Processing, Characterization and Applications of Polymer Nano Composites - A State of the Art Review

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ABSTRACT

This review provides some information about various polymer nano composites and also different processing techniques available. Metallurgical and mechanical characterization of the nano composites have been discussed in this work. Tribological properties of various nano filler reinforced polymer composites has been discussed in detail as well. This review outlines brief introduction on importance of wear mechanism map in understanding the wear behavior of polymer nano composites. Polymer nano composite finds vast applications in various industrial sectors such as automobile, aerospace, defense etc. This review also renders short information on various applications of polymer nano composites.

Keywords - Polymer Nano composites, Mechanical Characterization, Tribological properties, Wear mechanism maps.

1. INTRODUCTION

The polymer resins are broadly classified into two categories (i.e) thermoset and thermoplastics. Thermoplastic resin usually consists of long polymer molecules which may or may not have side chain. Therefore thermoplastics can be repeatedly melted or solidify by subsequent heating or cooling. On the other hand thermosetting polymers cannot be recycled. Some of the commercially available polymers are shown in Table 1.

Thermoset	Thermoplastic	
Epoxy	Polypropylene	
Phenolic	UHMWPE	
Polyimide	PEEK	
Polyurethane	ABS	
Vinyl ester	Polytetraflouroethylene	
Polycyanate	Polyvinylchloride	
Polyester	Polyamide	

Polymer nano composites are hybrid organic inorganic materials with at least one dimension of the dispersion phase less than 100nm [1]. Due to the nano scale dimensions nano composites process superior mechanical and tribological properties. The Polymer nano composites can be synthesized using following methods.

- a) Melt intercalation
- b) In situ polymerization
- c) Hot pressing

Melt intercalation involves preheating the polymer granules at high temperatures and then adding the filler and finally mixing using high speed mixer to achieve uniform distribution [1].

In situ polymerization involves penetration of filler in the liquid monomer or monomer solution [1]. Hot pressing involves the mixing of powder using ultra sonication assisted milling and pressing of the powder at high temperature and pressure.

2. SYNTHESIS OF POLYMER NANOCOMPOSITES

Liu et al [2] reported on the preparation of Nylon 6/clay nano composite using melt intercalation method. Addition of nano clay to the polymer (nylon 6) matrix increases the mechanical strength and heat distortion temperature without much affecting the impact strength. The composites were prepared by melt mixing method using twin screw extruder. The processing temperature has been set as 230^oC and the rotational speed was kept at 30 rpm. The extrudate was then pelletized using pelletizing machine and the pellets are injection molded into standard specimens for mechanical testing. The injection molded parameters set as temperature 220^oC and pressure 13.5MPa.

Al-Saleh et al [3] discussed about preparation and characterization of Carbon nanotube (CNT) reinforced

Acrylonitrile Butadiene Styrene (ABS) nano composites. The composites were prepared varying CNT up to 10% by melt mixing using twin screw extruder. The powders were dried in vacuum oven for 16 hours at 80°C and 130°C before mixing in extruder. The processing temperature was kept at 220°C at a rotational speed of 100 rpm. The pellets leaving the extruder are then compression molded at a temperature of 220°C and a pressure of 28MPa.

Diffallah et al [4] prepared Polycarbonate (PC) composites reinforced with solid lubricant (MoS₂) using injection molding machine at a injection pressure of 724 bar and at a temperature of 290°C and a screw rotation speed of 220 mm/s.

ABS/PA6 blend reinforced with short carbon fiber and nano $CaCO_3$ has been prepared using twin screw extrusion followed by injection molding. The processing temperature is kept at 235°C at speed of 100rpm [5].

Polyphenylene sulphide/ Polytetra flouro ethylene polymer blend reinforced with short carbon fiber were melted and blended using twin screw extruder. The temperature Profile from barrel to the die was varied as 265°C to 295°C in nine zones. The pellets from the extruder are dried and then injection molded to form mechanical and tribological test specimen [6].

Ultra high molecular weight polyethylene(UHMWPE) reinforced with talc particles has been synthesized using hot compression molding technique, in which polymer powder was mixed with talc using dry ball milling process. The mixture was then preheated in a mould for 10min and then hot pressed. The composite samples thus obtained were allowed to cool to room temperature before they were cut according to test dimensions [7]. Powders of PEEK and Al₂O₃ have been dried before they were mixed through magnetic stirring in an ethanol medium and then the resultant powder was dried in an oven to remove the ethanol. Pure PEEK and its composites have been prepared using hot press under pressure of 15MPa and 350°C [8].

