A review of the recent developments in the field of polymer composites

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Abstract

In the past few decades, a considerable amount of research in the branch of polymer nanocomposites has taken place which has revealed their astonishing benefits in multifarious applications. As a result of this, their uses in sports industry, automobile bodies, and in biomedical instruments have also increased. Furthermore, these advanced composites can be easily manufactured and tailored to impart the desired combination of electrical properties, mechanical properties, anti-corrosive properties, improved reliability, and thermal stability. This current research review paper focuses on multiple models, tools, and theories used to engineer the epoxy based nanocomposites. Apart from this, this review also accentuate the influence of fillers (nano sized) addition on mechanical, water resistance, anti flammable, morphology, and thermal properties on them. Prior research work depicts that the inclusion of nano particles such as metal based nanoparticles, carbon nano-tubes, layered silicates, and nanofibers, of varied dimensions in the thermoplastics and thermosetting plastics acquires an intense aspect ratio(i.e. surface area/volume), which results into improved properties. Hence, our analysis would intend to uncover future scope, highlight the gaps in research, and suggest methods for manufacturing of advanced nano polymers with controlled thermal, mechanical, and electrical properties.

Keywords: DMA(Dynamic Mechanical Analysis, Nano-materials, Electron Microscopy, XRD (X Ray Diffraction), TGA(Thermograviometric analysis), Polymer nanocomposites.

1. Introduction

Epoxy resins (a thermosetting polymer) owing to their cross linked microstructure, exhibits improved tensile modulus, remarkable adhesion properties, and anti corrosive as well as anti chemical resistance at elevated temperature. [1]. Nevertheless, like the majority of polymers, the epoxy is also fragile and present low impact resistance and lack of resistance to crack propagation. [2]. This issue of low fracture toughness can be resolved by incorporating thermoplastics and rubber in epoxy; [3,4], however, this could also lead to low glass transformation temperature, low strength, and loss of stiffness.[5]. Another technology to control this vulnerability of polymer composites is to use fibres in epoxy matrix to provide them adequate strength. This modification has lead to possibility of using epoxy based composites in various industries like marine, construction, aerospace, and automobile companies. FRPs( Fibres-reinforced polymers) are also found striking as they have not only got high specific stiffness and specific strength, but they also comprises low decomposition at an elevated temperature range. Major failure modes of FRPs are cracking of matrix, delamination at interfacial region, and fibre’s fracture. These both fractures takes place due to failure of matrix phase. [5,6]. Hence, understandably both academicians and industrialists are focused on improvement of matrix stage with incorporating
particulate fillers, to enhance various attributes. The modification in the properties is mainly dependent on the size of nano filler, nature of filler, weight percentage of filler, and facade treatment of the fillers. In the last two decades, there has been a strong importance given to the polymer based nanocomposites, i.e. at least one of the proportions of the filler particles should have size in nanometres. The ultimate manufactured product should not be of nano-scale, but it can be in macroscopic or microscopic shape[7]. The nanometric scaled molecule such as platelet clays, multi walled nano tubes of carbon, and fibers in nano size with extremely elevated aspects ratio with its nano-scaled distribution within the chemical compound matrix has proven to become the basis of structures because these substances lead to the growth of the polymer’s properties at a very low level fillers amount [8].

1.1 Polymer based nano clay composites

Nano-technology refers to manipulation and control of the materials having a constituent of the size one to hundred nanometres, where one nm is equal to one one-billionth portion of meter to fabricate and designing a novel material or structure that goes through enormous changes in engineering properties because of their large surface area and unique exfoliated and intercalated microstructure[9,10]. Any material which has one of the constituent material of nano scale level (10^{-9} meters) are constantly have features which are dissimilar than their bulk scaled part. [11].

Despite the fact that clay polymers and nanoparticulates are mixed to manufacture a layered silicate nanocomposite, always two dissimilar variants of morphologies are formed; which are called intercalation and exfoliation. Intercalation arrangement is a well-ordered and arranged multi-faceted composition where the associated polymer bond are sited into the space wedged among proportionate silicate layers separated merely by 1-3 nm. Although exfoliation or delimitation pattern is achieved when layers of clay are considerably disconnected from each other and scattered around the never-ending polymer array. The exfoliation of clay or delaminating pattern is of much importance for the motive that they exploit the clay-polymer boundary constructing the whole subsurface area of the layers within reach for the polymers. This probably would direct the generally remarkable progression in the physical and mechanical attribute [12].

