Miscible Transparent Polymethylmethacrylate/Cellulose Acetate Propionate Blend: Optical, Morphological, and Thermomechanical Properties

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To obtain a high transmittance blend within ultraviolet and visible regions, various transparent samples of ascending percentages of polymethylmethacrylate (PMMA)/cellulose acetate propionate (CAP) were prepared by melt blending using a twin screw extruder. These blends were characterised by ultraviolet-visible spectroscopy, and the curves illustrated that the blending ratio of 10% CAP in PMMA meets the required purpose. The morphological, mechanical, and thermal properties for pure PMMA and the PMMA/CAP 10% blend were investigated using X-ray diffraction, scanning electron microscopy, dynamic mechanical analysis, and thermogravimetric analysis. The results showed that the PMMA/CAP 10% blend has an amorphous structure and low stiffness than pure PMMA. The miscible PMMA/CAP 10% blend exhibited mechanical stability below the glass transition temperature (T_g), with a slight increase in T_g value relative to that of pure PMMA. The study also demonstrated that the intermolecular interaction between blend elements has an effective influence on the physical properties of the blend.

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INTRODUCTION

Polymer blends are regarded as an effective way to obtain new products, and for problem-solving by providing the ability to control characteristics without the creation or invention of new polymers. Physically mixing two or more polymers often yields immiscible or partially miscible blends (Manson 2012); however, miscibility in the polymer blend is the property we hoped to achieve in this study. Although there are a number of studies that have reported miscibility in polymer blends (Edgar *et al.* 2001; Bhat and Jois 2014; Bourara *et al.* 2014; Bao *et al.* 2015; Huang *et al.* 2015), it is an infrequent occurrence, so it is treated as a special case (Paul 2012). Some thermodynamic factors are interconnected in a complex way to the polymer-polymer interaction such as miscibility, adhesion, and interfacial energies (Park *et al.* 2014). Two-polymer miscibility is mostly caused by a negative heat of mixing. This can be achieved by particular interactions between the constituent particles of the blend (Nesterov and Lipatov 1998; Olabis 2012). Generally, miscible polymer blends are structurally homogeneous and

thermodynamically stable; this can be seen morphologically by the lack of interface between the blend phases, so the comparable term is used to describe single-phase behaviour (Olabis 2012; Paul 2012). Furthermore, a miscible polymer blend shows a single glass transition temperature (T_g) for its components (Gajria *et al.* 1996; Olabis 2012); otherwise, there will be several peaks for each component of the immiscible blend (Manson 2012).

Poly (methylmethacrylate) (PMMA) is an important thermoplastic engineering polymer because of its wide application in several areas, including optics. Its light weight and high transparency have made it a viable alternative to glass. As a result of direct contact with weather conditions, especially ultraviolet (UV) radiation, PMMA suffers from scission (Davis and Sims 1983; Choi *et al.* 1988; Torikai *et al.* 1990; Choi *et al.* 2001). It has been found that the photodegradation of PMMA in air leading to random scission starts with the decomposition of side-chains (ester side groups) and ends with main chain scission (Fox *et al.* 1963; Davis and Sims 1983; Caykara and Güven 1999). The most important products of PMMA scission are hydrogen, methane, carbon dioxide, and carbon monoxide. During exposure to radiation, the UV absorption of PMMA increases because of the chromophoric groups (Fox *et al.* 1963). Chromophoric groups such as the carbon-carbon double bonds (C=C) and carbonyl groups (C=O), which are able to absorb UV energy, will be involved in the photochemical degradation reactions that occur *via* free radical mechanisms, leading to the formation of hydroperoxides and chain scission (Davis and Sims 1983; Clough and Shalaby 1991; Dole 2013). The UV irradiation causes random chain scission, leading to variations in molecular mass, T_g, and spectra, as well as the loss of volatile particles from PMMA (Abouelezz and Waters 1978, Torikai *et al.* 1990).

