Enhancement investigations on thermal properties of PMMA/PE composite film reinforced with nano $\gamma$-Fe$_2$O$_3$ nanoparticles

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ABSTRACT

In the present study, PMMA/PE-$\gamma$-Fe$_2$O$_3$ nanocomposites of various compositions were produced through ultrasound-assisted technique. Thermogravimetric analysis and UV-visible results indicated that the thermal stability is enhanced distinctly, without a sacrifice in optical clarity. The improvement of thermal properties was attributed to the homogeneous and good dispersion of $\gamma$-Fe$_2$O$_3$ nanoparticles in PMMA/PE-$\gamma$-Fe$_2$O$_3$. And the excellent thermal properties performance of the $\gamma$-Fe$_2$O$_3$ fillers improved the tribological properties of PMMA/PE composites.

KEYWORDS
PMMA; PE; $\gamma$-Fe$_2$O$_3$; thermal property; degradation analysis

1. Introduction

In the last two decades, organic-inorganic nanometer composites have attracted great interest, both in academia and industry, because of their remarkable improvement in mechanical and other properties when compared with plain polymer or conventional micro and macrocomposites, such as high modulus, increased strength and heat resistance [1,2]. Polymers are filled with an inorganic component to increase their strength or impact resistance, to reduce their electrical conductivity and permeability of oxygen and other gases.

The introduction of $\gamma$-Fe$_2$O$_3$ into a PMMA/PE matrix received much attention due to improvements in the glass transition and thermal stability of the composites. Several methods have been used to prepare PMMA/PE-$\gamma$-Fe$_2$O$_3$ nanocomposites, including ex-situ sol–gel polymerization, radical polymerization and solution mixing [3]. The excellent friction and wear properties of fabric composites have drawn more and more attentions these years.

For nanocomposites prepared via in situ bulk polymerization it was found that the presence of $\gamma$-Fe$_2$O$_3$ retarded the thermal decomposition of the polymer [4]. This was attributed to the excellent interaction of the polymer chains with the $\gamma$-Fe$_2$O$_3$ nanoparticles and the barrier effect to the evaporation of small molecules generated during the thermal decomposition of the PMMA/PE matrix. The opposite trend, where the presence of $\gamma$-Fe$_2$O$_3$ in a PMMA/PE matrix did not enhance the thermal stability, was also observed and it was associated with the evaporation of physisorbed water [5–9]. Most of
the reported studies concentrated on commercial \( \tau \)-Fe\(_2\)O\(_3\) incorporated in PMMA, while little information was provided regarding incorporation of the rutile phase into PMMA. No systematic comparison of the properties of PMMA/PE–\( \tau \)-Fe\(_2\)O\(_3\) nanocomposites, containing respectively PMMA/PE and \( \tau \)-Fe\(_2\)O\(_3\), has been reported in literature. The purpose of this study was to prepare PMMA/PE–\( \tau \)-Fe\(_2\)O\(_3\) nanocomposites, through melt compounding, and analysing the sample morphologies as well as their degradation and thermomechanical behaviour. The fillers were prepared by using sol–gel combustion methods.

2. Experimental

2.1. Materials

\( \tau \)-Fe\(_2\)O\(_3\) nanoparticles were purchased from Shanghai Hongxing New Material Co., Ltd. PE film was purchased from Shanghai Gaobao Chemical Co., Ltd. PMMA was purchased from Shanghai Wangrong industry Co., Ltd. The particles are received as coated particles dispersed in a diester solvent mixture. The coating accounts for approximately 20 wt% of the dry-weight of the nano-\( \tau \)-Fe\(_2\)O\(_3\) and enables a relatively stable solvent dispersion.

2.2. Specimen preparation and compositions

A negative charged hydrophilic Si-OH layer was formed on the surface of the Si (001) substrate (dimensions: 4 \( \times \) 5 mm\(^2\)) after the substrate was ultrasonically cleaned in acetone and immersed into Piranha solution at 60 \(^\circ\)C for 20 min. Then, the negatively-charged \( \tau \)-Fe\(_2\)O\(_3\) was alternately immersed into three different solutions of PE and PMMA (70,000 g/mol, Aldrich). The thickness of the organic PE layers was controlled by the number of dipping cycles into PMMA/PE solutions, while two dipping cycles were carried out in the present work. The deposition time and temperature were 3 hours and 60 \(^\circ\)C, respectively.

