Mechanical properties of TiO$_2$-filled CNT/PMMA composites

He Runqin, Niu Fenglian and Chang Qiuxiang

School of Mechanical and Electrical Engineering, Ningbo Dahongying University, Ningbo, China

ABSTRACT
The present study investigated the effect of TiO$_2$ fillers on the mechanical properties of CNT/PMMA composites. TiO$_2$/PMMA/CNT composites were prepared by using twin screw extruder and test samples by injection moulding. Results indicated that incorporation of CNT in PMMA causes decreases in tensile stress, elongation at break, and on impact properties. It is observed that addition of CNT and TiO$_2$ seems to be beneficial in increasing mechanical strength via increasing the interface dispersed phase.

1. Introduction

Polymer and their composites are finding ever-increasing usage for numerous industrial applications such as bearing material, rollers, seals, gears, cams, wheels and clutches [1]. Different types of polymers show different mechanical behaviour. However, neat polymer is very rarely used as bearing materials and wear resistant materials because of unmodified polymer could not satisfy the demands arising from the situations wherein a combination of good mechanical properties is required [2]. Among the wear types, abrasive wear situation encountered in vanes and gears, in pumps handling industrial fluids, sewage and abrasive-contaminated water, roll neck bearings in steel mills subjected to heat, shock loading; chute liners abraded by coke, coal and mineral ores; bushes and seals in agricultural and mining equipment, have received increasing attention [3]. The bidirectional fabric reinforcement offers a unique solution to the ever-increasing demands on the advanced materials in terms of better performance and ease in processing [4].

On account of their high-specific strength and modulus, ease of fabrication and the facility for tailoring in component design, carbon/PMMA composite laminates have been accepted by the aircraft and aerospace industries. Once the composites are adopted for structural components, it is inevitable that the components are subjected to a dynamic environment. Among these, fatigue and impact are the two major dynamic loadings that challenge structural materials.

Unlike that in metallic materials, fatigue damage in polymeric composites is more complicated. The mechanisms of fatigue failure involve matrix cracking, interface debonding, delamination and fibre fracture. Although damage may appear very early during fatigue
testing, the composites can last for very long periods before fracture takes place. Many studies have been reported regarding this topic, but clear design criteria have not yet been established. When composites are accepted for structural components in the aerospace industry, unexpected impacts may occur. A bullet in ballistic impact can penetrate the materials and bird strike takes place at higher speeds. Such impact loads may result in very serious damage. On the other hand, dropped tools or runway debris impacts occur at relatively low velocity which may also cause damage. Damage produced by impact may be serious, especially if composites are subjected to compression loading. Efforts have been devoted to investigate the variation of mechanical properties of impacted composites [5–9].

Among these, composites and fibre-reinforced polymeric materials are the most attractive because of their abundant usage in mechanical components such as gears, cams, wheels, impellers, brakes, seals, bushes and bearings [10]. One of the commonly used composites is carbon-reinforced PMMA-based polymer material, since it possesses better mechanical and thermal properties [11].

2. Experimental

2.1. Materials and composite preparation

The TiO₂ particles used in this investigation were provided by nanostructured and amorphous materials, and their diameters are 10 nm.

The polymers were pre-dried in an air-circulating oven at 80 °C for 4 h and mixed physically for 2 min prior to blending. Blending of the polymers in different proportions was carried out by using 17.5-mm-diameter twin-screw co-rotating extruder (HAAKE Rheocord, Model No. 9000, Germany) having L/D ratio 1:18 in the temperature range 150–200 °C at 80 rpm just after the physical pre-mixing by tumbling action. The resulting blends were subjected again to pre-drying conditions before moulding into the appropriate specimens for tensile test specimens as per standard specifications by injection moulding in Engel, Austria (Type: ES330/80 HLS), computerised injection moulding machine, set at 80 t.

The PMMA used in the study was Diakon CMG302 supplied by Distrupol Ireland and produced by Lucite International Inc. with MFI = 4.4 g/10 min (ISO 1133), average molecular weight (Mw) 85,000 g/mol. (GPC) and \( q = 1.18 \text{ g/cm}^3 \) (ISO 1183). It is a general-purpose moulding and extrusion grade PMMA with high heat resistance used mainly in the production of optical parts, display items, and for tube and profile extrusion.

