon fabric its friction and wear properties are improved. When the surface of the carbon fiber was treated, the adhesion between the matrix and fibers are improved which ultimately leads to improvement of tribological properties of the composite.

Schutz *et al.* [16] investigated the improvement of the properties of phenolic resin nanocomposite. This nano composite also consist of silsesquioxane. The mechanical and thermal properties were studied for the prepared composite. From the morphological study of the composite it was found that silicon is evenly dispersed in phenolic resin and during the condensation of the precursor no large particles were formed. The bending strength and strain was improved by 36% and 51% because of the formation of silsesquioxane. Also the decomposition temperature of the nano composite is more as compared with the pristine resin.

Chen *et al.* [17] studied the characteristics of the nanoprepreg which were used for the preparing nanocomposites. The epoxy resin was used as a matrix phase and carbon nano tubes (CNT) was used as a reinforcing member. The reinforcing agent was treated with titanium(IV)n-butoxide to modify the CNTs. The properties of the prepregs were examined and found that the modified CNTs give more strength than unmodified CNTs. The reason for the improved strength is that the proper distribution of CNTs in the matrix phase and the proper interfacial bonding between the reinforcing phase and matrix phase. At the elevated temperature the strength of the material decreases also the cracks are formed due to different expansion coefficient. The mechanical failure is because of the fiber pullout and delamination. Moreover the conductivity of the material is enhanced with the addition of CNTs.

Ayatollahi *et al.* [18] studied the multi walled carbon nano tubes reinforced with epoxy nano composites. In their research work they investigated the boundary conditions using finite element analysis and these results were used to find the stress. With the addition of nano tubes the strength was improved except the elongation at break. They also found the toughness was improved when shear loading was applied on the specimen with the presence of nano tubes.

He *et al.* [19] examined the properties of carbon reinforced composite when the nano particles of calcium carbonate was mixed with epoxy matrix, the addition of nano particle improved the mechanical properties as well as thermal properties. The small amount of nano particles improved the properties of the composite because of the reason that nano particles were properly dispersed in the matrix phase which reduces the defects between the fibers and filler material.

Ku *et al.* [20] did a pilot study about the tensile properties of phenol formaldehyde Nano clay reinforced composites. Different samples of Nano clay with different percentage of weight was prepared. Afterwards cured in microwaves and ovens. Then tensile tests were performed on them. As per result, the composite with 5% wt of Nano clay produced the best result. It also boost the tensile strength and Young's modulus along with the acceptable fluidity for casting. The weight percentage ranging from 0 -3, the samples post cured in ovens ad more yield strength as compared to post cured in microwaves. Later, by extrapolation to 5 % wt

Nano clay, the results were totally opposite i.e. tensile strength and Young's modulus in oven was lower than in case of microwaves. ISO-527-1 standard was used for tensile strength. The reinforcer used was Cloisite 30B (Nano clay).

Alamri and Low [21] studied the effect of water absorbed by the composite material. They also studied the effect of various nano particles like silicon carbide, halloysitenano tubes and clay. They investigated the mechanical properties like toughness, impact and flexural strength. Their study showed that with the addition of nano particles the water absorption by the composite, flexural strength and modulus decreases, the reason for such behaviour was the nano particles formed twisted shape and plasticisation respectively. Whereas the impact strength and toughness increased with water absorption because of the mobility of the matrix phase.

Mittal *et al.* [22] reviewed about the various methods for producing carbon nano tubes and graphene which are used as a filler materials. They also studied about the effects of alignment of carbon nano tubes in the composites. The effects on the mechanical properties of these nano fillers are studied. Also the applications of these nano composites were discussed in their research work.

Zare [23] studied the mechanical properties of the nano composites with the addition of nano particles. The effects were studied on the various samples which were prepared from poly ether ether ketone, poly vinyl chloride, polypropylene and polypropylene with maleic anhydride. The nanofillers of silicon dioxide and calcium carbonate were added to these polymer composites and their effects were studied. From the results it was found that with the addition of fillers and reducing the size of filler materials will increase the aggregation level and will also reduce the effective volume fraction and will result in less effectiveness of nano particles in composites.

Bhattacharya [24] compared the different nano fillers to prepare the composite. He reviewed the various methods to process the carbon nano tubes, graphene and clay to prepare nano composite. He highlighted the benefits of various filler material in the composite. He discussed about the mechanical properties of carbon nano tubes and graphene based nano composites, electrical and thermal conductivity, thermal stability and glass transition temperature.

Aviles *et al.* [25] studied the properties of vinyl ester polymer nano composites which consist of carbon nano tubes, graphene oxides and graphene shells, these all are of different topology. They also investigated the properties of the hybrid composites which were prepared from these combinations. From the results it shows that the composites with carbon nanotubes and hybrid composite with carbon nano tubes and graphene oxide shows highest mechanical properties because of the reason that the flake like structures of graphene oxide favours the transfer of stress concentration. This combination also provided highest piezoresistive sensitivity. Whereas the hybrid combination of carbon nanotubes and graphene shells provided highest electrical conductivity.

Li *et al.* [26] in their study compared the mechanical properties of the composites in which carbon nano tubes and sheet of graphene was used as a reinforcement phase and poly methyl methacrylate was used as a matrix phase. The pull out simulations were performed on the models prepared from the specified material and the tensile properties were analysed. The

result shows that the graphene sheet samples provide high young's modulus, tensile strength and surface crack energy, these are 18%, 8.7% and 5% respectively, more than the samples from carbon nano tubes.

Rempeet *al.* [27] studied the effect of 3D nano particles in the composite material. A new technique was proposed to analyse the volume of unfilled polymer and degree of agglomeration and uniformity was analysed using free space length and pair correlation function. The silica filler material was added to matrix phase and were analysed using the mentioned techniques.

3. Summary

In this paper the effects of the nano filler material on the nano composites were reviewed. The various properties were analysed and it has found that the mechanical and electrical properties are improved with the addition of nano filler materials. The research till date has been done on the polymer composites which can be extended to the hybrid composites. The future scope of this study is that the effects of nano filler materials can be investigated on the hybrid composites. Also the various properties can be compared for different hybrid composite. Firstly one filler material can be considered and then its effect can be studied on the different polymer hybrid composites and then the filler material can be changed and the same study can be done on the hybrid composites.

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