

Polysulfone/Cellulose Acetate Butyrate Environmentally Friendly Blend to minimize the Impact of UV Radiation

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Abstract

An eco-friendly transparent blend for ultraviolet and visible light rays from polysulfone (PSF) and cellulose acetate butyrate (CAB) was prepared by melting and re-molding. Some optical, mechanical, thermal and morphological properties of the blend were studied by means of UV-Vis spectroscopy, dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), scanning electron microscope (SEM) and X-ray diffraction (XRD). The UV-Vis spectroscopy results showed that the blend became more transparent in the ultraviolet region with an increase in CAB concentration, especially at the damage threshold (268 nm). The preferable blend sample contained 0.2% w/w CAB in the PSF/CAB blend, signifying low ultraviolet light absorption while preserving the transparency of the blend. The results also demonstrated that the amount of 0.2% CAB in PSF increased the modulus and thermal stability while decreasing the value of the glass transition temperature.

Keywords: Blend; Cellulose acetate butyrate (CAB); Polysulfone (PSF); Ultraviolet

Introduction

Polymer blend is a combination of two polymers or composites at least. The purpose of polymer blending is to obtain a new material with different physical properties to meet performance requirements that cannot be satisfied by the currently available polymer. There are two ways to blend polymers. One is by blending the compound component in the molten state; the other is to blend them in common solution [1]. Melting by using the twin screw extruder (used in this work) is the other method. The twin screw extruder is preferred for melt-blending polymers with added materials instead of using a single screw extruder because of several issues, including its extraordinary mixing ability, the high degree of process resilience, better control of process parameters, and higher process productivity. Therefore, mixing and melting two materials for the purpose of forming a homogeneous blend or composite will be easier and more accurate by using the twin screw extruder [2,3].

In recent years, much attention has been focused on environmentally friendly materials as a renewable source to reduce the amount of waste that accumulates on the Earth. Therefore, inserting renewable polymeric materials in the blend has become the focus of many academic studies and industrial undertakings [4-7]. Renewable polymeric materials carry a higher grade of complexity than artificial ones. This is the result of nature's long growth in terms of material design, which is of great importance to many applications. Natural polymers have numerous positive properties compared to artificial polymers that make them ideal applicants for different applications.

Conversely, there are numerous disadvantages of biodegradable polymers obtained from renewable sources, such as unacceptable mechanical properties especially under wet conditions, solubility in water, and the rapid degradation rate. Although there is no ideal polymeric blend or composite from renewable resources, the properties of polymer blends can notably improve by blending synthetic polymers with natural polymers [8,9].

Bio-based cellulose acetate butyrate (CAB) is a thermoplastic polymer, obtained from the esterification of acetyl and butyryl group.

This polymer has showed its significance in different applications in terms of transparency and weathering resistance when used as a coating to repair or re-finish, and especially for ultraviolet protection, in addition to the high usability of casting and molding. Therefore, CAB is used as biodegradable inhibitor with polymers. The biodegradation inhibitor has postulated that the change in the biodegradability of the blend with CAB was caused by the new structural phase formed when CAB is added to the blend [10-13].

Polysulfone (PSF) is also a thermoplastic polymer like cellulose acetate butyrate (CAB). It is well known for its transparency, toughness, high strength and high thermal stability. In some applications, it is used as a substitute for polycarbonate because of its unique properties, but its low resistance to a number of solvents and rapid weathering restricts its applications [14,15].

Studies have confirmed that the microstructure and the performance of PSF are affected by ultraviolet irradiation within a very short time of exposure, leading to simultaneous chain scission and crosslinking [16]. PSF photooxidation in an oxygen atmosphere leads to an oxidized surface with an increase in the relative amount of sulphur on the surface. This change is attributed to rapid oxidation at carbon sites in the polymer [17]. At temperatures below 140°C, long heating times cause little changes in the PSF properties, but exposure to ultraviolet light results in greater changes, as indicated by broad absorption in both the carbonyl and hydroxyl areas [18].

The purpose of this work is to make the PSF/CAB blend more

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transparent in the UV region in order to reduce the damage that is caused from trapped radiation inside the material, and to withstand weather conditions.