2. Materials Types (Nano)

In the modern world numerous style of nano particles exist, that are integrated in the array to obtain particular outcome to alter the physical proportions and chemical arrangement. A few of the nano particles are discussed below in depth.

2.1 Nanoclay

The majority and the most usually in use as well as considered for researched nano particle is Nano clay in the category of polymer nano composites. They are artificially made from physically existing clay natural resources. Clay based minerals can also be categorized as montmorillonite (MMT), kaolinite, chlorite, and illite pertaining to their class in crystalline structure [13]. MMT has extensive applications in the manufacturing of matrix nano composites, reason being the elevated exfoliation properties and aspect ratios. It contains two ratio one of sheet structure, two numbers of tetrahedral laminates of silica,
and into the centre of it carries an octahedral mass of alumina [14]. The grouping of these three different types of sheets has single layer of clay which is also well-known as ‘tactoid’, and have thickness of around 1nm. The sideways dimensions of these layers relied upon process chosen for production, resource of clay, and its size might vary from 350Å to many microns, as a consequence achieved an extremely elevated aspect ratio. The force which holds covers the layer of clay is exceedingly debilitated and is named as Van der waals force. [15]. Predominantly, really elevated superficial area of tactoid of exfoliated nano composites proven to be the best combination for the enrichment of features.

2.2 Carbon Nanoparticles

Before three decades ago it was well famous to the science community that there two allotropic shapes in which carbon exists in the world i.e. diamond and graphite. The tertiary variety of carbon that subsist is called fullerenes and this was found in 1986 [16]. However, few years later the nano tubes, both singular wall and multiple walled were discovered.[17]. Subsequently on micro-mechanical working of graphite sheds grapheme, that is the honeycomb like pattern of carbon particle and all atoms are related to one another by feeble Van der waal forces [18]. Singular walled nano-tubes and multiple walled nano-tubes both have a cylindrical shape. The only significant difference between both of them is that, the single walled nano tubes are made up of rolling up only a single sheet of grapheme. On the other hand, in multi walled carbon nano tubes further than one sheet is secured with Van der waals unit. Fullerenes have pentagonal and hexagonal faces in the form of hollow spheres of carbon [19].

Carbon black is also another enforcement material utilised in the polymer. They are acquired by incomplete burning and thermal disintegration of the hydrocarbons in the nuclear reactors and are ball-shaped in existence and its molecules are nano or micro-metric. These are enclosed in the polymer array because of their quality of enhancing the thermo-mechanical attributes [20].

2.3 Oxides

Silicon oxide, aluminium oxide, and titanium oxide in ball-shaped shape have nano porose structure and they possess a substantially elevated circumstantial surface area and considerably smaller dimensions (5 to 40 nm in dia.) are largely in use nano oxide powders in modern polymers [21]. This procedure includes the production of minute oxidized compound particles, i.e. Hydrolysis at an elevated temperature range, silica molecules, for instance, are derived from silica tetrachloride, and aluminum oxide from alumina tri-chloride and titanium from titania tetra-chloride. Oxidized compound formed from these processes are called oxidised fumes. Some of the other sophisticated methods concerned in microstructure of this nano permeable molecules are sol-gel process and chemical change procedure.

Various functional groups residing on the nano materials surface are responsible for nano silicon and aluminium particles dispersion in water. OH group emerges property hydropholic in silica. Strong aggregates due to hydrogen present lested to major disadvantage. Weak Inter particle forces tends hamper the dispersion [22]. This hydrophilic behaviour could be modified with technique of surface assimilation of shortened ligament polymers with the aid of electrostatic interaction and hydrogen
attractive force. [23].

Functional groups upon the superficial area are the key factors deciding aluminium to be hydrophilic or hydrophobic. Nano alumina can perform effectively in presence of hydroxyl group, assisting it to dissipate in polymers and polar solution. Varying temperatures during manufacturing of nanotitania fumes results different structures. Titanium dioxide emerges into two different crystalline forms with hydrolysis at 1300K[24]. Optics and photocatalytic operations are its major applications. UV rays improves the photovoltaic effect. Modification on the surface of semiconductors can improve the capability of titania nanoparticles.

