The preparation and characteristic of maleic anhydride grafted polyethylene (PE-g-MA) filled CNT/PMMA composite film

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ABSTRACT
In order to improve the tribological properties of PMMA, the PMMA composites incorporated with CNT powders were prepared. The effect of CNT content on tribological properties of the composites was investigated. When CNT content is 0.5 wt%, the friction coefficients of the 0.5%CNT/PMMA composite are the smallest, which are about 0.15 and are 67% less than those of the pure PMMA composite, and its wear resistance remains the same as the pure PMMA composite. Incorporating 0.5 wt% CNT into the PMMA composite may develop a continuous transferred film on the worn surface. As a result, the friction coefficients of the composite are reduced and its wear mechanism is mainly fatigue spalling. The addition of PE-g-MA improved the friction and wear properties of CNT/PMMA composite.

1. Introduction
Polymeric materials have been used as biomaterials in the last decades. However regardless materials’ application, polymer mechanical properties and its surface characteristics must be adequate for the purpose intended. Particularly, for biomedical applications, among all the other important properties, the biocompatibility of the surface acquires extreme importance and can dictate its rejection. One of the issues regarding biocompatibility is cytotoxicity which strongly depends on the contamination level at surface [1–3]. Polyolefins such as polyethylene (PE) exhibit good barrier properties to water vapour and biaxial orientation can be achieved in a wide temperature range up to the melting point. PE displays a largely predominant orthorhombic crystalline form with little trend for martensitic-like phase transition into a monoclinic form under imposed strain [4].

Polymer based nanocomposites represent a radical alternative to conventionally filled polymers because of the dispersion of nanometre-sized sheets or tubes and these nanocomposites have improved properties when compared with conventional polymers and their microcomposites. The characteristic properties of nanocomposites are usually observed with nanofiller contents as low as 1%–5% [5]. These improvements include increased electrical conductivity, high mechanical strength and decrease in oxygen...
permeability. So, polymer nanocomposites based on carbon nanotubes are of current interest due to their potential application in various fields [6,7]. CNTs have attracted great interest because of their unique physical and chemical properties, such as high mechanical strength, electrical, thermal stability and chemical stability [8,9] as compared to the virgin matrix. As a result of their large aspect ratio and superior electrical conductivity and mechanical strength, CNTs have been widely considered as one of the most promising filler for making of novel composite materials.

PMMA is often used as an alternative to glass and is preferred for many applications because it is easy to handle and process, with useful properties such as good impact strength, good stiffness, high transparency. Compared to other plastics, it is also cost effective and possesses excellent environmental stability. PMMA is most suitable polymer for the optical coatings as well [10,11].

In this paper, the PMMA composites incorporated with various amount of CNT were prepared and the effects of CNT content on microstructure, hardness and tribological properties of the composites were studied. The effects of CNT on friction and wear mechanisms of the PMMA composites were investigated to provide theory and experimental foundation for application of CNT to improve the properties of PMMA composites in surface engineering.

2. Experimental procedure

2.1. Materials

Maleic anhydride (MAH; Shanghai Lingfeng Chemical Solvent Factory) was used as the grafting monomer and a radical initiator of PE. Single-walled carbon nanotubes were purchased from SRL (Mumbai, India) with diameter of 1.5 nm and length 2 μm (aspect ratio ≈ 1333). A linear low density polyethylene grafted with 0.16 mol% of maleic anhydride (PE-g-MAH), Yparex 9403 from DSM was used as tie-layer or coupling agent. The LLDPE-like backbone of this polymer is thoroughly compatible with the PE layer, whereas the MAH side groups are likely to buildup covalent bonds with the amide groups of the PMMA layer.

2.2. Irradiation of PE film

PE film was cut into small strips of size (2 cm × 4 cm), washed with methanol, dried and weighed. The film was irradiated with gamma rays from 60Co source housed in Gamma chamber-900 at a constant dose rate of 2.052 kGy/h for different time periods.