Experimental

Materials

Transparent pellets of polysulfone (PSF; average $M_w \sim 35,000$ by LS, average $M_n \sim 16,000$ by MO) and white powder cellulose acetate butyrate (CAB; average $M_n \sim 12,000$) were supplied by Sigma-Aldrich(USA).

Methods

The samples were prepared using twin screw (three zones, electric heating and air cooling) Thermo-Haake Poly Drive Internal Mixer (Germany) (D=19.05 mm) and Hsin-Chi Machinery Co. Ltd. hot press (Taiwan). The materials were dried in a vacuum oven at 50°C for 4 h before mixing. The CAB/PSF blends were prepared by adding a fixed weight of PSF to different weight ratio of CAB. Firstly, the polymer pellets was melt-kneaded in the extruder at a rotation rate of 50 rpm at 225°C for 10 min. Then, variable percentage weights of CAB (0.1%, 0.2%, 0.3% and 0.4%) were added to the molten of PSF. Mixing continued until reached to constant torque, which took about 10-15 min. The samples were transparent and homogeneous in their outward appearance. After that, each blended sample was pressed in a hot press at 110 KPa and 130°C to form a sheet 70 mm × 90 mm, 1 mm thick.

Measurements

The character of the transparency and absorbance of the samples was determined using ultraviolet-visible (UV-VIS) spectroscopy (Shimadzu UV-3600 spectrophotometer, Japan). Surface analysis was obtained out by scanning electron microscopy (SEM) studies on a Hitachi S-3400N (Japan) microscope. Sample morphology and crystallinity identification were determined by XRD analysis using a X-ray diffractometer (Philips/X'Pert Pro Panalytical - PW 3040/60 MPD, Netherlands). The diffractometer data were obtained from $2\theta = 20^\circ$ to 80° at a scanning speed of 5°C/min. Dynamic mechanical analysis (DMA) was made on a PerkinElmer Pyris Diamond (USA) apparatus in tension mode at a frequency of 1 Hz and a heating rate of 5°C/min in a liquid nitrogen atmosphere. Thermal gravimetric analysis (TGA) was undertaken on a TGA/DSC1 STAR System (USA) at a heating rate of 20°C/min from room temperature to 1000°C in a continuous highly pure nitrogen atmosphere.

Characterization

Complete scans over the ultraviolet and visible spectra were made from 220 nm to 800 nm for highly transparent pure PSF samples using a Shimadzu UV-3600 spectrophotometer. The results show that the absorbance peak in the ultraviolet range for pure PSF was at 268 nm, which represents the UV damage peak for the polymers [19-21], whilst the transmittance peak in the visible range for pure PSF was 712.5 nm. The transmittance peak indicates the real effectiveness for pure PSF [21]. The absorbance and transmittance peak values were adopted for all subsequent measurements on the blended samples under study, as well as the sample transparency.

Results and Discussion

UV-VIS spectroscopy

The absorbance and transmittance curves, in addition to the spectra and the visual appearance of the PSF and PSF-CAB blends are shown in Figure 1.

The CAB concentration in PSF was 0.1, 0.2, 0.3 and 0.4%. Figure 1a shows the relationship between absorbance and concentration for PSF at 268 nm. It is clear that an increase in the CAB concentration in PSF reduced the optical absorbance in the ultraviolet area, especially at the damage threshold (268 nm). The retention of ultraviolet radiation within PSF molecules leads to the breakdown of bonds in the polymeric chain and disintegration over time. Therefore, a change in physical properties will take place, which reduces the lifetime of utilization [18]. On the other hand, the optical transmittance in the visible region, especially at a wavelength of 712.5 nm, was relatively stable at the first two concentrations, then declined from 0.2% to 0.4%; this is evident from the foggy samples shown in Figure 1d. Therefore, 0.2% CAB was the best concentration of PSF in terms of the lack of absorption in the mid-ultraviolet region and the maintenance of optical transmittance with the required transparency.