Yi-Lan-You et al [9] prepared polyamide nano composites reinforced with nano TiO_2 and PTFE by using twin screw extruder under processing temperatures of $210^{\circ}C$ to $240^{\circ}C$ in nine zones of the extruder barrel. The extrudate was cooled in water and then pelletized to produce granules, which is then placed in the injection molding die and is injection molded to produce tribological test samples.

3. RESULTS AND DISCUSSION

3.1 Microstructure

Jiang et al [10] prepared wrapped Graphite nano sheet reinforced PEEK composites and characterization of the composite was done using TEM image (Fig 1), which indicated that surface modification has no effect on the diameter of the GNS.

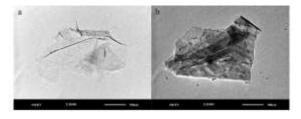


Fig. 1 TEM micrographs of GNS & wrapped GNS [10]

Kuo et al [11] studied the distribution of alumina nano particles into PEEK polymer using TEM image as shown in Fig. 2. From the above figure it can be inferred that alumina nano particles have been uniformly dispersed in the PEEK matrix.

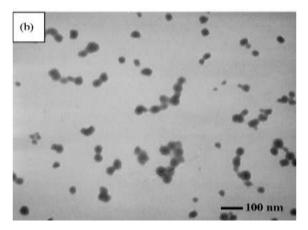


Fig. 2 TEM image of PEEK/alumina [11]

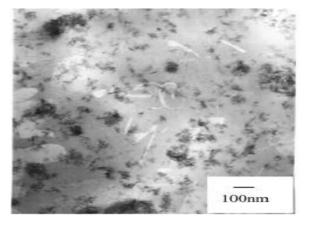


Fig. 3 TEM image of Epoxy-modified nano clay composite [12]

The dispersion of surface modified nano alumina in the epoxy resin was studied by Ya-Ping-Zheng [12] and it can be seen from the image (Fig. 3) that nano particles disperse uniformly in the resin.

The alumina nano particles appear well separated and also uniformly distributed with the polymer as shown in Fig. 4 [13].

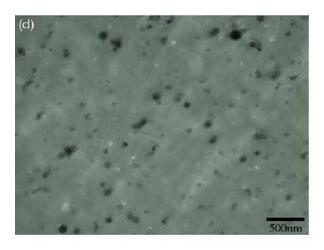


Fig. 4 TEM image of Polyethylene/nano alumina composites [13]

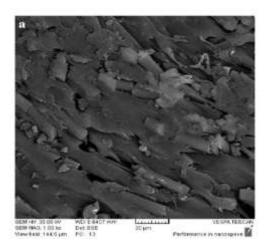


Fig. 5 SEM image of PEEK/SCF/nano silica hybrid composite [14]

Tourani et al [14] discussed the dispersion of nano silica and short carbon fiber in Polyetheretherketone (PEEK) polymer during extrusion using SEM (Fig. 5). During melt mixing the SCF breaks into small length and also white zones in image indicates the presence of Silica.

3.2 Mechanical Properties

The mechanical behavior of PEEK composites reinforced with SCF, graphite and various nano fillers

was studied by Harsha et al [15]. Table 2 show the tensile properties of various PEEK composites

Sample Code	Young's Modulus (MPa) LD TD	Tensile Strength (MPa) LD TD	Elongation at Break (%) LD TD
А	2490 ±76.6	102.2±0.9	38.9±2.9
	2518.2±50.2	102.8±1.4	34.2±3
В	4696.8±279.2	126.8±6.3	4.7±0.5
	3925.9±194.9	111.3±4.5	4.8±0.5
С	7279.3±300.8	136.2±7.4	3.0±0.1
	5617.8±190.8	111.3±4.0	3.0±0.5
D	6580.2±105.9	139.4±9.5	3.7±0.2
	4869.3±55.3	115.8±2.9	4.2±0.6

From Table 2, it can be inferred that the mechanical properties of PEEK reinforced with various fillers shows improved mechanical properties as compared to neat PEEK.