2.3. Measurement of glass transition temperature

Glass transition temperatures are measured using differential scanning calorimetry (DSC, type TA instruments Q1000) with a heating/cooling rate of 10 \(^\circ\)C/min.

2.4. Thermogravimetric analysis

Thermogravimetry (TGA) was performed using a Perkin Elmer TGA-7 thermobalance. Finely powdered (about 10 mg) samples were heated at 10 \(^\circ\)C/min with N\(_2\) purging (70 ml/min). Two degradation methods were used to analyse the thermal parameters. The first method was applied to 1%–5% non-isothermal different weight loss with constant heating rate to get average activation energy. The second method used different heating rate for each degree of conversion to measure activation energy.
3. Results and discussion

Figure 1 shows the DRIFTS spectra on nano-Fe$_2$O$_3$ films at 320 °C, in which the bands at 3736, 3447, 3067, 2935, 2349, 2305, 1594, 1487, 1413, 1354, 1255 and 1150 cm$^{-1}$ were observed. The intensities of most of the adsorbed species change obviously. The two (OH) modes of different types of isolated hydroxyl groups (3736 and 3447 cm$^{-1}$), as above, were due to the dissociation of water to form two distinctive hydroxyl groups: one OH—group bridges two surface vicinal Fe$^{3+}$ and the other forms a terminal Fe$^{3+}$ OH—group. The band at 2935 cm$^{-1}$ was assigned to the characteristic peak of dioxymethylene. The sharp absorption bands at 1594, 1487 and 1354 cm$^{-1}$ observed at higher temperature can be associated with COO asymmetric stretching, CH bending and COO symmetric stretching vibrations in the formate structure. In this case, the spectra in the lower frequency region, showing very intense absorptions at 1150 cm$^{-1}$, indicate that formaldehyde is polymerized to linear polyoxymethylene. The bands at 1413 and 1255 cm$^{-1}$ were assigned to molecularly adsorbed formaldehyde on the Fe$_2$O$_3$ film. The peaks that were attributed to carbon dioxide appeared obviously. Therefore, most of the species were found at this temperature, which indicated that the reactions went actively with temperature increasing.

Figure 2 shows the dielectric strength of the PMMA/PE-$\gamma$-Fe$_2$O$_3$ hybrid films with different $\gamma$-Fe$_2$O$_3$ content. It can be seen that the dielectric strength were slightly increased with the $\gamma$-Fe$_2$O$_3$ content increasing and then decreased gradually.

The hybrid film with 2 wt% of $\gamma$-Fe$_2$O$_3$ shows the dielectric strength of 199 MV/m, which is about 6% higher than that of pure PMMA/PE film (188 MV/m). As the $\gamma$-Fe$_2$O$_3$ content increased to 20 wt%, the dielectric strength of the hybrid film reduced to 159 MV/m, which is 20% lower than the hybrid film with 2 wt% of $\gamma$-Fe$_2$O$_3$. It can be

![Figure 1. DRIFTS spectra on nano-Fe$_2$O$_3$ films at 320 °C.](image-url)
concluded that the nano $\gamma$-Fe$_2$O$_3$ aggregates at relative high $\gamma$-Fe$_2$O$_3$ content, and the impurity cause some defects to deteriorate the dielectric strength.