2.3. Graft copolymerisation

The peroxidised and weighed PE film was placed in a standard joint two necked flask, fitted with water condenser and a thermometer. To it was added definite amount of water (2.5–30 ml), followed by the addition of known amount of monomer mixture (MAAc + AAm) taken in definite proportions and the initiator, benzoyl peroxide (4 × 10 − 2 − 28.9 × 10 − 2 mol/L). The reaction mixture was placed in Rota mental maintained at constant temperature (130 °C) and refluxed for definite time periods, under constant stirring.
After the reaction was over, the grafted film was washed with acetone/water solvent (1:1 v/v) mixture and water to completely remove any homopolymer or the copolymer, poly(MAAC-co-AAm). The grafted film free from homopolymer/copolymer was dried till constant weight was obtained.

2.4. Specimen preparation

The Langmuir–Blodgett films of PMMA, Mw-120,000 (Sigma–Aldrich), were prepared by vertical deposition on polished silicon wafers using a KSV Langmuir trough (Model: KSV-2000). Prior to deposition, substrates were ultrasonically cleaned by acetone followed by iso-propanol and Milli-Q water (>15 MΩ cm). Then, the substrates were soaked in a basic piranha solution for 1/2 h, to make them amphiphilic in nature, followed by thorough rinsing with Milli-Q water. PMMA films were fabricated by spreading solution of PMMA in chloroform (HPCL grade) of concentration 0.3 g/1 L to water (deionised (Milli-Q) water) subphase of LB trough. The pH of subphase was maintained at 5.8. About 70 µL of the solution in chloroform was spread on subphase surface. The surface pressure of monolayer was measured using the Wilhelmy plate method with an accuracy of 0.05 mN/m. The movable barriers were employed to enclose an area of the water surface by compressing the PMMA monolayer with a predetermined value of barrier speed. By compressing the barriers, a plot of surface pressure against surface area can be obtained. During experiment the target pressure was maintained at 20 mN/m and dipping speed was 1 mm/min in both upward and downward directions with a relaxation time of 300 s in air for all the samples. The films were deposited as a function of number of deposition strokes.

2.5. Tribological tests

Friction and wear tests were done using a ball-on-block reciprocating UMT-2MT tribometer at room temperature with a relative humidity of 45%–55%. The specimens were cleaned ultrasonically with acetone and dried before testing. The counterbody consisted of a 2 mm diameter GCr15 stainless steel ball.

3. Results and discussion

The friction coefficients of the PMMA as a function of CNT content are shown in Figure 1. As the loads increase from 6 to 12 N, the friction coefficients of the pure PMMA are between 0.39 and 0.48, which are higher than those of the composites incorporated with CNT. When the CNT content is 0.5 wt%, friction coefficients of the CNT/PMMA composite decrease to 0.15, which is 67% less than those of the pure PMMA. As CNT content exceeds 1.0 wt%, friction coefficients of the composites thereupon increase. Moreover, when the loads are less than 10 N, the friction coefficients increase to 0.35. If the load is 12 N, friction coefficients will increase to 0.25.

Figure 2 shows the wear losses of the PMMA as a function of CNT content under loads of 6–12 N. With the increasing of CNT content, the wear losses gradually increase. The wear loss of the pure PMMA is the smallest. The wear resistance of the 0.5% CNT/PMMA composite is almost the same as the pure PMMA. But the wear losses of the
1 wt% CNT/PMMA composite increase by about 31% compared with those of the pure PMMA. And those of the 1.5 wt% CNT/PMMA composite and the 2 wt% CNT/PMMA composite respectively increase by 68% and 88%.

It can be concluded that the addition of CNT to the PMMA can greatly reduce its friction coefficient. When CNT content is 0.5 wt%, the composite presents the lowest friction coefficient, and its wear resistance is similar to the pure PMMA.