Recent research has focused on the use of biodegradable materials such as cellulose esters in the formation of layers or blends to handle some of their polymer optical, mechanical, and thermal properties (Nobukawa *et al.* 2014; Park *et al.* 2014; Kunthadong *et al.* 2015; Nobukawa *et al.* 2015). Cellulose acetate propionate (CAP) is an amorphous, transparent, and thermally stable polymer belonging to the cellulose ester family that has attracted attention from scientists because of its biocompatibility and properties intermediate between cellulose acetate and cellulose acetate butyrate. In CAP, a hydrogen bond with the presence of hydroxyl groups and ester carbonyl groups plays an important role in forming a homogeneous polymer blend (Edgar *et al.* 2001; Bhat and Jois 2014; Bourara *et al.* 2014). It was reported that the orientation birefringence behaviour of cellulose ester blends with polymers has a significant influence on the optical properties of the blend, whereas the unusual wavelength distribution of the orientation behaviour of CAP macromolecules is due to the polarisability anisotropy of ester groups. In addition, the orientation birefringence of CAP is reliant on the ratio of draw and draw temperature; furthermore, the molecular mass also affects the orientation birefringence (Rinderknecht and Brisson 1999; Park *et al.* 2005; Yamaguchi *et al.* 2009). It is noteworthy that the interaction of the two phases enhances the synergistic effect, which leads to improved thermal stability of the CAP/polymer blend (Souza *et al.* 2012). The aim of this work was to reduce the photochemical reaction between transparent samples of different percentages of PMMA/CAP blends and UV radiation by making use of the unusual optical properties of CAP. Reducing the ability for interaction comes through looking for the best blending ratio of CAP into PMMA to make the blend more transparent in the UV region (less absorbance for UV radiation). The blend is supposed to be transparent in the UV area while maintaining transparency in the visible region.

EXPERIMENTAL

Materials

White powder CAP (average M_n ~15,000) and white powder PMMA (average M_w ~120,000 by GPC) were supplied by Sigma-Aldrich (USA).

Methods

Sample preparation was performed in two steps. The first was kneading the basic components of each concentration and the second was moulding the mix. The polymers were pre-dried in a vacuum oven at 50 °C for 4 h. The CAP/PMMA blend was prepared using a Thermo HAAKE PolyDrive Internal Mixer (Germany) ($D = 19.05$ mm).

To prepare the PMMA/CAP samples, a fixed weight of PMMA was melt-kneaded in the extruder at a rotation rate of 50 rpm at 130 °C for 10 min. Then, variable percentage weights of CAP (5%, 7%, 9%, *etc.* up to 20%) were added to the molten PMMA. Mixing continued until a constant torque was reached, which took about 15 min. The samples were transparent and homogeneous. After that, each blended sample was pressed by a hot press from the Hsin-Chi Machinery Co., Ltd., (Taiwan) at 110 kPa and 130 °C to form a sheet 70 mm × 90 mm and 1 mm thick.

Measurements

The transparency and absorbance nature of the samples were determined using ultraviolet-visible (UV-VIS) spectroscopy (Shimadzu UV-3600 spectrophotometer, Japan). Surface images were obtained using scanning electron microscopy (SEM) studies on a Hitachi S-3400N (Japan) microscope. The amorphosity of the samples was investigated using X-ray diffraction (XRD). The XRD patterns were recorded with an X-ray diffractometer (Philips PANalytical X'Pert Pro MPD – PW 3040/60, Netherlands). The diffractometer data were obtained from $2\theta = 20°$ to $80°$ with a scanning speed of 5°/min at room temperature. The thermal behaviour of the prepared samples was examined by a TGA/DSC1 STAR System (USA) thermogravimetric analyser at a heating rate of 10 °C/min from 50 to 1000 °C in nitrogen atmosphere. Dynamic mechanical analysis (DMA) was carried out on a Perkin Elmer Pyris Diamond (USA) device in tension mode at a frequency of 1 Hz a nd a heating rate of 10 °C/min in a liquid nitrogen atmosphere.

Characterisation

The optical characteristics within the UV and visible spectra were evaluated from 220 to 800 nm for transparent pure PMMA samples using a Shimadzu UV-3600 spectrophotometer. Results revealed a clear absorbance peak in the UV region for pure PMMA at 226 nm. The absorbance of high photon energy within the UV region led to scission in the polymer chain. More precisely, chromophoric groups, which are capable of absorbing the UV energy involved in the photochemical degradation reactions that occur *via* free radical mechanisms, led to the formation of hydroperoxides and chain scission of the polymer (Charlesby and Thomas 1962; Abouelezz and Waters 1978; Michelson *et al.* 2012). The transmittance peak for pure PMMA in the visible region was 798 nm. The transmittance peak in the visible region signifies the actual performance for pure PMMA (Moore and Ferreira 2006; Osuagwu and Ogbuehi 2014). The sample transparency as well as absorbance and transmittance peak values were relied upon for all subsequent measurements on the blended samples under study.

RESULTS AND DISCUSSION

UV-VIS Spectroscopy

The absorbance and transmittance spectroscopy curves, in addition to the spectra and visual appearance of the PMMA/CAP blends, are shown in Fig. 1.

A preliminary study of the optical properties was carried out, investigating specifically the absorbance and transmittance within the UV and visible regions. Initial concentrations of CAP in PMMA were 5%, 10%, 15%, and 20%. The absorbance *versus* concentration curve for these four concentrations demonstrated that the lowest value of absorbency was at 10% CAP, *i.e.*, approximately 2.572 (the absorption of pure PMMA is 3.408), with transparency up to 87.561%. New samples were prepared and added (7%, 9%, 10%, 11%, 13%, and 15%) to make a full examination of the low absorbance area (10% CAP). Three samples were tested from each concentration, and then the average for each concentration was determined to calculate the values of absorbance and transmittance.