2.4 Nanocarbides

Carbide is a well known refractory material as it melts at a high temperature. It also has high hardness and are used in powdered form as abrasives. Few examples of carbides are SiC and B₄C, these both have same crystalline structure as diamond. Boron carbide in terms of hardness comes just after diamond. The generation of these carbides is done in an electric arc furnace. During heating oxides reacts with carbon as their thermal reduction takes place[25]. Finally, to achieve the desired size milling of the obtained carbide is done.

Oftentimes popularized carbides are silicon, boron, and carbide. The nano-metric molecules of carbides possesses the ability to upgrade the wear opposition of the polymers [26]. That is likewise utilized as coverings on carbon and different structures for its utilization at elevated temperature and amend thermal obstruction [27]. Clay coverings of zirconium are utilized to amend protection from oxidation [25]. For graphite holding at higher temperature, phenolic sap is utilized as cement with smaller scale enforcement as B₄C to direct it towards higher temperature range and it was seen that it displays its most elevated capability at 1000°C [28].

2.5 Other Nanoparticles

These days, if nature mindfulness is considered, the for the most part utilized materials for development of nanostructures are the inexhaustible assets and biodegradable lattices of polymers. The promptly accessible wide assortment of biodegradable/natural source is vegetables to be specific cellulose, starch, and some more.

Cellulose Nanocrystals, the filaments existing in plants in cell divider and every fiber comprises of crystalline microfibrils prepared of unbending cellulose existing in lignin (shapeless stage). Cellulose, a polysaccharide, its rehashing parts are alluded in the form of cellobiose [29]. Their measurement shifts in length from 4-10 nm and angle proportion exists somewhere in the range of 6 and 50. They contains attribute to give higher obstruction from acids [30] and have developed rigidity, modulus of elasticity and low effects of thermal extension [29]. Fuse of cellulose noncrystalline as filler in polymer network form them dissolvable in H₂O because of quality of hydroxyl bunch on its subsurface. While its filiation by hdrolysis, if sulfuric acid is included, it reduces the thermal stableness also [31].

Afterwards cellulose, the promptly accessible natural chemical compound is lignin. It is accessible in
shapeless structure and acquired from p-coumaryl, coiferyl and sinapyl with radical polymerization strategy. Contingent upon filiation technique, the quantity of practical gatherings (macromolecules) joined to lignin and their sub-atomic weight differs [32].

As of late, the handling of numerous metals with nanoparticles just as nano fillers in mixes in polymer resuled in astonishing outcomes in branch of mechanical, optics and, gadgets, and so on [33]. The bundling of bio-medicinal items has gotten conceivable with silverish nanoparticles because of its outstanding attribute of against microbial strength yet it can respond with liquid and could get ionized [34].

3. Fabrication techniques

Various strategies which are utilized for the arrangement of assortment of nanomaterials have been discussed. This acquire enthusiasm because of remarkable climb in the attribute of the material consolidated in nanoparticles in their framework. So the most basic factor is the way the scattering of nanoparticles ought to be consistent.

For creation of composites of CuO and polyester, ultrasonic exhibitor was used for two hours and in the wake of mixing, it was set in rotational shaker for homogenized blending for an additional 4 hours [35]. The shear blending procedure utilized for epoxy/graphite nanoplatelets composites [36]. Cross breed nanocomposites of MWCNT/MMT were dissipated in epoxy by sonicating and attractive mixing [37]. Scattering of zinc nano particles in epoxy composites was accomplished with ultrasonicator and vacuum warmer [38]. For composites of polypropylene, consideration of natural montmorillonite was handled utilizing twinned extruder at 190-200°C pursued by 110-170 rpm of screw speed [39]. Epoxy supported composites in nano powders of alumina and silica included shear blender and sonicator at higher vitality at low temperature [40]. In organoclay-polyester, composites at first mixing performed pursued by degassing, which is performed to expel globule development of the sap [41]. For scattering of CNTs in activated carbon filaments with CH3 and 2CO was finished by tar move embellishment and restoring was performed for various temperature and timeframe [42]. Epoxy with changing stacking used to produce dirt nanocomposites, utilizing high shear blending pursued by degasification invacuum and afterward relieving at 170°C [43]. Change composites with clay and unifacial E-glass strands was finished utilizing the most well-known technique for example manual layup strategy [44].