Figure 3 shows the time to failure of PMMA/PE-$\gamma$-Fe$_2$O$_3$ hybrid films in electrical aging test, which determined by detecting the breakdown time of the films as a voltage of constant electric field applied. The PMMA/PE-$\gamma$-Fe$_2$O$_3$ hybrid films show improved electrical aging performance as compared with pure PMMA/PE film. Especially, the hybrid PMMA/PE film with 10 wt% of $\gamma$-Fe$_2$O$_3$ exhibited a significant enhancement, the time to failure of the hybrid film with 10 wt% of $\gamma$-Fe$_2$O$_3$ in electrical aging at 1 kV is 208 h, which is 3.4 times longer than that of pure PMMA/PE film (61 h). We suppose that the improved electrical aging performance of PMMA/PE hybrid film is related to the highly dispersion and adequate addition of $\gamma$-Fe$_2$O$_3$ particles in the matrix resin, which exhibited excellent effect to prevent the corona damage.
3.1. Thermal degradation analysis

Figure 4 shows the weight loss versus temperature curves of PMMA/PE/\(\gamma\)-Fe\(_2\)O\(_3\) at different heating rates. It is interesting that degradation shows only one degradation step in different heating rate procedures. Both results show that the thermal behavior is obviously different from traditional ones and also suggest that the different end groups maybe have different behavior as proposed by Manring, because PMMA/PE/\(\gamma\)-Fe\(_2\)O\(_3\) has an end group which is less stable and generates a radical unzipping the polymer chains via the chain transfer process. Most researchers agree that the unstable ends present in the polymer prepared by a radical mechanism are unsaturated ends resulting from termination by disproportion. For PMMA samples with different molecular weights, possibly, some termination occurs leading to unsaturated ends normally degrading around 270 °C as explained before. For the two molecular weights investigated, the peak has a similar magnitude indicating that the initiation of this degradation step is of the same kind for the two polymers. It may be assumed that the initiation is caused by similar species probably involved in the polymerization process for which unfortunately no information was available. Figure 4 also shows that PMMA/PE/\(\gamma\)-Fe\(_2\)O\(_3\) with the highest molecular weight degrades more at lower temperatures than PMMA/PE/\(\gamma\)-Fe\(_2\)O\(_3\) with the lowest molecular weight confirming previous observations.

3.2. Effect of \(\gamma\)-Fe\(_2\)O\(_3\) groups on thermal stability for PMMA/PE/\(\gamma\)-Fe\(_2\)O\(_3\)

The relationship between the activation energies and the degree of conversion is reported in Figure 5. These values fall within the range of activation energies for PMMA/PE/\(\gamma\)-Fe\(_2\)O\(_3\) degradation reported previously. The activation energy values of pure PMMA/PE/
\(\gamma\)-Fe\(_2\)O\(_3\) and its nanocomposites generally showed an increase with the degree of conversion.

Radical polymerization gives a polymer with two initiator fragments as its chain ends if no transfer reactions occur and mutual termination proceeds only by recombination. However, in ordinary radical polymerization of many monomers, the chain transfer reactions are known to be important, in other words, the number of initiator fragments per polymer molecule is always less than 2 that there exist vinyl end groups due to the chain transfer of end group to monomer. As compared to the polymer chain structures, the end group had a weaker bonding chains, and the end groups started to degraded at about 220 °C. As the temperature rises above 300 °C, the mechanism of degradation becomes random scission, and the depolymerisation rate increased due to the main chain scission. From the TGA curves, the degradation rate increased more rapidly with the whole of the polymer unzipping completely above 300 °C. The significance of the shift of the maximum transition temperature, however, is due to the effect of the main chain unsaturation. The new system has the degradation temperature about 100 °C higher than other systems.

The presence of \(\gamma\)-Fe\(_2\)O\(_3\) shows higher activation energy of degradation values between 20 and 70% weight loss than those of without. The observation supports the increase in thermal stability of the PMMA/PE–\(\gamma\)-Fe\(_2\)O\(_3\) nanocomposites observed in TGA. However, the presence of the rutile phase generally shows lower activation energy of degradation values. The decreased activation energy suggests that \(\gamma\)-Fe\(_2\)O\(_3\) may have acted as a catalyst for the thermal decomposition of the composites.

