A review on the effect of processing techniques and functionalization of filler on mechanical properties of polymer nanocomposites

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Polymer nanocomposites with carbon fillers are widely used for electrical, mechanical and thermal applications due to their excellent intrinsic properties along with their light weight. Carbon fillers with higher aspect ratio have limitations of higher agglomeration and non-uniform distribution in polymer matrix due to high vander Waals forces acting between them and also due to lack of compatibility between polymer and filler. This results in poor properties of the fabricated composites, hence limiting their application. With proper selection of processing method and optimization of processing parameters, mechanical properties of the polymer nanocomposites can be improved. Functionalization of carbon fillers can enhance the compatibility of filler and the polymer matrix, which can further increase the mechanical properties like tensile strength and young’s modulus. This can result in polymer nanocomposites which may have the result in substitution of metals in various applications. This paper reviews about effect of various processing techniques used for dispersion and fabrication of composites and functionalization of filler which can improve mechanical properties of fabricated nanocomposites.

Keywords: Polymer nanocomposites, functionalization, mechanical properties, fillers, matrix, mechanical properties

1. INTRODUCTION

Polymer nanocomposites have received much attention to enhance the properties of engineering polymers while retaining their ease of processing. Polymer nanocomposites need very low dispersant loadings as compared to conventional composites to enhance mechanical properties like modulus and strength [1,2]. Now-a-days, carbon fillers like carbon nanotubes, carbon fibers and carbon black are used due to their intrinsically high mechanical properties like high tensile strength and elastic modulus. Even though, carbon filler have high mechanical properties, there are various factors which affect the mechanical properties of carbon filler based polymer nanocomposites. Factors which affect the mechanical properties of polymer nanocomposites are a) Interfacial load transfer by Mechanical Interlocking, Chemical Bonding, Weak Vander waals Force, b) Dispersion of filler, c) Type and content of filler [3-5]. In order to form a nanocomposite material with the excellent mechanical properties, strong chemical bonding between the reinforcement and matrix is a necessary condition. There might be significant difference in mechanical behaviors between a long fiber-reinforced composite and nanofiber reinforced composite, even both have strong interfacial bonding [6]. Xu et al. [7] studied the effect of duration of sonication on ultimate tensile strength of Graphitic nano fiber (GCF)/epoxy nanocomposites and they found that for lower sonication energy, nanocomposites show higher young’s modulus and tensile strength as compared to higher sonication energy. This may be
due to lesser damage to CNF for lower sonication energy. They also stated that for higher sonication energy, lower duration of sonication will show better mechanical properties. Salomet et al. [8] studied the effect of functionalization of graphene nanoplatelets (GNP) by amine group in epoxy/GNP nanocomposites. Tensile strength of nanocomposites having functionalized GNP was 5 MPa larger than that of nanocomposites having un-functionalized GNP. Thus we can see that as the bonding between filler and matrix improve, mechanical properties of polymer nanocomposites increases. Bonding between filler and the matrix is affected by the choice of processing techniques and by improving the compatibility between them. One of the ways to improve compatibility between filler and the matrix is functionalization of the filler. Therefore, this paper reviews about effect of functionalization and processing methods on mechanical properties of polymer nanocomposites.

2. Critical Length of fiber

Even with strong interfacial bonding, there might be significant difference in mechanical behavior between a long fiber-reinforced composite and nanofiber reinforced composite [9]. Long fiber-reinforced composite can effectively stop the propagation of a major crack whereas short nano fibers may not have this kind of effect. Material failure is governed by a main crack nucleating from defects inside the matrix or at the interface between the matrix and the reinforcement. In other words, tensile strength of polymer nanocomposite depends on the fiber length rather than on amount of fibers [10]. Failure of the nanocomposite depends on the number of fiber ends, as under tensile loading condition, the crack initiate at the fiber end and passes through the fiber-polymer interface to the polymer matrix, therefore more no of fibers will result in increased number of stress concentrating points in the form of fiber ends [11,12]. For lower concentration of smaller sized filler there will be insufficient hindrances for crack propagation. While the crack will be mainly constrained by strong long fibers so the strength and toughness values along fiber direction in these composites are much larger than the values of the pure matrix. Zheng et al. [13] stated that the length of fiber must be longer than a certain length known as a load transfer length. This critical length \( L_c \) is mainly determined by the fiber tensile strength \( S_f \), the fiber diameter \( d \), and the interfacial shear strength \( \tau_i \) between the fiber and the matrix.

\[
L_c = \frac{d \times S_f}{\tau_i}
\]

For strong interfacial bonding between the fiber and the matrix, the critical length should be smaller in order to prevent rupture of the fiber. This can be achieved by either functionalization of filler or by use of proper processing technique.

