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Thermal and structural characterization of Acrylonitrile butadiene styrene (ABS) copolymer blended with Polytetrafluoroethylene (PTFE) particulate composite

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ABSTRACT

A novel thermally sustainable polymer composite was fabricated with Acrylonitrile Butadiene Styrene (ABS) as the matrix and Polytetrafluoroethylene (PTFE) particle as the filler, using injection molding process with 10 and 20 wt. % PTFE filler. The composites were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Thermogravimetric analysis (TGA). The composites were also tested for their visco-elastic properties using Dynamic mechanical analyzer (DMA). The ABS/PTFE composites exhibited high thermal stability, conductivity and good coefficient of linear thermal expansion. The composites exhibited better visco-elastic properties than the ABS matrix. Consequently, this hybrid blended polymer can be a suitable alternative material for tribological applications in both automobile and aerospace industries, among others.

Keywords: Acrylonitrile Butadiene Styrene (ABS); Polytetrafluoroethylene (PTFE) particle; Thermal properties; Injection molding; Visco-elastic properties.

1. Introduction

In recent years, polymers play a vital role in the engineering applications, because of their excellent properties. Owing to their better functional and processing properties, Acrylonitrile-butadiene-styrene copolymer (ABS) is widely used in the industry as an engineering plastic among other thermoplastics (Tang et al., 2002). It composes of varying quantities of styrene (40-60%), butadiene (5-35%) and acrylonitrile (15-30%) (Vail et al., 2011) and finds applications in many fields such as aerospace, automotive, defense, computers, electrical and telecommunications (Ramaraj, 2006). ABS is a hard and tough thermoplastic polymer with a good impact strength and smooth surface. However, it has a lower thermal stability, poor flame retardancy, thermal conductivity and chemical resistance (Liu et al., 2007). Because of the lower thermal properties, ABS cannot effectively dissipate heat and its higher coefficient of thermal expansion leads to thermal failure (Lee et al., 2006). In order to improve the these properties and also to make cost-effective polymer products, organic or inorganic particulate fillers are reinforced with the polymer matrices (Jiang et al., 2005). It is always necessary to choose the right filler, its composition in the polymer matrix and the suitable fabrication process to make an improved polymer composites for some specific applications (Ben Difallah et al., 2012).

Polytetrafluoroethylene (PTFE) is a kind of hydrophobic fluoropolymer with many advantageous characteristics, such as low coefficient of friction, high chemical resistance, fire-retardant properties and high thermal stability. These properties make it ideal for filler reinforcements in composites fabrication for many high-end applications (Sawyer et al., 2003).

However, PTFE has a very low resistance to wear and this is attributed to the long chains of PTFE that are oriented on the transfer surface, while sliding which forms a low shear strength interface with the other material. Furthermore, the helical molecular structure of PTFE makes its surface smooth for other molecules to slide easily (Bijwe et al., 2000). PTFE can be used as a storage and packaging container for reactive and corrosive chemicals. Also, it can be used as an insulator in cables, connector assemblies and can be employed as substrate for printed electrical circuit boards (Khan et al., 2009).

Therefore, the combination of both properties of ABS and PTFE materials to produce an enhanced synergistic polymer composite necessitates this study. With better thermal and visco-elastic properties of the composite, it has a high and wide potential engineering applications, especially where creep and creep recovery, stress relation, thermal energy and energy absorption are very significant. This study mainly comprises of three aspects: fabrication of the ABS/PTFE composites with varying concentrations of PTFE (10 and 20 wt.% of ABS), followed by characterization of the fabricated composites using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Thermogravimetric analysis (TGA). Finally, study on the thermal and visco-elastic properties of the composites was carried out with an extensive discussion of results obtained.

2. Materials and methods

2.1 Materials

The ABS polymer matrix in pellet form was supplied by M/s. Shree Meenakshi Plastics Company, Madurai, Tamil Nadu, India. PTFE powder was procured from M/s. Modoplast Company Pvt. Ltd, Kolkata, and West Bengal, India.

2.2 Preparation of ABS/PTFE composites

An injection molding technique was used to fabricate the ABS/PTFE composites, with a 50T double screw injection molding machine (DGP Windsor). The ABS pellets and the PTFE powders were dried at 100 °C in a hot air oven for 24 hours to remove the moisture. The dried ABS pellets and the PTFE particles were fed in the hopper to make rectangular molded composites. A mold with dimensions of 200 x 140 x 3 mm was used. The mold and processing temperatures were maintained at 35 °C and 220 °C, respectively. The fabricated composites were then cut into different sizes for various tests, using water jet machining.