In the PSF-CAB blends, it was noted that the samples were transparent down to 0.3%; after that, the samples started to become hazy with an increasing CAB concentration in PSF. Samples with concentrations more than 0.4% were discarded because they did not meet the required purpose.

Scanning electron microscopy

The SEM images taken for the internal morphological study of pure PSF and PSF/0.2% CAB blend are shown in Figure 2. The SEM images for each sample are shown at three different magnifications (2, 5, 10 μm). As can be seen in the pure PSF images, there were uniform morphological features, indicating a single material (Figures 2a-2c) [22].

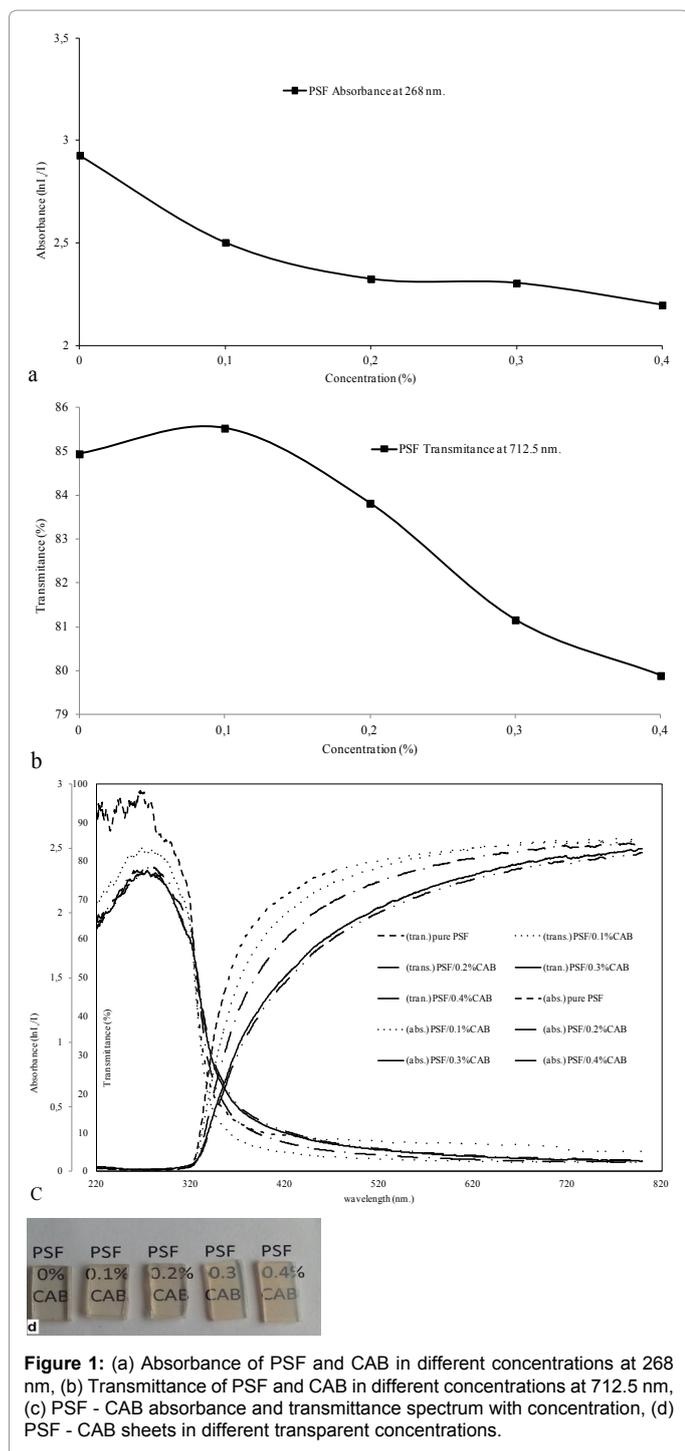
The morphology of PSF/0.2% CAB blend shown in Figure 2d-2f. It is easy to see the size reduction of the CAB components and separation from the continuous phase of PSF. Figure 2f shows that the size of CAB sphere not more than (99.5 nm). In polymer blends, if the concentration of one components is small, it tend to present in spherical droplets dispersed all over the matrix and the polymer nature determined the size [23]. The clear difference in the size of the spherical shapes may be due to variation in the interaction between functional components that led to an increase or decrease the surface tension [24,25]. As a result foggy appeared as early as in low concentrations of CAB in PSF.