3. Functionalization of filler

CNTs have excellent tensile strength in axial direction, whereas in radial direction they are rather soft. First TEM observation of radial elasticity displayed that Vander Waal’s forces can deform two adjacent nanotubes [14]. This radial direction elasticity of CNT is important for CNT nanocomposites for mechanical application where the mixed tubes are subjected to large deformation in the transverse direction when the load is applied to a composite structure [15]. Though incorporation of carbon filler in polymer matrices increases their mechanical properties but very low amount of filler is desirable as increase in the filler content has drawbacks of increased cost of composite and difficulty of fabrication [16,17]. Decrease in mechanical properties of composite at higher filler content is due to
agglomeration of CNT and CNF owing to their higher aspect ratio and vander Waals forces. To overcome this problem functionalization of CNT is done to enhance the bonding between filler and matrix [18,19]. Du et al. [20] reviewed that for unfunctionalized CNT, composites having aligned CNTs show higher tensile strength and elastic modulus as compared to randomly oriented CNTs. Also these properties improve with increasing content of aligned CNTs. On the contrary, for randomly oriented CNTs, properties increases up to critical filler loading and then it start decreasing. Mechanical properties of nanocomposites having randomly oriented CNTs after critical loading may even reduce to values lower than pure polymer. This probably is due incomplete coverage of CNT by polymer matrix due to increase in viscosity of polymer matrix and large surface area of CNT. This makes uniform distribution and load transfer more difficult. Functionalization of CNT is done to enhance de-agglomeration and bonding between filler and matrix [21,22]. Various authors have observed different effects of functionalization on mechanical properties and it can be summarized that the mechanical properties of composites having treated MWCNT depends on the temperature, time and composition of functional group. There are different ways of functionalization of CNTs like covalent and non-covalent functionalization. Covalent functionalization is done by attaching desired groups on to the side walls of CNT permanently. Few of the functional groups are antharcene, 3aminopropyltriethoxisilane (3APTES), aminophenyl (C6H4NH2), nitrophenyl (C6H4NO2), poly (g-azidopropyl-L-glutamate)s (PAPLGs). Advantage of using these functional groups is that uniform dispersion of filler in the matrix can be achieved, however the limitation is that it introduces defects in CNTs. Non-Covalent functionalization is based on Vander-Waals’s forces. Advantage of non-covalent functionalization is that they do not damage or modify CNTs. Common examples of this type of functionalization are use of surfactants and non-covalent protein interactions [21-23]. Detail review of interfacial characteristics of CNT based polymer nanocomposites has been done by Chen et al. [24]

Madni et al. [25] discussed the effect of functionalization on pristine MWCNTs. Pristine MWCNTs was in the form of agglomerates, but addition of surfactants like SOCT and DTAB resulted in deagglomeration of MWCNTs, best dispersion was observed where mixed surfactants were used and for lower concentration. This may be attributed to stable dispersion owing to synergistic behavior in a mixture of anionic and cationic surfactants [25]. Alshammariet al. [26] prepared PET/MWCNT composite by melt mixing method with as received MWCNT and functionally treated MWCNT, they found that the tensile modulus increased from 1073.3 MPa for pure PET to 1302.7 MPa and 1343.2 MPa for 2 wt% of as received MWCNT and treated MWCNT composites respectively. Tensile modulus of nanocomposite increased with addition of MWCNT as a result of high aspect ratio and high modulus of MWCNT. Higher tensile modulus of PET/treated MWCNT as compared to PET/as received MWCNT is may be due to shortening of MWCNT length causing lesser agglomeration and better dispersion of treated MWCNTand separated MWCNTs after treatment. But at the same time the tensile strength and % elongation decreased with the addition of MWCNT in PET matrix, this may be due to start of failure at MWCNT agglomeration. Similarly, Sadeket al. [27] studied the effect of surfactants on PVA/MWCNT composites and found that for low surfactant percentages (0.01 wt%), tensile strength, elongation at break and Young’s modulus increased to 94.85 MPa, 160% and 67.05 MPa as compared to 40 MPa, 50% and 30 MPa for pure PVA. This may be because surfactant may have broken the MWCNT bundles into individual tubes resulting in increased hydrophobic interaction of CNT and PVA and uniform distribution of CNT in PVA matrix.