Figure 6 shows the FTIR transmittance spectra of PE, PMMA/PE composite and \(\gamma\)-Fe\(_2\)O\(_3\)/PMMA/PE films. PPANI shows absorption at 1500 and 1600 cm\(^{-1}\) which are assigned to C–C stretch of benzenoid and quinoid groups respectively. In addition, the appearance of band at 2950 cm\(^{-1}\) is assigned to saturated C–H stretch which indicates the partial loss of aromaticity during plasma polymerization. The appearance of bands at 697 cm\(^{-1}\) due to 1,3 di-substituted aromatic ring (meta) and 758 cm\(^{-1}\) due to 1,2 di-substituted aromatic ring (ortho) suggest branched structure of PE. The strong absorption
at 1040 cm\(^{-1}\) may be due to in-plane C–H deformation. The band at 3330 cm\(^{-1}\) is assigned to secondary amine N–H stretch and the bands in the range 3448–3855 cm\(^{-1}\) present in all films are due to OH stretch of absorbed water. The sputtered nano \(\gamma\)-Fe\(_2\)O\(_3\) has absorption bands at 741 and 612, 526 cm\(^{-1}\), which are assigned to Ti–OH and Ti–O stretch respectively. The intensity of the band at 526 cm\(^{-1}\) is weakened in the composite form. The C–C stretch at 1600 cm\(^{-1}\) is slightly shifted to 1586 cm\(^{-1}\) and the band at 1500 cm\(^{-1}\) disappears in the composite form. This means due to additional ion bombardment of sputtering, benzene rings are broken down in the composite form. From the above findings it is clear that the initiation of polymerization takes place through the substitution of benzene rings and the benzene rings are broken down by the glow discharge energy. So under continuous bombardment of plasma species, the precursors are broken down seriously and the deposited film structures are usually crosslinked and a few functional groups are retained and form unique polymeric structure.

Since the nano-scale morphology of the system with ordered domains are probably preferred under the slow-drying regime of blend films, annealing only improves the crystallinity and further percolation/clustering. If the blend film is dried immediately after spin casting (in fast-drying regime), the polymer chain of PE grows into comparatively large crystalline domains along with the formation of clusters. The growth of interpenetrating nano-scale domains under the slow-drying regime and subsequent annealing at appropriate temperature to improve the crystallinity is perhaps ideal to ensure the maximum dissociation of the photoinduced excitons and also results in low mechanical properties for such morphology.

The low angle XRD patterns of all blend films (Figure 7) have a sharp peak in the 2\(\theta\) range of 5 and 6 corresponding to the PE and the best performing blend films have optimal peak intensity i.e. crystallinity rather than having very large crystalline domains of PE in comparison to PMMA/PE that will forbid efficient charge separation. If the polymer blends have a large proportion of amorphous matrix, the entangling of polymer chains also contributes to the enhanced mechanical properties. Therefore, we attribute the lowest
Young’s modulus and hardness of 1:1 wt/wt ratio blend film processed to the optimal morphology of crystalline. However, PMMA/PE–$\gamma$-Fe$_2$O$_3$ film on the substrates are bent or stretched, and it may adjust the film morphologies and impact device performances. With the measurement of mechanical properties, we can more easily monitor the film quality and maintain the device performances in roll-to-roll production process.

4. Conclusion

(1) Dielectric strength were slightly increased with the $\gamma$-Fe$_2$O$_3$ content increasing and then decreased gradually. And the addition of PE further improves the thermal properties of PMMA/PE/$\gamma$-Fe$_2$O$_3$ composite. The improved electrical aging performance of PMMA/PE hybrid film is related to the highly dispersion and adequate addition of $\gamma$-Fe$_2$O$_3$ particles in the matrix resin, which exhibited excellent effect to prevent the corona damage.

(2) The presence of $\gamma$-Fe$_2$O$_3$ shows higher activation energy of degradation values between 20 and 70% weight loss than those of without. The coefficient of thermal of PMMA/PE/$\gamma$-Fe$_2$O$_3$ is slightly less than that of PMMA/PE. When $\gamma$-Fe$_2$O$_3$ was added to PMMA/PE composite, the coefficient of thermal property was lowered further.

Disclosure statement

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