3.3 Tribological Properties

Luo et.al discussed the effect of addition of carbon fiber on the wear behavior of PPS/PTFE [16]. The addition of carbon decreases the coefficient of friction. As the carbon fiber content is low the carbon fibers can easily come out of the polymer matrix and hence coefficient of friction increases. Once the content of Carbon fiber (CF) increases it becomes difficult to break the hard CF particles which in turn lead to reduce in friction coefficient.

The incorporation of zirconia (ZrO_2) particles into the PI polymer matrix seems to reduce the friction coefficient of the composites. But when exposed to AO (Atomic oxygen), the friction coefficient of the composites slightly increases which can be attributed to the formation of ZrO_2 rich layer.

Wear rate and friction coefficient of PEEK reinforced with nano ZrO_2 increases with increase in load. This is due to high plastic deformation and scuffing mechanism. With the addition of SCF into the composite the wear rate and coefficient of friction of the composites decrease at higher load. This is because SCF supports most of the stress during sliding process, so that the hybrid composites exhibit superior wear resistance [17]. Tribological performance of PEEK composites reinforced with various micro fillers and PEEK reinforced with micro as well as nano fillers was studied. It is studied that the addition of nano powder reduces the friction coefficient. The increase in pressure increases the wear rate in both the composites. However the nano filler reinforced composites show less increase in wear rate with increase in pressure as compared to composites filled with traditional fillers [18].

The addition of WS_2 nanoparticles to the PEEK resulted in reduced wear rate. Addition of WS_2 (Fullerene shaped) showed 10% less wear rate as compared to neat PEEK, whereas WS_2 (needle shaped) particles reduce the wear rate approximately by 60% [19]. But the wear rate increases with addition of CNT and Graphite nano particles. The addition of CNT increases the wear rate of composites by 20% and wear rate of Graphite nano particles reinforced composites is almost three times higher than that of neat PEEK. These changes are mostly due to hardness of the reinforcing materials.. While WS_2 particles enhances the hardness of the composite, addition of CNT and GNP reduces the hardness thereby prone to more plastic deformation leading to higher wear rate.

ABS Polymer reinforced with graphite particles shows more wear resistance as compared to neat ABS polymer. ABS /7.5% graphite composite showed highest wear resistance [20]. Pure ABS shows poor wear resistance due to severe adhesive wear, whereas addition of graphite particles helps in reducing the adhesive and ploughing wear.

Addition of PTFE as reinforcement to PA6/GF composites helps in reducing the coefficient of friction and the wear rate. This can be attributed to the formation of the transfer film by PTFE which reduces the exposure of GF and also reduces contact between polymer and counter face [21]. The addition of UHMWPE as solid lubricant increases coefficient of friction and wear rate, which is mainly due to interface debonding between UHMWPE and PA6.

Tribological behavior of Carbon filled PPS composites were studied by Golchin et.al [22]. Three different carbon fillers namely SCF, MWCNT and Graphite are used as reinforcements. The results show that addition of short carbon fibers as reinforcement resulted in reduction of wear rate by 60% as compared to unfilled PPS. However addition of graphite and MWCNT did not improve the wear resistance significantly due to the pur bonding carbon fiber and the polymer matrix. Khare et al [23] experimented the tribological behavior of PEEK and its composites in water lubricated conditions. The results show that the COF as well as wear rate is minimum in PEEK + 30% CF followed by PEEK + 10% PTFE+10% graphite+10% CF.

Sliding wear tests of Polybenzimidazole were conducted at three different temperatures of 100, 150 and 200°C and at six different contact pressures (1 to 6 MPa) [24]. The results show that up to 3 MPa, the COF increases with increase in temperature and beyond 3MPa to 6MPa the COF decreases with increase in temperature. This is because at higher pressure and temperature the frictional heat reaches a stage at which the surface layer starts melting thereby reducing the COF.

Sudeepan et al [25] studied the wear behavior of ABS polymer reinforced with Tio_2 powder. Wear tests were conducted on block on roller tribotester and multi parameter optimization of the wear behavior is carried out using grey relational analysis [25]. From the results it is observed that normal load is the most significant factor followed by filler content and sliding speed.