Figure 1(a) shows the absorbance *versus* concentration curves for pure PMMA and PMMA/CAP% blends. The decline in the value of the absorption curve is clear at 10% CAP. This decline in the value of absorption corresponds with a transmittance peak in the same concentration, 10% CAP, at the threshold of 226 nm. Figure 1(b) shows two transmittance peaks, one at a concentration of 10% CAP and the other at 15% CAP. The peak value of transmittance at 15% CAP was higher than at 10% CAP (89.41 and 88.64, respectively), but at 15% CAP the peak value had a high absorbance within the UV area (3.003), as can be seen in Fig. 1(a). Therefore, 10% CAP was chosen as the highest concentration. The selection of PMMA/CAP10% as the best blend concentration met the required purpose of the work, which was to achieve the lowest absorbency of optical radiation within the UV region, especially at the damage threshold of PMMA (226 nm). The absorbance and transmittance curves for pure PMMA and all concentrations are shown in Fig. 1(c). From the transmittance curves, it seems clear that the optical transmittance of pure PMMA and PMMA/CAP10% are approximately compatible, with some shifting into the visible region at 10% CAP. This demonstrates that the transparency behaviour of the PMMA/CAP10% blend matches that of pure PMMA.

Making the PMMA/CAP10% blend more transparent to UV radiation led to a reduction in the amount of damage that resulted from photochemical degradation reactions (Davis and Sims 1983), meaning that it reduced the severity of the interaction between UV radiation and the carbonyl groups (chromophoric groups) of the PMMA/CAP10% blend (Salamone 1998). The PMMA/CAP10% blend minimises peroxide formation and chain scission (Torikai *et al.* 1990; Caykara and Güven 1999; Dole 2013). It seems obvious from the absorbance curve that 10% CAP concentration in PMMA gave less absorbency in the UV region. This may be due to the nature of the chemical bonding between CAP and the PMMA backbone in the composition (Edgar *et al.* 2001; Manaf *et al.* 2011), while a high transparency of the sample of about 88.64% was maintained.

The difference in the absorbance and transmittance values with concentration variation, as shown in Fig. 1 (a,b), can be attributed to the polarizability anisotropy of ester groups (Yamaguchi *et al.* 2009). That means, with respect to the wavelength dependence of the propionyl or acetyl group, one can expect unusual dispersion with positive or negative orientation birefringence.
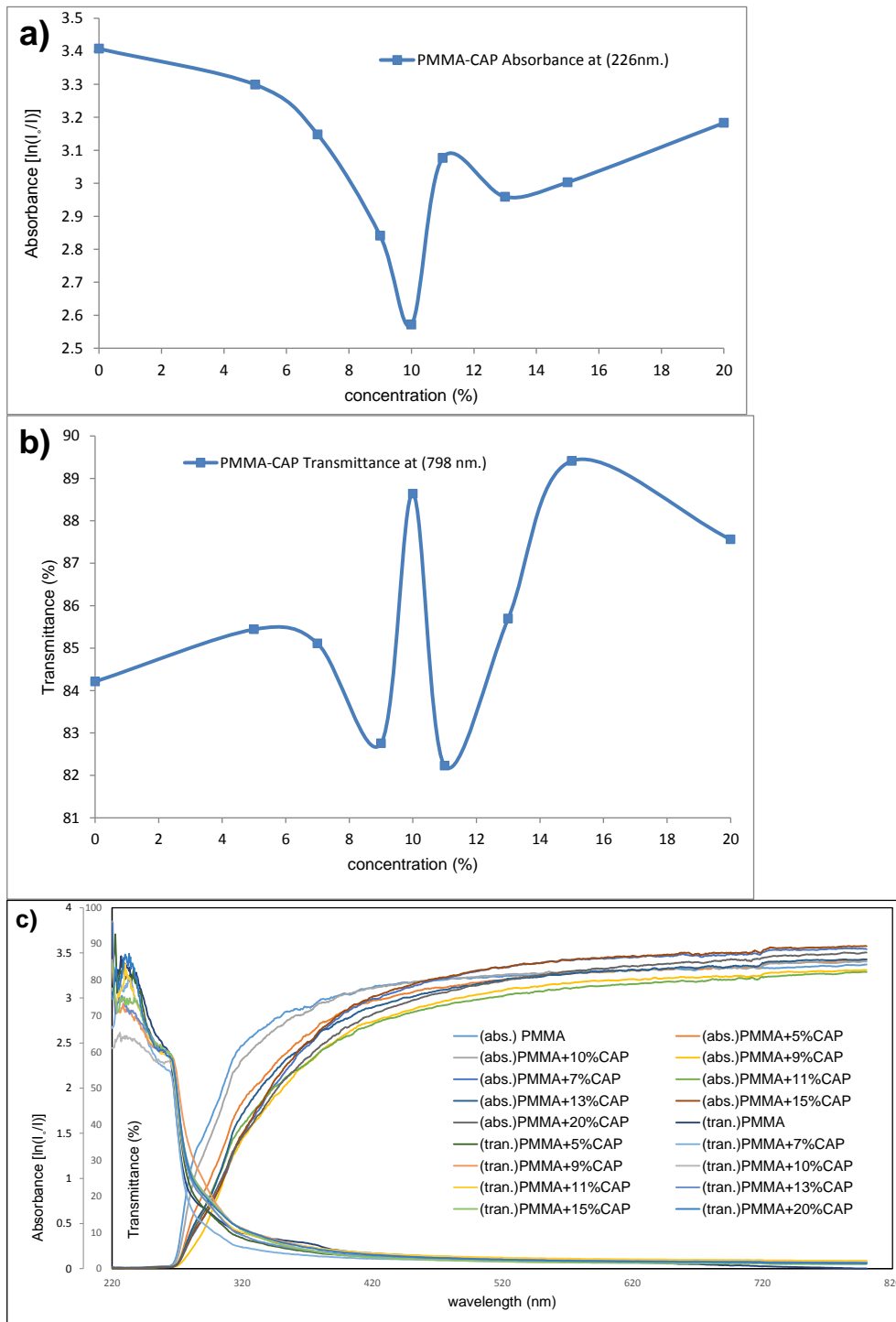
Fig. 1. (a) Absorbance of PMMA and CAP in different concentrations at 226 nm; (b) transmittance of PMMA and CAP in different concentrations at 798 nm; (c) PMMA/CAP absorbance and transmittance spectrum with concentrations; (d) PMMA/CAP sheets in different concentrations