4. Methods used in characterisation of composites

The fewest modern and recognized methods all over the world to evaluate the distribution of nanoparticles in the polymeric and their diverse properties will be discussed in this section.

4.1 X-Ray Diffraction

The examination of the diffraction design in broad edge X-beam diffraction is finished utilizing Bragg’s law that grants recognizing the crystalline periods of nanoparticles assessing the area between layers of crystalline structure. The perspective, wideness and power of distinguishing peak in XRD spectra can be changed by altering the breadth of layer and this grants to get to the class of nanoparticles foundation.
According to the Bragg's law, “the variances of related peak continuing to lower or higher point of diffraction is brought about by change in d-spacing”. Level of shedding/intercalation could be dictated by evaluating the situation of peak in the nanocomposites. Intercalation designs that with relative abatement in relative point, there is climb in d-dispersing and in peeling, estimation of d-space and peaks are unrealistic because of scattered structures. This method could be used to appraise the spreading of fillers and non-crystalline particles such as silica [45].

Epoxy/MMT composites are presented to X-beam optical phenomenon and it was presumed that variances of top to bring down points proposes that clay is gently intercalated all through the lattice yet the filler isn't altogether peeled as translated by pinnacle. For assessment of intercalation of clay in frameworks, this system is utilized; however, now its utilization is extended up to peeling of shedding and scattering of graphene, graphene oxide nanoplatelets and cellulose nanocrystals separately [46,47,48]. nano platelets, graphene and its oxides, and nanocrystals of cellulose.

XRD has been utilized for examination of polypropylene fused nanoparticles made of iron and natural clay (OMMT) and this was seen that there is consistent scattering of particles in the network [39]. In other sample of epoxy with nanoclay and unidirectional strands and the outcome showed that there was intercalation between layer of clay [44]. The nanoclay is scattered with monomer I-28E alongside E-glass strands and aftereffects of XRD indicated peeling of platelets with increasing Inter planar space in the samples[49].

4.2 Electron Microscopy

TEM and SEM, especially two advanced methods utilized for getting amplified high resolution of scattered particles in the system. The essential distinction of the standards of two strategies is in TEM, picture is delivered by electronic cooperation by an electrical signal through ultra thin component, and on opposite side, amplified filtering is taken by concentrating a beam of light on the sample. Sample components for TEM should be kept thin safekeeping in thought that measurements are basically indistinguishable from mean free way of electrons which relocate all through specimens. For thermoplastics, a cryomicrotome is alluded as it permits to keep away from plastic decrement in the examples while it's coated. In SEM, the static charges are aggregated to anticipate that specimens should be semiconductive. For plastics ultra thin covering got from sputter covering or dissipation is being covered on it.TEM and SEM were led on Zno composite and it was noticed that the particles were very much scattered in the network of epoxy [50]. SEM assessment is directed on ether of bisphenol A organic compound was untreated with natural MMT nano and the outcome showed that it frames an non-miscible stage in epoxy lattice [51]. Crystal clear proof from epoxy fortified with E-glass filaments expressed that there is advancement in interfacial attraction of the soecimens made up of composites [49]. One more examination was directed on polystyrene gum with consideration of copper oxide and to examine about the smaller scale basic conduct SEM was utilized and the outcomes demonstrated that with increment in mass percentage the microstructure become better [52].

4.3 TGA analysis

This assessment is a trial methodology where proportion of progress in aggregative of test and to distinguish the procedures whether concoction or corporeal change that occurred in the wake of
heating[53]. The straightforward plan of TGA fuse systematic offset with elevated exactness to which test pan is united. Test skillet is usually abeyant inside a warmer, that is managed electronically. There are a few varieties in test and balance climates; however, they share managed condition created for the most part with having nitrogen gas. There are a few methods that gives variation environments and manages strain to adjust and test/warmer zone. This strategy is extremely helpful in looking at the procedures manages mass misfortune for example dynamic procedures of fluids and solids.