4. Processing Method for fabrication of polymer nanocomposites
Duration of mixing of filler and matrix and the processing method affects the mechanical properties of polymer nanocomposites. Compression molding has the ability to orient fiber in 0° as compared to extrusion method. It has been observed that fibers aligned at 0° showed maximum mechanical properties [28]. Also, compression molding has the ability to keep the filler in the matrix and have the laminate structure of composite which enhances the mechanical properties of composites. Higher shear stresses involved in extrusion causes the breakage of fiber which reduces the mechanical properties of composites [29]. Enqvist et al. [30] suggested that with increase in milling time, distribution of the filler improves and thus mechanical properties improve. The tensile strength of composites mixed for 1 h with 1 wt% MWCNTs is lower than that of composites mixed for 2 h with 0.5 wt% MWCNTs. This shows that, even lower concentration of filler may result in better mechanical properties with increase in milling time. In the same way, Zha et al. [31] studied the effect of sonication time on tensile strength and % elongation of PVDF/MWCNT nanocomposites. They found that with increase in the duration of ultrasonication, tensile strength increases while elongation at break decreases, showing enhanced mechanical strength of the composite but with reduced toughness. Tensile strength of nanocomposites was improved by 23% as compared to pure PVDF for sonication duration of 30 min. For same duration of sonication, elongation at break reduced by 50%. Increase in sonication time leads to uniform dispersion and interfacial adhesion between MWCNT and the matrix.

Zheng et al. [32] studied the morphology and tensile properties of PMMA/ MWCNT nanocomposites fabricated by anti-solvent precipitation (ASP) method where the solution of PMMA and MWCNT was precipitated out in methanol solvent and after drying it was hot compacted. Functionalization of MWCNT was done to find out its effect on tensile properties of nanocomposites. It was observed that the tensile strength of nanocomposites containing as received 0.5 wt% MWCNT and 1 wt% functionalized MWCNT resulted in similar (~14%) increase in the tensile strength. This according to authors is due to good dispersion of filler in the matrix in case as received MWCNT and decrease in the size of MWCNT due to functionalization. Mondal et al. [33] compared mechanical properties of Chlorinated Polyethylene (CPE)/CNF nanocomposite fabricated by two different methods namely solution method and solution cum melt mixing method. They observed that the tensile strength of the nanocomposites were 16.6 MPa and 11.75 MPa for 1 wt% MWCNT fabricated by solution cum melt mixing method and melt mixing method respectively as compared to 7.4 MPa for pure CPE. As sonication was involved in solution cum melt mixing method, surface roughness of MWCNT increased resulting in increased contact points between MWCNT and CPE polymer matrix which in turn resulted in better interfacial bonding and mechanical interlocking. Table 1 compares the mechanical properties of various polymer nanocomposites prepared by different processing techniques for same filler loading i.e. for 1 wt%.
Table 1: Comparison of mechanical properties of polymer nanocomposites prepared by different processing methods [6,25-26,32-35]

| System          | Filler content | Method of processing | Tensile Strength [MPa] | Elongation at Break [%] | Young’s Modulus [MPa] |
|-----------------|----------------|----------------------|------------------------|------------------------|-----------------------|
| PET/MWCNT       | 1 wt%          | Melt extrusion       | 30.0 ± 3.8             | 2.6 ± 0.3              | 1252.6 ± 31.3         |
| PET/treated MWCNT| 1 wt%          | Melt extrusion       | 25.6 ± 6.0             | 2.7 ± 0.8              | 1222.5 ± 105          |
| CPE/MWCNT       | 1 wt%          | Melt mixing          | 11.7                   |                        |                       |
| CPE/MWCNT       | 1 wt%          | Solution cum melt mixing | 16.6                  | -3.2                   |                       |
| PVA/MWCNT       | 1 wt%          | Solution mixing      | ~90                    | ~160                   | ~60                   |
| PC/MWCNT        | 1 wt%          | Melt mixing          | ~74                    | ~65 %                  | ~1425                 |
| PVDF/CNF        | 1 wt%          | Melt mixing          | 47.13                  | 12.02                  | 1284                  |
| EMA/SCF         | 1 wt%          | Melt mixing          | 9.1                    | 1203                   | 1.9                   |
| UHMWPE/CNT      | 1 wt%          | Ball milling         | 39.4                   | 686                    | 21.7                  |
| PP/MWCNT        | 1 wt%          | Melt mixing          | 34.5                   |                        | 283                   |

5. Conclusion

From literature review, it was observed that the mechanical properties depend on factors like interfacial load transfer between filler and matrix, type and content of filler and agglomeration of filler. Mechanical properties of nanocomposites can be improved by avoiding the agglomeration of filler and maintaining the proper length of filler material by employing proper processing methods. All papers suggested that elastic modulus increases with the increase in the filler content however tensile strength, toughness and strain at break decreases with increase in filler content, this may be due to agglomeration of fillers and poor interfacial bonding between filler and the matrix.

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