X-Ray diffraction

The X-ray diffraction pattern of pure PSF and PSF/0.2% CAB blend are shown in Figure 3. The patterns in Figures 3a and 3b show that there were no clear peaks. The broadened background scattering areas of pure PSF indicate their amorphous nature and non-crystalline structure [26-28]. So, change absence that observed in the pure polymer to the blends indicates that CAB did not change the essential random compositional structure of the original polymer. This corresponds with previous data indicating that the spherical clusters were no larger than 99.5 nm in PSF/0.2% CAB, i.e., are not crystalline regions.

Dynamic mechanical analysis

The dynamic mechanical analysis is a technique involves studying the properties of materials as they are deformed under periodic stress by applying a variable sinusoidal stress under thermal conditions. Most polymers are viscoelastic and exhibit a phase difference between applied stress and the resultant sinusoidal strain. This phase difference, together with the amplitudes of the stress and strain waves, is used to determine a variety of parameters, including storage modulus E' (the ability of the material to store potential energy), loss modulus E'' (energy



dissipation in the form of heat upon deformation) and phase angle $\tan\delta$ (the mechanical damping or internal friction in a viscoelastic system). The dynamic modulus indicates the intrinsic stiffness of the material under dynamic loading conditions. Some polymeric blends are well-suited to this test due to their single phase. Nevertheless, most polymer blends form two phases because of incompatibility between the blend elements [29].

The curves of the storage modulus E' , loss modulus E'' and phase angle $\tan\delta$ vs. temperature for pure PSF and PSF/0.2% CAB are

shown in Figure 4a-4c. The storage modulus E' curve for PSF and the PSF/0.2% CAB blend showed three main regions, but in the glassy region there is a significant appearance of the three deformation phases (secondary dispersion at 82.6/23.9°C, γ -relaxation at 90.4/30-40°C and β -relaxation at 187/164°C) for pure PSF and the PSF/0.2% CAB blend, respectively. It was clear that adding CAB to PSF led to significant changes in molecular motion, so that two γ -relaxation processes were observed (30-40°C) because the substituent in the CAB component introduced phenylene rings [30]. At 187/164°C, the E' curve for pure PSF and PSF/0.2% CAB went into the transition region with a steep slope in order to meet with the $\tan\delta$ curve at the glass transition temperature (T_g) region for each curve, after that went into the rubbery region. The melt temperature of PSF was 220°C, which has been observed in several experiments. The sulfone with two neighboring benzene rings in PSF contains a highly conjugated diphenyl structure, with significant rigidity of the molecular chains of pure PSF, which led to a high T_g at 177.3°C, with the peak of $\tan\delta$ curve within the rubbery region [31].

The increase in the modulus value for the PSF/0.2% CAB blend indicated improved storage of potential energy but decrease in T_g value, so the addition of CAB increased stiffness and made the blend technologically compatible to some extent even though molecular level