Composition of epoxy nanocomposites  with graphite particles were prepared and the investigations uncovered that thermal constancy of the composites were upgraded with expanding measure of filler for the most part because of high coefficient of conductivity just as has generally finer interfacial similarity of the nanocomposites [36]. Nanocomposites  were created and by TGA analysis it was seen that it has high soundness and change temperature in correlation with unadulterated epoxy [50]. Glass fibre fortified epoxy with tubes made of carbon innano size (CNT) show improvement experiencing significant change in temperature [54]. One more nanocomposite was made utilizing particles of oxides of titanium and alumina and greater progression was observed in T_g [55].

4.4 DMA

The portrayal of attribute that manages visco-elasto beahaviour of polymer is found by Dynamic Mechanical Analysis. This procedure inquire about the attribute of material distorted under strong pressure and found about modulus and damping. The data of material's presentation can be gotten through these measures. Assessment of wide scope of materials could be led utilizing this method, for example, coatings, different sorts if polymers, strands, and so forth. This system is erogenous for assessment of glass change range and auxiliary relaxations are promptly watched utilizing this procedure and cause trouble in different ones.

DMA is performed on epoxy having nanoplatelets of graphite and the results got displayed developed glass transformation temperature with expanding measure of fillers [36]. MMT and MWCNT composites were presented to DMA and it reasoned that utilization of half and half nano particles in epoxy showed increment in glass transition temperature[37]. Epoxy having TiO_2 or AL_2O_3 uncovered a move of top in damping towards higher temperature, stockpiling modulus was likewise seen to be elevated [54].

5. Attributes of Polymer Composites affected by addition of fillers in nano size

In this portion, attributes of chemical compound nano composites and their impact has been talked about. According to the above report, it very well may be effectively marked that with presentation of nanofillers there is improvement by and large proportions of nanocomposites, for example, wear opposition, mechanical toughness properties, electrical, optical and thermal attributes, and so forth. Even scattering of fillers brings about progressively developed attributes in composites particularly mechanical attributes as they go about as split arrestors. Hence, in network scattering and dissemination of nano- fillers are the imperative elements.

5.1 Mechanical Properties
Young’s modulus of the polymer composites could be developed by incorporation of hardened nano particles in polymeric networks. In support network, delicate polymer grid is replaced with a stiff nano particle which prompts move of stress from matrix frame to filler.

The to the highest degree developed filling nano particles in nano materials that was examined was dependent on the clay. The comprehensively bordered favorable position utilizing clay in nano form is it can prompt different polymeric frameworks. Critical enhancements could be made by incorporation of clay in nano form moderately in littler extents and they are of higher quality, sturdiness and rigidity [55, 56, and 14]. Unadulterated epoxy resin when contrasted and nanocomposites with clay in nano form implanted in it showed improvement in modulus[57]. Nanoclay in blend with nanocomposites formed by polypropylene prompts upgrade in moduli (tractable and flexural modulus), enhancements in yield quality that yet indicated decrease in greatest strain [58].

By and large, the pattern of augmentation of mechanical attributes with expanding use of nanoclay is on the rise; however, this conveys up to few of the constrained measure of reinforcement in nano size. A lot of nanoclay could prompt deficient peeling of clay which may leads to permanent flaws in material. Intercalated arrangement of clay particles and epoxy resin incomparable the break conduct when contrasted with shed one as extra surface for spread of splits was shaped with filler [59]. The nearness of silicates inflexibility get upgraded yet it unfavorably influences durability and relinquishing at purpose of break, which can cause development of enormous emptiness and splits [60].