Even in the case of a single polymeric material, not polymer blends, one may observe unusual dispersion (Yamaguchi *et al.* 2009). The transparency curve shows that there was a clear creep towards the visible region from 10% CAP down to 15% CAP concentration. This property has wide applications in different optical fields (Edgar *et al.* 2001; Yamaguchi and Masuzawa 2007a; Manaf *et al.* 2011). The PMMA/CAP blend samples started to become cloudy with increasing CAP concentration in PMMA. Samples with concentrations higher than 20% were discarded because they did not meet the required purpose (Fig. 1(d)).

X-Ray Diffraction

The XRD diffractograms for pure PMMA and the PMMA/CAP10% blend are shown in Fig. 2. The amorphous structure of pure PMMA and the PMMA/CAP10% blend did not have long-range order and therefore made broad scattering peaks**.** Broad peaks in XRD diffractograms are a typical characteristic of amorphous materials and are known as amorphous humps (Guinier 1994). The values obtained from the diffractograms show that there was a difference in the intensities of pure PMMA and PMMA/CAP10% peaks.

The intensity of the PMMA/CAP10% peak was approximately three times higher than the peak of pure PMMA. Moreover, there was a clear shift of the peaks after the addition of 10% w/w CAP to PMMA increasing towards 2θ. This implies that 10% w/w CAP has maintained random situation and that complication took place between the CAP composition and PMMA structure in the amorphous region. The increasing intensity and shift of the peaks confirm the occurrence of stereochemistry complication between PMMA and CAP (Gupta and Singh 1996; Ramesh *et al.* 2010). In other words, the shift of the peaks confirms that interactions happened between PMMA and CAP structure (Ramesh and Arof 2001).The intensity of characteristic peaks increased after 10%CAP addition because of increase the arranged areas in the PMMA backbone (Ramesh *et al.* 2010).
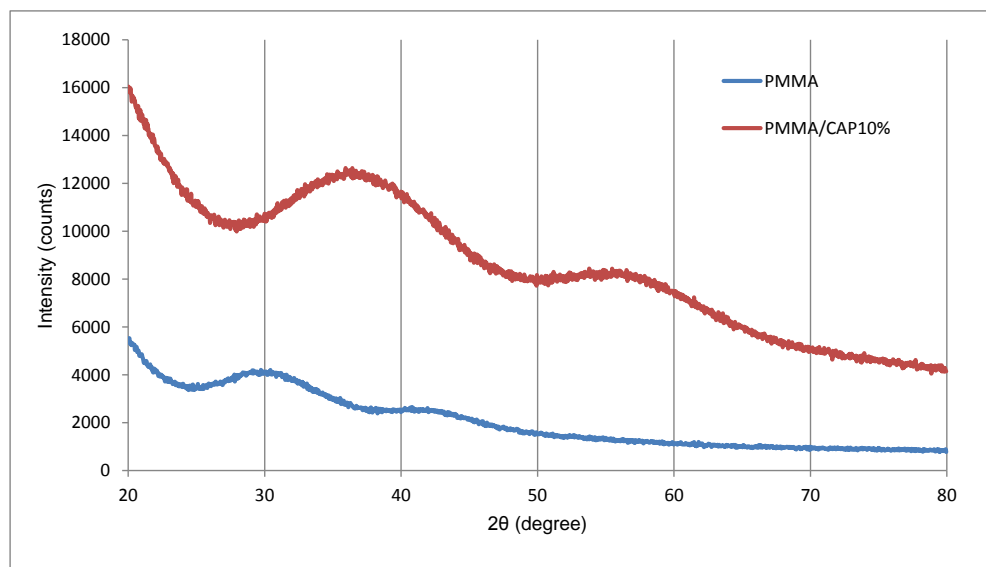