PTFE powder when added with Kevlar fabric reduces the wear rate and friction coefficient up to PTFE content of 20% and thereafter increases. Similarly addition of graphite up to 15 wt% decreases the wear rate and friction coefficient of the Composite [26]. Both PTFE and graphite helps in formation of transfer film on the counterpart thereby reducing the wear rate and Friction coefficient.

Wang and Gao [27] studied the tribological behavior of PEEK and CF reinforced PEEK under sea water lubrication. The tests were conducted with a rotational speed of 100r/min, load of 100N and duration of 2h. It is inferred that PEEK/CF composites has lower friction coefficient.

Rajmohan et al [28] analyzed the wear behavior of MWCNT reinforced PEEK composites prepared using melt mixing technique. A linear regression model was developed to predict the wear rate of the composites and desirability based approach was applied to optimize the sliding wear parameters.

Plumlee et al [29] studied the wear resistance of UHMWPE reinforced with zirconium particles. The composites were prepared using compression molding at a pressure and temperature of 100MPa and 230^oC. The results indicate that with the addition of zirconium

particles the wear rate of the composite can be reduced without affecting its impact strength.

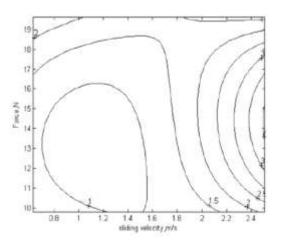


Fig. 6 Wear rate maps for long glass reinforced plastics [30]

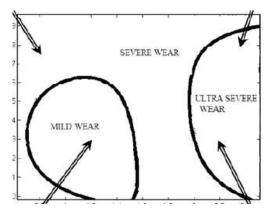


Fig. 7 Wear transition map [30]

The various wear mechanisms and wear regions as well as transition in sliding wear of long and short carbon fiber reinforced composites were identified using wear rate maps and wear transition maps as shown in fig 6 and Fig. 7 [30]. The different wear mechanisms were identified by SEM observation of worn surfaces. Wear transition map is developed by classifying the contour from contour maps based on the wear mechanisms Wear transition is observed from the change in direction of contour lines.

Fakhar et al [31] studied the improvements in tribological properties of polyoxymethylene by reinforcing aramid short fiber and PTFE. It is found that addition of aramid fiber and PTFE drastically reduces the wear rate.

Srinivasan et al [32] applied probabilistic neural network (PNN) for developing wear processing maps for glass fiber reinforced epoxy composites. Wear processing maps indicates the wear rate as well as mild wear, severe wear and ultra-severe wear and also transition between each mechanism as shown in Fig. 8 and 9.

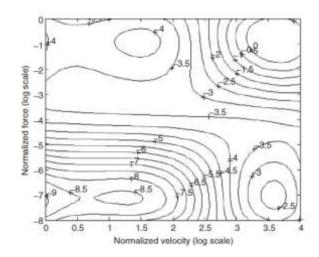


Fig. 8 Wear rate map for GFRP [32]

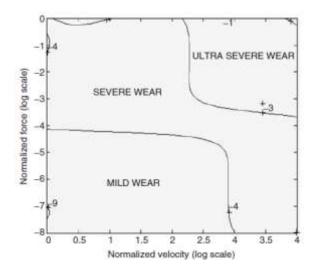


Fig. 9 Wear Transition map for GFRP [32]

4. APPLICATIONS

The use of plastics in automotive applications in Europe is 7 to 10% of mass of the automobile. The engineering plastic has mostly been used in automobile field for exterior body parts for decorative and aerodynamic requirements [33].

ABS plastics are mostly used in Refrigerator Lining Automotive parts and highway safety devices. Polyamide plastics are most commonly used in bearings, gears, cams and belt reinforcement. Carbon fiber reinforced polymer composites are most widely used in aerospace applications. CFRP are used in side panels of number of aircrafts including jaguars, Tornados, Boeing and harriers. Carbon fiber reinforced PEEK has been used in designing helicopter blades and in reducing overall weight [34].

5. CONCLUSIONS

The following inferences are derived from the aforesaid discussions.

- a) Extrusion and injection molding are the most commonly methods for preparing polymer nano composites.
- b) Processing parameters and surface modification of the nano particles play a vital role in dispersion of nano particles in polymer matrix.
- c) Addition of nano fillers tends to increase the tensile strength of the composites.
- d) Wear maps are most helpful in identifying various wear mechanism involved and also the wear transition.

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