2.2. Tensile properties

The strength, modulus and elongation at break of the blends were determined under ambient conditions according to ISO 527-2. Tensile properties were done using a Universal Testing Machine model INSTRON/3366 with the cross head speed of 5 mm/min. Five specimens were used for the testing, and the average was reported in each case.
2.3. **Flexural properties**

A flexural test was carried out using Llyod tensile machine (Model 5533) accordingly to ASTM D 790, Test Method 1; Procedure A. The three-point bending test was preferred. The distance between the spans was set according to the standard (4.96 cm), and the strain rate was 3 mm/min. The flexural properties were measured at room temperature (25 ± 2 °C) and 50% ± 5% relative humidity. Five samples were tested for each composition and the average values were reported.

2.4. **Izod impact test**

The impact test was done according to ASTM D 256A by using a Ray-Ran Izod impact tester, pendulum-type model (Model RR2500, Houston, TX, USA). The test specimen obtained from the injection moulding, then notched using a notching machine. The notch depth was fixed at 2.5 ± 0.05 mm. The impact strength was calculated by dividing the indicator reading (energy) by the cross-sectional area of the specimen. The results were reported in J/m of notch for notched specimens. Ten specimen test values were carried out for each blend sample. This test was measured at room temperature (25 ± 2 °C) and 50% ± 5% relative humidity.

3. **Results and discussion**

3.1. **Tensile properties**

Figure 1 shows that tensile stress at yield of composites decreases with the increased content of CNT. A sharp drop of around 5 MPa was observed in the tensile stress at break on 10 vol% addition of CNT. A further 20 and 30 vol% addition of CNT produced continues decrement of tensile stress at yield to 49.2 and 47.6 MPa, respectively. With increase of filler contents, the size of the voids formed when the polymer matrix becomes detached.

![Figure 1. The tensile stress at yield of composites.](image-url)
from the filler particles due to deformation will become critically large and may initiate the main crack.

In addition, the inevitably increased agglomeration of dispersed filler particles results in decreased mechanical strength due to low strength of the agglomerates themselves. Many researchers believed that the addition of TiO$_2$ is the most universal modern coupling agents, which may improve filler/matrix adhesion, protect the filler surfaces from micro-flaws that initiate failure, reinforce the interface layer and improve the filler wetting and dispersion.

The tensile modulus increases linearly with the increase of CNT content for both CNT/PMMA and CNT/TiO$_2$/PMMA composite. Tensile modulus of PMMA is 1037 MPa and addition 10, 20 and 30 vol% of CNT to the composites cause an increment of 1162, 1310 and 1619 MPa, respectively. From Figure 2, it is clearly observed that 30 vol% of CNT show a strong increase in tensile modulus compared to other two formulations. The addition of CNT did not cause much difference in the tensile modulus of these blend materials if the TiO$_2$ was not used.

The poor interface behaves as a flaw where initiated the failure at the interface, which resulted in low tensile strength and elongation at break.

Elongation at break values of CNT/PMMA and CNT/TiO$_2$/PMMA composite are revealed in Figure 3. Elongation properties of CNT/TiO$_2$/PMMA composite decreased to 9%–62% with the increasing CNT content up to 30 vol%. This decrease indicates that the blends become brittle with increase in CNT loading owing to the stress concentration effect of CNT. The decrease in elongation at break with increasing CNT content is to be expected due to development of cracks around the filler particles and possible formation of particles agglomerates and voids resulting local detachment of the matrix from the particles.

Data analysis following the CNT surface treatment indicates no apparent change in elongation at break for 10 vol% loading. On the other hand, it seems that the silanisation was found to be more effective for CNT/PMMA having 20 and 30 vol% due to its higher elongation at break. The increase in the elongation at break of the blends in the presence

![Figure 2. The tensile modulus of composites.](image-url)
of TiO₂ was expected due to the plasticiser effect. TiO₂ enhanced the strain properties of CNT/PMMA composites. The development of elongation properties can be a consequence of homogeneous structure and improved adhesion between the matrix and filler via the modified interface.