Fig. 2. XRD patterns for pure PMMA and PMMA/CAP10%

Dynamic Mechanical Analysis

Thermomechanical behaviour is commonly studied using the DMA technique. This technique is based on applying a small deformation (oscillatory force) to a sample in the cyclical mode and reporting changes in stiffness. A DMA scheme includes three basic curves (the storage modulus E' curve—the ability of the material to store potential energy, loss modulus E'' curve—energy dissipation in the form of heat upon deformation, and the phase angle tan δ curve—the mechanical damping or internal friction) in a viscoelastic system *versus* temperature (Mathur *et al.* 2003; Menard 2008).

The storage modulus, loss modulus, and phase angle *versus* temperature within a range of −10 to 130 °C for pure PMMA and the PMMA/CAP10% blend are shown in Figs. 3(a) and (b). The storage modulus E' curves for pure PMMA and the PMMA/CAP10% blend were similar in general appearance, and they showed a marked decrease with increasing temperature. Moreover, the E' curves did not show any clear milestones for the three deformation stages in the glassy region, as one can see them move smoothly from secondary dispersion passing through Hookean behaviour (gamma relaxation) to the second transition (beta relaxation). The onset temperature for pure PMMA and the PMMA/CAP10% blend moved from the glassy region to the rubbery region (glass transition) at 80 °C. The rubbery region started with a primary transition (alpha relaxation); in this region the E' curve strongly descended down to the high visco-rubbery region (visco-elastic fluid); it did not stay long in this area, moving to the flow (melt) region. The E'' curve for the PMMA/CAP10% blend was close to that of pure PMMA, and through T_g they were at a maximum.

Generally, E' curves are typical for amorphous thermoplastics. Therefore, at low temperatures, pure PMMA and PMMA/CAP10% blend molecules are unable to resonate with the oscillatory loads and hence remain stiff. This is apparent on the E' curve by the absence of the three deformations within the glassy region. In other words, the polymeric side groups are not able to rotate about the C—C bonds, so the molecular side groups behave as rigid crosslinks (Heijboer *et al.* 1987; Menard 2008; Merenga and Katana 2010). At 80 °C, the pure PMMA and PMMA/CAP10% blend molecules moved to the alpha relaxation region, which is the main chain motion area. In this region (the glass transition region), the E' curve fell during heating to a level a thousandth of its original value. The E' curve left the alpha relaxation region at 120 °C for the rubbery region (Fekete and Pukánszky 2005; Merenga and Katana 2010). The addition of 10% CAP to PMMA led to a clear decline in the values of E' and E'' at lower temperatures.

There is a slight shift for tan δ curve peak for PMMA/CAP10% blend, which suggested that the presence of CAP molecules caused a decrease in the free volume related to the segmental motion of PMMA at high temperatures near T_g. With decreasing of the free volume, the amplitude of the local motion for beta relaxation becomes smaller (Yamaguchi and Arakawa 2007b; Nobukawa *et al.* 2013).