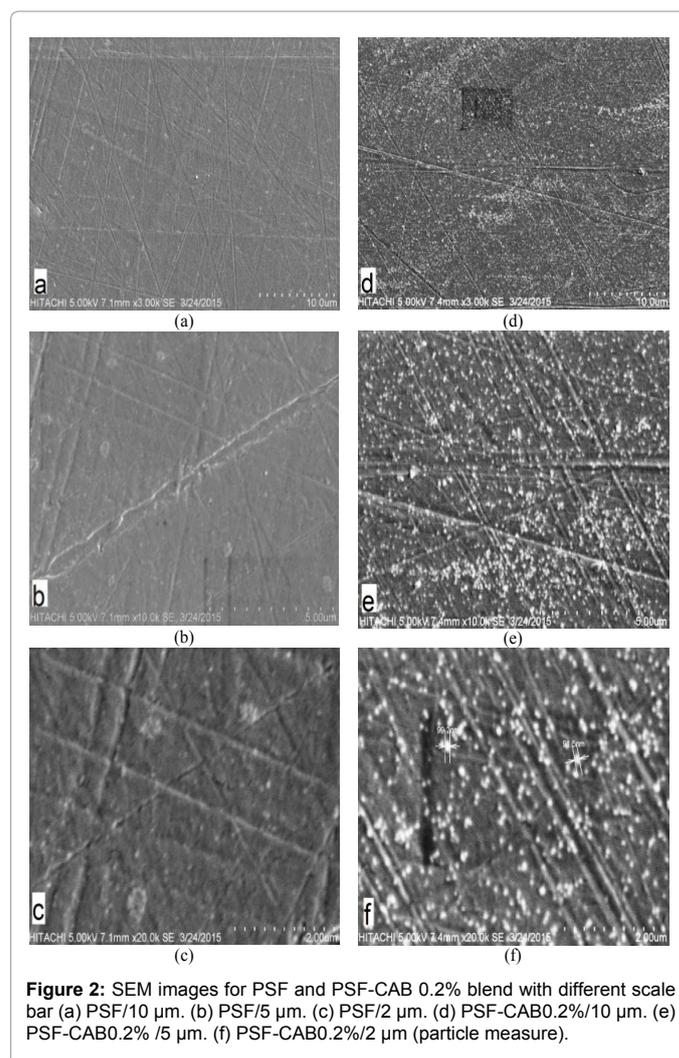


Figure 2: SEM images for PSF and PSF-CAB 0.2% blend with different scale bar (a) PSF/10 μm. (b) PSF/5 μm. (c) PSF/2 μm. (d) PSF-CAB0.2%/10 μm. (e) PSF-CAB0.2%/5 μm. (f) PSF-CAB0.2%/2 μm (particle measure).