### 3.2. Flexural properties

Figures 4 and 5 show the effect of CNT content on the flexural properties of composites. As the CNT content increased, the flexural strength decreased. Figure 4 shows the variation of flexural strength values of blends simultaneously filled with unsilanised and silanised CNT fillers. The addition of CNT into PC/PMMA composition either with treatment or without treatment causes a decrease in flexural strength. It can be seen that the

![Graph](image-url)
optimum flexural strength was achieved at 10 vol% of CNT loading. Carbon fibre incorporation in the range of 20–30 vol% caused the flexural strength to drop slightly, which can be attributed to the reduction of interaction due to agglomeration of the CNT as shown later in morphological study. Interestingly, the addition of TiO₂ increases the flexural properties of the CNT/PMMA composite.

The degree of filler–polymer loading or adhesion can be increased through the use of an appropriate coupling agent, thereby providing functional reinforcement from otherwise non-functional filler. In this regard, silicone and silane coupling agents have been widely used on various fillers with reasonable success. The flexural modulus of a polymeric material has shown to be remarkably improved when CNT content is increased. From Figure 5, it was found that 30 vol% was the optimum quantity to be incorporated into CNT/PMMA composite to achieve maximum value of flexural modulus. This implies that fillers can contribute significantly to a stiffness increase. The results, therefore, are in agreement with those of a previous researcher, where the flexural modulus is usually inversely proportional to flexural strength, which means that increasing the modulus of filled material usually contributes to a decrease in flexural strength.

However, for the presence of CNT, the flexural modulus of the blends decreased significantly for all formulation. The flexural modulus of the blends containing 10 vol% CNT significantly gave a higher decrement than those containing either 20 or 30 vol%. Generally, TiO₂ can minimise the incompatibility between the polymer matrix and the filler by improving interactions at the polymer/mineral interface.

3.3. Izod impact strength

Figure 6 presents the influence of CNT content on the impact strength of the composites. As the filler content increased from 0 to 30 vol%, the impact strength is reduced by about 25%. Toughness of the blends decreases with the CNT loading, as blends having 10 vol% CNT exhibits lower toughness. Moreover, a further 10 vol% addition of CNT to PMMA blends caused Izod impact strength to continuously decrease, which can be attributed to the reduction of interaction due to agglomeration of the CNT.
The CNT fillers tend to agglomerate and to resist dispersion as the filler content increases. These factors weaken the interfacial adhesion between filler and polymer and become potential sites for crack growth because of inability of filler to support stress transfer to the polymer matrix. Voids in the matrix may also become sites for crack initiation. All these reasons are likely to contribute to lower impact strength value of the composites.

This provides evidence that the polyimide–CNT hybrid blends were reinforced by TiO$_2$, and aggregations of CNT at high content with more than 10 vol% resulted in decreasing toughness and strength. A compound becomes more resistant to bending as the filler’s surface area, aspect ratio and resin adhesion restrict the ability of the polymer chains to move relative to its surface. A filler-stiffened compound is, however, in most cases more brittle, and therefore, more prone to crack initiation and propagation at point of stress concentration, such as notches, bends and voids. Filler that is truly coupled to the polymer generally provides the most stiffening, but at the expense of impact resistance.

Interestingly, Izod impact strength of CNT/PMMA filled with TiO$_2$ are higher for all compositions. PMMA composite filled with 10 and 20 vol% CNT show the increment of 6% and 5%, respectively. Although surface treatment of 30 vol% CNT to the PMMA blend exhibits the highest value of Izod impact strength with the increment of 17%. These results further confirm the importance of strong interaction between matrix and CNT, which ultimately leads to better overall Izod impact strength. Based on these observations, the Izod impact strength can be tuned, to some extent, by changing the composition of these materials with TiO$_2$. Bond breaking and reformation at the filler surfaces under stress often occur. As a result, it is sometimes found that both ultimate elongation and impact resistance are improved.

The flexural properties of CNT reinforced PMMA composites increased with content of TiO$_2$ (Figure 7). All tested specimens underwent compressive buckling failure on the top surface of the tested laminates. When TiO$_2$ was incorporated into the blends, the flexural strength increased greatly.

Izod impact tests were carried out to determine the effects of adding TiO$_2$ and/or PMMA on the sample toughness. The results are included in Figure 8, and reveal that the

![Figure 6. The impact strength of composites.](image-url)
high content of TiO$_2$ filled PMMA blend exhibits lower impact strength than their parent polymers due, once again, to the immiscible character. However, the incorporation of acid TiO$_2$ resulted in an obvious increase in the blend’s impact strength, indicating a toughening effect. In addition to the rubber nature of PMMA, the reason for this remarkable enhancement is believed to be associated with the compatibiliser role played by the TiO$_2$.