The identical tan δ curve peak at 105 °C for PMMA and PMMA/CAP10% represents the T_g for atactic miscible PMMA (Bosma *et al.* 1988; Teng *et al.* 2009; Olabis 2012). The decrease in the values of E' and E'' for the PMMA/CAP10% blend is a sign of more freedom in the polymer chain movement (Heijboer *et al.* 1987), leading to decreased hardness of the blend.
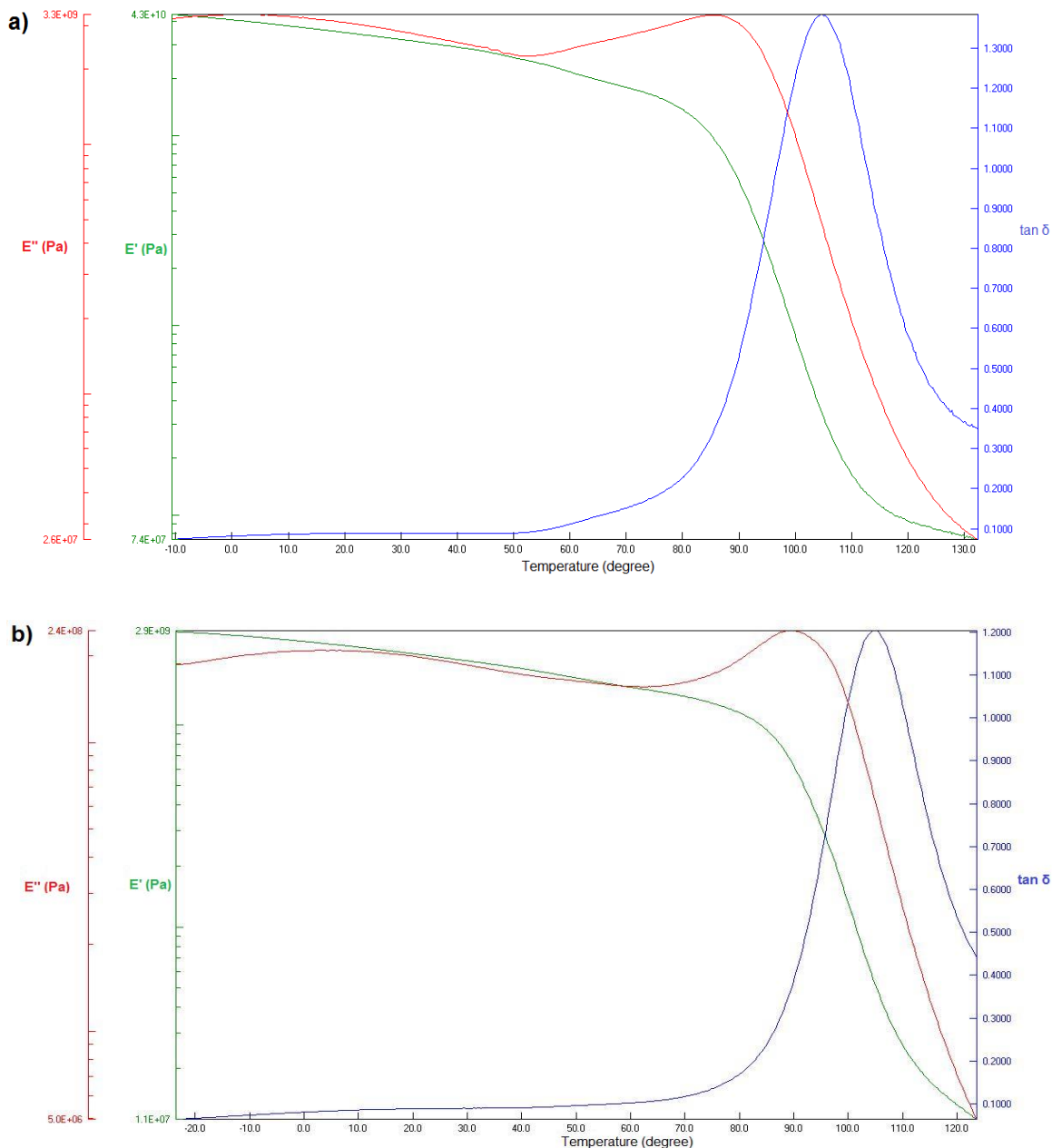
Fig. 3. Storage modulus *E*', loss modulus *E*'', and tan *δ* trace for (a) pure PMMA and (b) PMMA/CAP10%

Thermogravimetric Analysis

The mass loss rate *versus* temperature thermograms for pure PMMA and the PMMA/CAP10% blend are plotted in Figs. 4(a) and (b).

The thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) thermograms of pure PMMA show three thermal degradation areas beginning at 280 °C with a total mass loss of ≈27% due to head-to-head linkage scission (weak links) (Kashiwagi *et al.* 1986; Manring *et al.* 1989), then at 384 °C with a total mass loss ≈47% because of unsaturated vinyl end decomposition that leads to cleavage from the chain end (Kashiwagi *et al.* 1986; Wang *et al.* 2005). The third and last degradation at 525 °C with

a total mass loss of ≈15% was caused by PMMA main chain random scission (Kashiwagi *et al.* 1986; Manring *et al.* 1989).

The first order reaction must have occurred during thermal degradation after random chain and/or chain-end scission. Random scission is caused by the pre-oxidation of PMMA as a result of air exposure. At high temperatures, during depropagation, intramolecular transfer is responsible for oligomer formation by the elimination of an unsaturated end group and thus for molecular weight degradation (Lehrle and Place 1997; Holland and Hay 2001; Hu and Chen 2003).