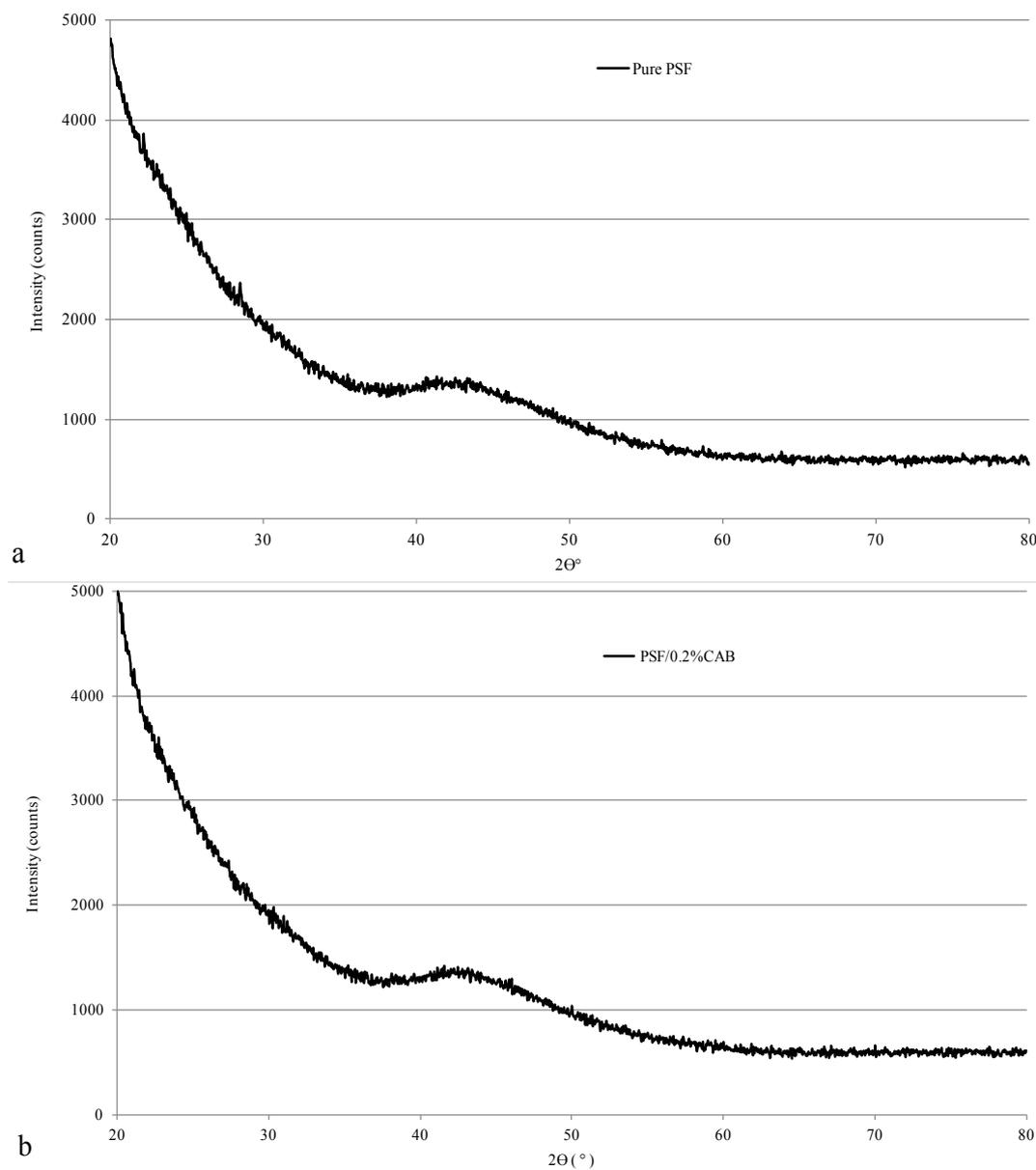


Figure 3: XRD pattern for; (a) pure PSF (b) PSF/0.2% CAB.

miscibility could not be achieved [28,32].

The position of a peak maximum in the $\tan \delta$ versus temperature curve can be attributed to T_g . It was seen that the addition of 0.2% CAB shifted T_g of pure PSF towards a lower value by about 15°C Figure 4c. This result suggested that the presence of CAB molecules caused an increase of molecular mobility in PSF at high temperatures near to T_g due to decrease in van der Waals bonding forces between PSF and CAB chains [33].

Thermogravimetric analysis

The thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) diagrams for pure PSF and the PSF/0.2% CAB blend are shown in Figures 5a and 5b. All the DTG peaks represent degradation point for each stage. The total weight loss for pure PSF

amounted to ~27% from 89°C-245°C and for the PSF/0.2% CAB blend was ~5% from 70 to 430°C, due to the residual water bound to the hydrophilic imidazole moieties [33]. Pure PSF (Figure 5a), showed a lower degradation temperature at 389°C, because of the loss in sulfonic acid groups and this represents the most important thermal degradation in polymer chains. The second at 527.8°C as a result of carbonization of the degraded residuals (polymeric backbone degradation) [34,35]. The high degradation temperature at 527.46°C for PSF/0.2% CAB blend was attributed to decomposition of the imidazole group without phase inversion components [33,36].

It has been observed that there is thermal stability due to CAB addition therefore CAB contributed to the improvement of thermal stability of polymer although not change the degree of decomposition of the main chains temperature. The break in each thermogram