The acid TiO$_2$ is also responsible for building up bridges between the nanoparticles and the matrix. Consequently, the impact strength of TiO$_2$/PMMA increased with a rise in TiO$_2$ content. The synergetic toughening effect is enhanced by the increased amount of the *in situ* interfacial reactions. For the TiO$_2$/PMMA composites, the nanoparticles are encapsulated by excessive PMMA. Such a core–shell structure in which the nanoparticle inclusions have high affinity to the elastomer encapsulation favours the absorption of impact energy and prevents the propagation of cracks at the interface. When TiO$_2$ weight

Figure 7. The flexural properties of PMMA composites with TiO$_2$ content.

Figure 8. Impact strength of PMMA composite as a function of TiO$_2$ content.
ratio remains constant, an increase in TiO\textsubscript{2} content is equivalent to an increase in the amount of the elastomer-like spheres. Toughness of the composites increases with TiO\textsubscript{2} content as a result. Since there is no chemical bonding between the elastomer and the matrix, the synergetic toughening effect was observed in CNT/TiO\textsubscript{2}/PMMA. The latter has to show lower impact strength than the former at the same TiO\textsubscript{2} content. Comparatively, the particulates in untreated TiO\textsubscript{2} have neither elastomer shell nor good adhesion to the matrix. The improvement of toughness under high-speed deformation is thus negligible in the composites, no matter how many TiO\textsubscript{2} particles are added. The TiO\textsubscript{2} again dominated the impact strength performance of the samples. Without the addition of TiO\textsubscript{2}, the PMMA composites did not show obvious improved mechanical properties compared with PMMA composite.

FTIR spectra of the modified CNTs compared with the clean unmodified CNT are shown in Figure 9. Although attributing specific chemical functional groups to band assignments are difficult, it was still found that all of the surface-modified fibres did exhibit new bands directly associated with the surface modification process. All samples displayed a peak at about 3500 cm\textsuperscript{-1} indicative of an increase in surface hydroxyl groups, expected to have resulted directly from the use of colloidal titanium and/or sol/gel chemistries. This is in contrast to the cleaned CNT that exhibited no band at all in this region. Another band that clearly relates to surface modification is the large peak at around 1100 cm\textsuperscript{-1}. This band was observed in the spectra for all of the surface treatments that used colloidal titanium and was therefore attributed to an O–Ti–O stretching vibration. The chemical attachment of TiO\textsubscript{2} to the CNT is less clear with the relevant peaks likely being masked by the presence of the titanium species. The peaks at 879 and 1664 cm\textsuperscript{-1}, clearly evident in the TiO\textsubscript{2}, can be attributed to hydroxyl groups originating from titanium and are comparable with the peaks obtained after colloidal titanium surface modification. The presence of the TiO\textsubscript{2}, however, can be inferred from the multiple small peaks

Figure 9. FTIR spectra of the CNTs after chemical modification.
in the fingerprint region between 1000 and 1200 cm\(^{-1}\), illustrating the additional surface functionality compared with the clean fibre.

The spectra from the surface treatment method also exhibits clearly the hydroxyl peak originating from the colloidal titanium, but also has an additional unique peak at 869 cm\(^{-1}\) and therefore likely to reflect an additional chemical modification of the surface arising from the amine species. The reduced size of the hydroxyl peak at 3500 cm\(^{-1}\) for the system may reflect removal from the surface of the fibre. Overall, FTIR spectroscopic analysis shows that this systematic approach has indeed resulted in either chemical or physical surface modification of the fibre surfaces, enabling comparison with resulting mechanical property evaluations.

4. Conclusions

From the studies of the tensile properties, it can be concluded that the optimum fibre loading was at 20 vol% for CNT/PMMA composite. The flexural strength of the composites increases with increasing TiO\(_2\) content in the CNT/PMMA composite. The results show that the addition of TiO\(_2\) helps to improve the fibre–matrix adhesion leading to higher flexural properties. Appropriate amount of TiO\(_2\) arrive the high-impact strength for the 20 vol% CNT/PMMA composite.

Disclosure statement

No potential conflict of interest was reported by the authors.

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