In Fig. 5(b), the PMMA/CAP10% blend TGA and DTG diagrams show two thermal degradation stages. The first at 310 °C with a total mass loss of ≈1% was caused by the degradation of the substitute parts of the CAP chain, and the second at 400 °C with a total mass loss of ≈98% is attributed to the degradation of the blend backbone (polymer main chain) (Jeon *et al.* 2012; Allue and Botaro 2012). The TGA trace shows that PMMA has a high residue (7.1853%) and thermal stability than the PMMA/CAP10% blend (0.6222%).
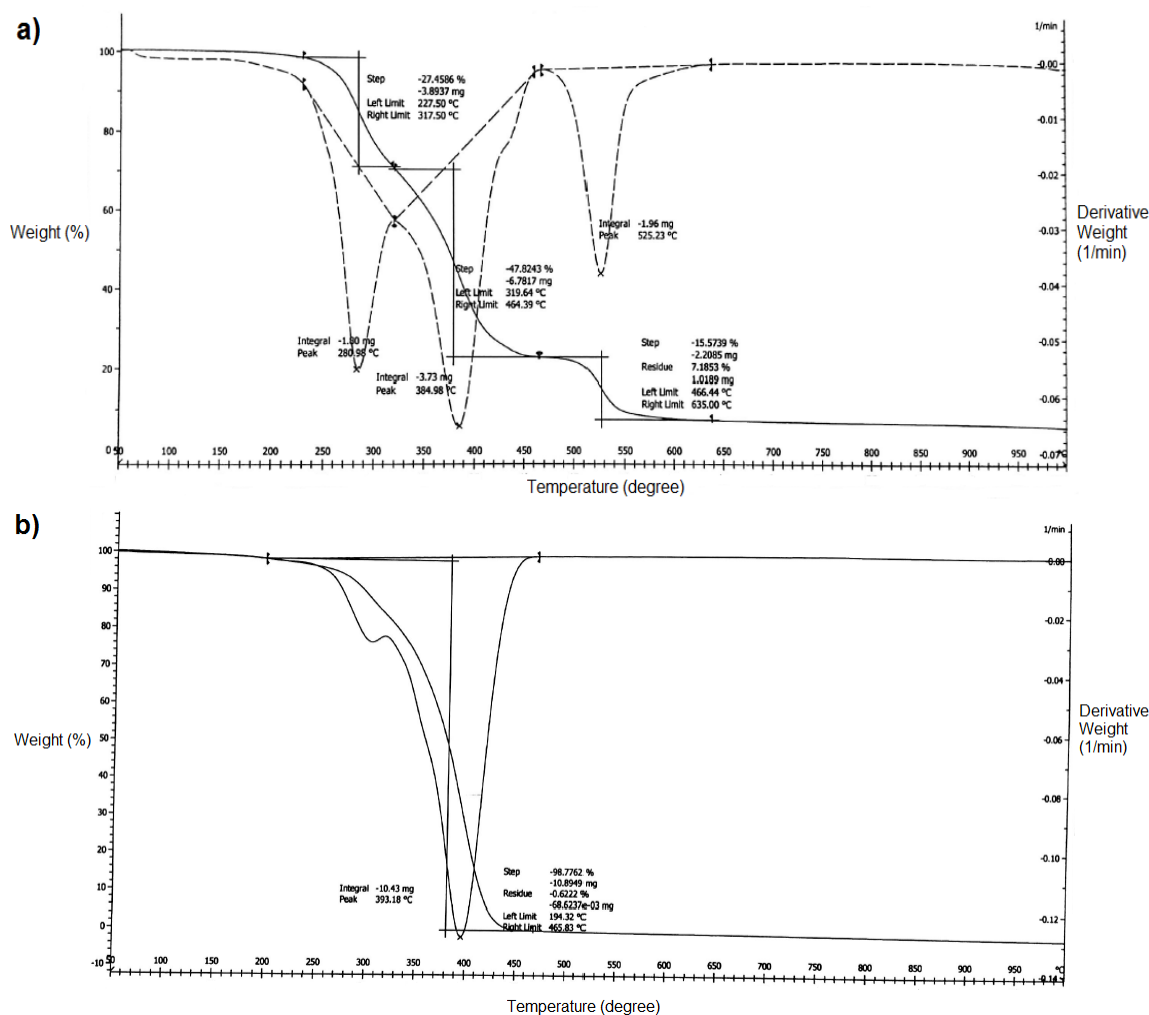

Fig. 4. TGA and DTG thermograms for (a) pure PMMA and (b) PMMA/CAP10%

Scanning Electron Microscopy

The characteristic features of pure PMMA and the PMMA/CAP10% blend obtained from SEM are shown in Fig. 5. The SEM images for each sample are shown at three different magnifications (2, 5, and 10 µm). The pure PMMA surface images illustrate, unambiguously, uniform morphological features, representing a single material (homopolymer) (Fig. 5(a–c)) (Silverstein *et al.* 2014).