For the thermosettings and thermo-plastics, silica, alumina and titania in the form of nano particles, perform as reinforcement agent and improve strength because of their nanospherical construction that expands the break direction [61]. By consolidation of aluminium oxides nano powder in polytetrafluoroethylene, the improvement in wear bearing characteristics was observed [62]. Different carbides and oxides which have hardness as a unique feature of their existence, reinforce the tribiological attribute and upgrade protection from wear. An ascent was observed in modulus of rigidity and consolidation of limited quantity of tubes made of carbon in nano size in epoxy likewise when contrasted and unadulterated epoxy the strength was additionally improved [63]. Augmentation in the Young’s modulus and quality was seen in common composites of elastic with tubes made of carbon in nano size and pliability was diminished [64]. Significantly, nanoplatelets of graphene are preferable in execution over tubes made of carbon in nano size in epoxy tar regarding different properties like sturdiness, break, modulus, and so forth [65]. Polyethylene terephthalate mix with polypropylene on shed graphene indicated advancement in tractable and sway quality [66]. Graphene is demonstrated as better strengthening object as opposed to dark carbon [67].

Polymer in nano structure incited its preferable consequences for grain gluten and polylactic corrosive as far as thermal-mechanical properties. These property were improved as its consuming develops low heat and it additionally represents extension/adaptability in the composition [68]. Cellulose nano crystals(CNC) because of development of inflexible hairs particularly over the glass change temperature encourage move of stresses that makes them alluring as fortification of polymers[69].

5.2 Electrical attributes

Polymeric can be changed over into conductive by incorporation of carbon nano-particles, for example,
nano-tubes of carbon, carbon nano-fibers of carbon, carbon dark and grapheme. In permeated anatomical structures, inclusion of conductivity is considered as least separation between subatomic particles. [70]. By fusing 0.3% by mass of carbon fibers in polyunsaturated polyester, raised the electrical conduction by six percent [71]. Scattering by 0.07 volume % of grapheme, conduction was made conceivable in ultra high atomic poly-ethylene [72]. Epoxy solution with the nano particles of graphene and nano tubes made up of carbon were accomplished and this was gotten that decrease in permeation and an elevated electrical conduction [73].

Expansion of carbon nano fiber in creation of fiber strengthened composites with fecundation of synthetic resin to glass filaments actuates detecting capacity to it. The application of carbon fibres has been featured that it powers the elastic strain of the manufactured composites when it is expected to utilized under high current passing situations. Moreover, fibers of glass strengthened with epoxy resins and carbon nano tubes prompts semi conductive properties which has been demonstrated advantageous for checking the harm brought about by electrical force [74].

5.3 Properties of thermal barrier

Chemical compound made up of plastics being exposed to an elevated temperature, the substance bonds existing between the atoms get interruption that reason debasement of chemical compound polymer and discharge smoke and different gases. For handling such problems, fire retarding chemical added substances ought to be added to it because thermal steadiness of the plastics gets developed [75]. There has been wide utilization of nano-clays in progress of thermal attribute. Nano-clay in epoxy prompts ascend in the thermal barrier security and fire attribute [76,77]. As the consideration of fired nanoparticles is done, upgrade of thermal attribute was ascertained, for example, covering of nano oxide. Fuse of different types of silica particles in plypropylene can decrease the discharging pace of warmth and loss of mass[79]. The utilization of nano- silica nano powders in phenolic/glass composite materials essentially form thermal barrier properties unrivaled and impede the pace of disintegration and weight loss[78]. Particles of alumina additionally amend warm dependability of epoxy network. Attributes of polymer materials with the joining of carbide materials are imaginative [80]. Boron carbide (B₄C) contribution in chemical compound changes in thermo steadiness and opposing heat attribute of complex chemical compounds with carbon nano particles[80].

6. Conclusion

At last this is reasoned that the scattering of nano-particles, being significant component for improved properties, if there should arise an occurrence of polymer nanocomposites. In addition, it has been seen that most extreme degree of fillers in nano size rate in polymers ought to be underneath five, to such an extent that dissipating is consistent. Contingent on the scope of attributes improvement there are many practical uses of composites. For example, carbon tubes in nano size as nano-fillers in the polymer made from epoxy help solidness and quality, because of this it very well may be used in tennis playing rackets and stick used in hockey. Butyl elastic as polymer by joining of moment amount of it shows penetrability bar along these lines and could be utilized for assembling football’s balls and tires used in automobiles. In forthcoming years, polymer nano-composites can be additionally overhauled by using
option of at least two sorts of nano-particles and also by chemically treating nano-particles or filaments, in order to accomplish different mix of thermo-mechanical and hindrance properties.

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