To illustrate the influence of PE-g-MA on the friction coefficient for of PMMA polymer, see Figure 3. It is clear from these figures that the coefficient of friction reaches the

![Figure 1. Friction coefficients vs. CNT fraction.](image)

![Figure 2. Wear losses vs. CNT fraction.](image)
lowest levels using of PE-g-MA. This is followed by CNT/PMMA and PMMA. This behaviour could be explained due to the less presence of transfer film for CNT/PMMA which most of it was quickly rubbed away. This is quite clear in the optical microscopy results of the disc worn surface examination. In fact the presence of the PE-g-MA avoids the adhesion and transfer film of PMMA.

Figure 4 presents the variation of coefficient of friction and specific wear rate with combined pressure and speed effect known as PV factor. It is clear from this figure that the coefficient of friction and specific wear rate for PE-g-MA filled CNT/PMMA composite is increasing with the increase in PV factor values. There is an increase of 100% in coefficient of friction and specific wear rate for a 1000% increase in PV factor at both dry and water lubricated conditions. It can be deduced from this figure that PE-g-MA filled CNT/PMMA composite is sensitive to conditions with varying load and speed under both dry and lubricated conditions.

In the friction test, the outline peak of the harder steel ring ploughed on the surface of the softer monomer casting PMMA and formed a furrow. With the increase of load, the wedge depth of the outline peak on the PMMA surface increased and more material was removed. Whilst, the plastic transfiguration of the material was enhanced; the friction surface temperature rose; the sample surface was intenerated and viscous flow occurred. Consequently, the tendency of conglutination and the transfer of PMMA increased while the adhesive power decreased, resulting in difficulty with the formation of film, increasing the wear rate/amount of the material thus forming large quantities of wear debris.

The SEM examination of worn surfaces of PMMA polymer pin against AISI 304 L stainless steel disc at 150 N applied load and at 1.0 m/s sliding speed test for both dry and
water lubricated conditions are given in Figure 5(a,b), respectively. In this figure, the worm surface is wrinkled with wavy morphology and the wrinkling is denser with deep grooves for dry condition. This is due to the high temperature reach on the polymer surface. The high temperatures in polymer surfaces result in softening the polymer surface and wrinkling present on the surface.

In Figure 5(a), the worn surface suffered from severe plastic deformation because PMMA transferred to the worn surface of the counterpart as a result of severe adhesion between the couples during friction progress. The worn surface morphology of the
PE-g-MA filled CNT/PMMA composite is shown in Figure 5(b), it is clear that a dense transferred film developed on the worn surface.

The FTIR spectra of unmodified and modified PMMA were illustrated in Figure 6. The broad peak at 3000–3800 cm\(^{-1}\) was assigned to hydroxyl (–OH) groups of PMMA. The hydrophilicity of PMMA was reflected in this peak as the presence of –OH groups on the surface of PMMA. The intensity of –OH groups absorption band was significantly reduced in modified PMMA. The indicated that the hydrophilic properties of PMMA were reduced as the –OH groups are reacted with CNT. Furthermore, the peak at 1727 cm\(^{-1}\) was assigned as carboxyl (C = O) groups from hemicelluloses of PMMA. The intensity of the peak is increased after modified with CNT. This is due to the additional peak attributed by the covalent bond between CNT and PMMA.

**4. Conclusions**

When CNT content is 0.5 wt%, the friction coefficients of the 0.5%CNT/PMMA composite are the smallest, which are about 0.15 and are 67% less than those of the pure PMMA, and its wear resistance remains the same as the pure PMMA. Incorporating 0.5 wt% CNT into the PMMA composite may promote a continuous transferred film on the worn surface. As a result, the friction coefficients of the composite are reduced and its wear mechanism is mainly fatigue spalling. However, when the CNT content exceeds 1.0 wt%, the continuous transferred film may hardly develop on the worn surface because the wear resistance of the composites decreases, so the friction coefficients of the composites increase and the wear mechanism of the composites becomes brittle fracture. The addition of PE-g-MA improved the friction and wear properties of CNT/PMMA composite.
Disclosure statement

No potential conflict of interest was reported by the author.

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