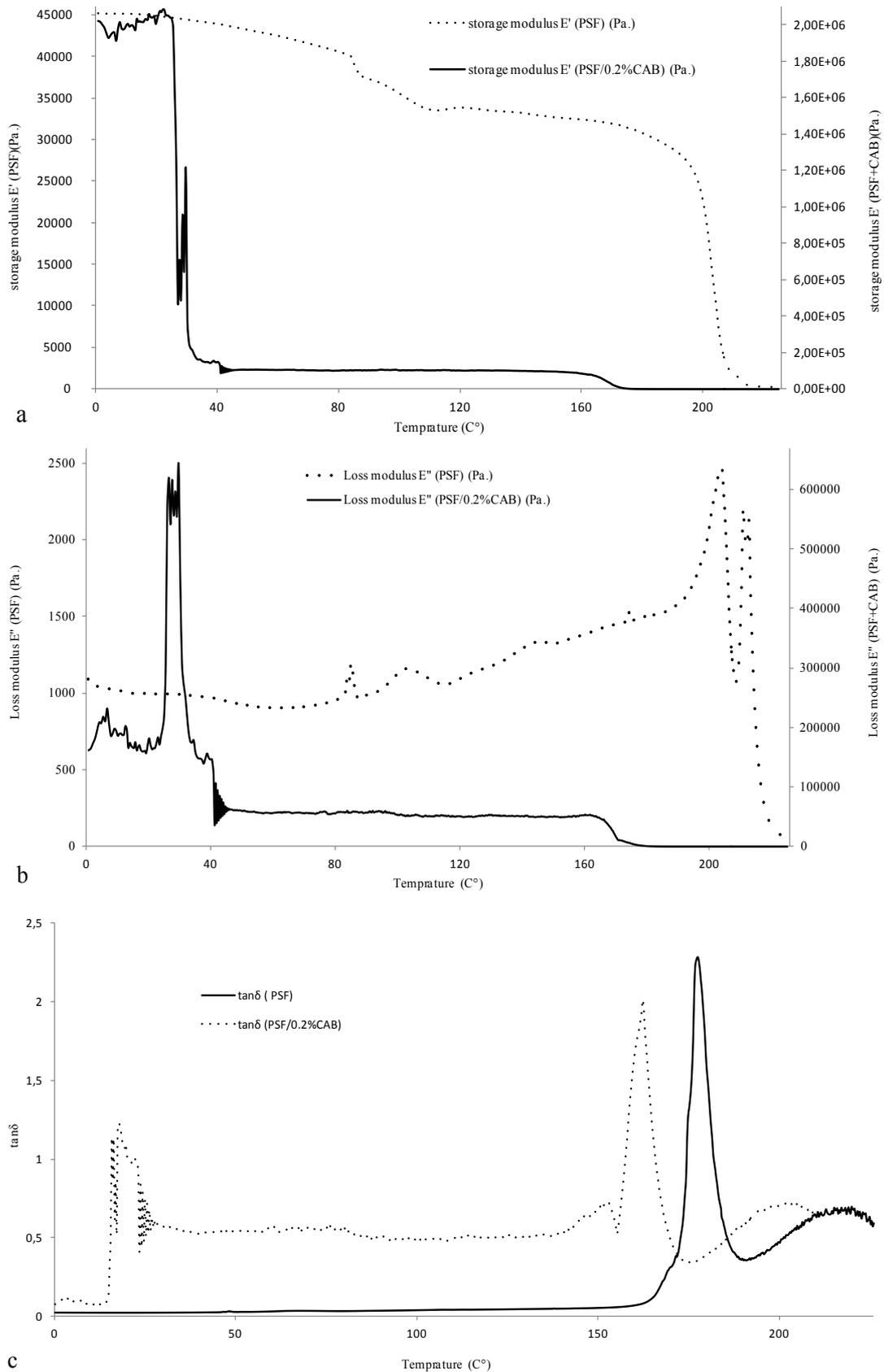


Figure 4: (a) Storage modulus E', (b) loss modulus E'' and (c) tan δ trace for pure PSF and PSF-CAB 0.2% as a function of temperature by DMA.