No collective configuration and boundary were noted in the PMMA/CAP10% blend images (Fig. 5(d–f)). The homogeneity of the blend can be seen as evidence of its miscibility. The polar interactions between the blend components and the nature of their spread in the blend matrix have an active role in making the blend homogeneous and stable against phase separation. Furthermore, the formation of hydrogen bonds in the carbonyl group of PMMA helps the amorphous phases in the blend to become miscible (Jeong *et al.* 2000; He *et al.* 2004; Bhat and Kumar 2006; Dixit *et al.* 2009; Bourara *et al.* 2014). The high homogeneity polymer blend shows homopolymer behaviour. This seems to be in agreement with the DMA and TGA results. In DMA, there was no change in the overall shape of the curves, nor to the constancy of T_g after adding 10% CAP. As for TGA, the improvement in thermal stability was very clear (Bourara *et al.* 2014).
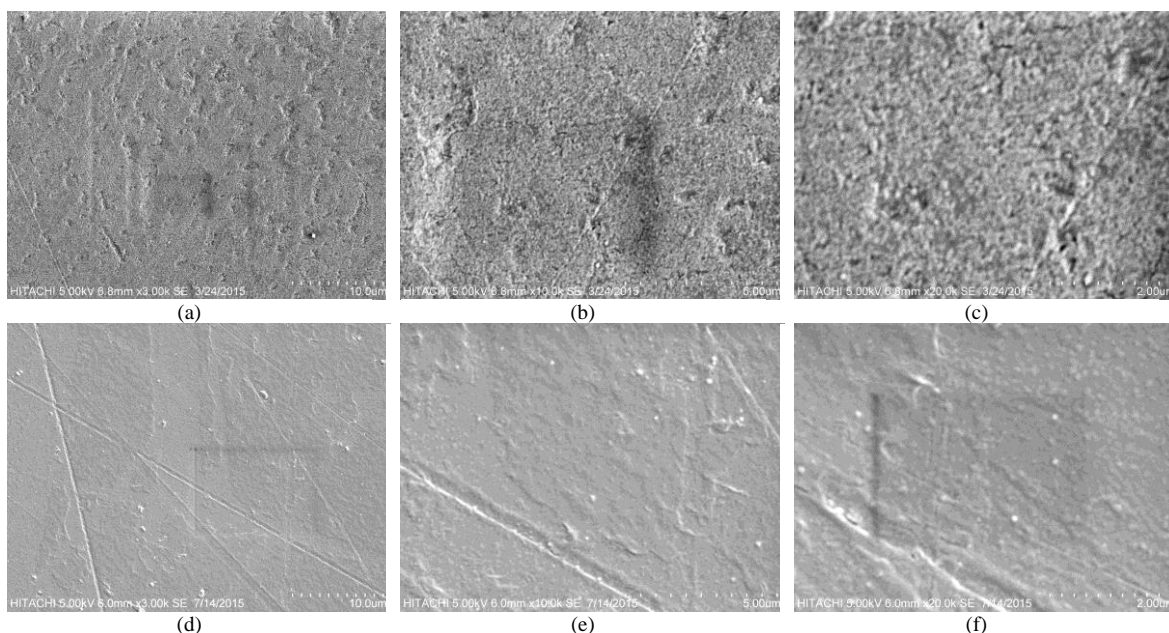

Fig. 5. SEM images for PMMA and the PMMA/CAP10% blend with different scale bars;
(a) PMMA/10 µm; (b) PMMA/5 µm; (c) PMMA/2 µm; (d) PMMA/CAP10%/10 µm;
(e) PMMA/CAP10%/5 µm; (f) PMMA/CAP10%/2 µm

CONCLUSIONS

1. Transparent blends of PMMA and CAP were achieved by melt blending. The UV-VIS spectrum showed that pure PMMA has an absorbance peak (3.408) at approximately 226 nm with transmittance up to 84.29% at 798 nm, whilst blending 10% CAP with PMMA provides less absorbency in the UV region (2.572), with high transmittance (88.53%) at the same wavelengths.

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2. The TGA investigations show that the PMMA/CAP10% blend has less thermal stability than pure PMMA. This could be attributed to the rearrangement that occurred during the mixing process.

3. The DMA results confirmed that the modulus of the PMMA/CAP10% blend was lower than that of pure PMMA, and that both of them were mechanically stable below T_g. The tan δ curve peak at 105 °C clarified that PMMA is an atactic miscible polymer.

4. The amorphous structure of pure PMMA and the PMMA/CAP10% blend can be explained by amorphous humps in XRD curves with an increase in the intensity of the peaks and creep in the PMMA/CAP10% blend. As a result, CAP provides a high level of enhancement to protect PMMA from UV radiation.

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