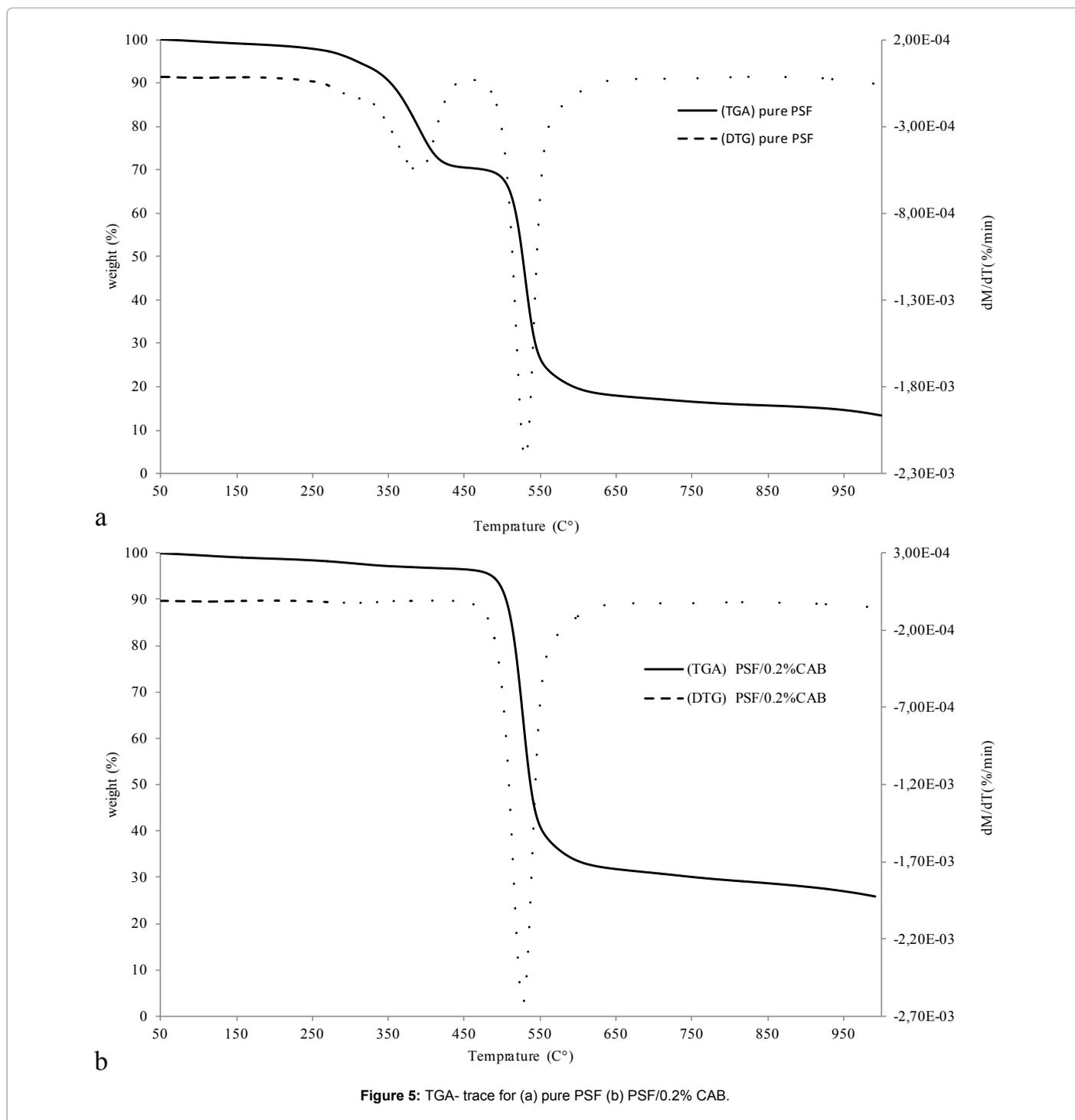


Figure 5: TGA- trace for (a) pure PSF (b) PSF/0.2% CAB.

indicates the onset of the decomposition process involving a rapid loss in weight [37].

Conclusions

In this paper, different concentrations of cellulose acetate butyrate (CAB) were mixed with polysulfone (PSF) using Internal Mixer for transparent blend of ultraviolet-visible area, and investigations of some optical, morphological, mechanical and thermal properties were carried out. The study revealed that PSF has absorbance peak at 268

nm and a transmittance peak at 712.5 nm. The value of these peaks decreases with increasing CAB concentration in PSF. The addition of CAB to PSF does not change the random structure of the blend, and this seems clear in the sample transparency. It was found that PSF/0.2% CAB blend representing low ultraviolet light absorption and high transparency, for this purpose, was chosen as the best concentration. The PSF/0.2% CAB blend showed an obvious thermal stability with an increase in the value of the modulus, but the value of the glass transition temperature decreased after adding CAB. The properties of

the blends were a function of CAB concentration in PSF. Additionally; environmentally-friendly CAB improved the PSF properties while maintaining the transparency of the samples, at least to some extent.

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