2.3 Fourier transform infrared spectroscopy

The FTIR spectra of the ABS matrix, PTFE filler and the ABS/PTFE composites with 10 and 20 wt. % of PTFE filler were recorded using an IR Tracer (Shimadzu, Japan) in reflection mode. All the spectra were recorded in the range of 4000-500 cm^{-1} with 32 scans in each case, at a resolution of 4 cm^{-1} .

2.4 X-ray diffraction

The X-ray diffractograms of the ABS matrix, PTFE filler and the ABS/PTFE composites with 10 and 20 wt.% of PTFE filler were similarly recorded using a D8 Advanced ECO X-ray diffractometer (Bruker, US) in the range of 10 to 80° at a scan rate of 4°/min.

2.5 Thermogravimetric analysis

The primary and derivative thermograms of the ABS matrix, PTFE filler and the ABS/PTFE composites with 10 and 20 wt.% of PTFE filler were recorded using a Thermogravimetric Analyzer (Mettler Toledo, US) in the temperature range of 25 – 600 °C in nitrogen atmosphere at a heating rate of 10 °C/min.

2.6 Dynamic mechanical analysis

The visco-elastic properties of the ABS matrix, PTFE filler and the ABS/PTFE composites with 10 and 20 wt.% of PTFE filler were tested, using a dynamic mechanical analyzer (Mettler Toledo, US) single cantilever mode at frequency of 1 Hz and a displacement of 10 μm . The tests were carried out at an ambient temperature (30 $^{\circ}\text{C}$) to 150 $^{\circ}\text{C}$, at a constant heating rate of 3 $^{\circ}\text{C}/\text{min}$.

3. Results and discussion

3.1 FTIR Spectroscopic analysis

In order to investigate the functional groups and the specific intermolecular physical and chemical interactions in the ABS/PTFE composites, the FTIR spectra of ABS matrix, PTFE filler and the ABS/PTFE composites were recorded, and are presented in Fig. 1. The sharp and high intense peak of ABS matrix at 3127 cm^{-1} is attributed to the aromatic and aliphatic C-H stretching vibrations. The band at 2237 cm^{-1} corresponds to the CN stretching of acrylonitrile component (Charles and Ramkumaar, 2009). The characteristic spectra at 1601, 1598, 1491 cm^{-1} corresponds to the aromatic ring of styrene (Aid et al., 2017). The spectra at 1401 cm^{-1} may be due to the scissoring effect of CH_2 groups.

Furthermore, the C-H deformation of the hydrogen atoms corresponding to the alkenic carbons in poly(butadiene) can be observed in the peaks at 962 and 908 cm^{-1} (Desrousseaux et al., 2015). Considering the FTIR spectra of PTFE, the high intense spectra at 1253 and 1151 cm^{-1} corresponds to the stretching vibrations of CF_3 and CF_2 , respectively. Similarly, the peak at 640 cm^{-1} may be attributed to the rolling vibrations of CF_2 (Yamauchi et al., 2011). The characteristic spectra at 2378 and 2347 cm^{-1} are assigned to the CF_2 backbone. Furthermore, the vibration of the hydrogen bonded COOH group can be observed at 3123 cm^{-1} . The band at 984 cm^{-1} is

probably due to the reaction of chain radical and the mobility of CF_3 (Dorschner et al., 1998). The ABS/PTFE composites possessed the characteristic bands of both ABS matrix and the PTFE filler. The shift in the spectra from 1090 cm^{-1} to 1201 cm^{-1} indicates hybridization state of the ABS/PTFE composites. Further, the changes in the intensities indicate the changes in functional groups associated with the molecular bonds.

3.2 XRD analysis

Figure 2 shows the XRD diffraction spectra of pure ABS and PTFE and their composites with ABS+10%PTFE, and ABS+20%PTFE. The measurement was recorded from 10° to 80° . From the spectra, a dominant peak was absorbed initially between the ranges of 18° to 21° in all the materials. It indicates the crystalline nature of materials in all the cases. Compared to all other peaks, a sharp and sharp narrow peak was observed at 18.1° for pure PTFE which indicates the long-range order in (100) lattice plane (Shen et al., 2013). The remaining higher peaks at this range of 2θ angle are seemed wider. This indicates the presence of low crystallinity index on their materials. The crystallinity index (CI) of all the polymer materials was calculated separately for ABS, PTFE, ABS+10%PTFE, and ABS+20%PTFE and they were found as 31.96%, 90.60%, 42.25%, and 31.58%, respectively. The CI values of all the polymer materials were calculated using the following formula (Mayandi et al., 2016).

$$\text{CI} = \frac{(I_{002} - I_{\text{am}})}{I_{002}} \times 100 \quad (1)$$

Where, I_{002} and I_{am} are peak intensities appeared at 2θ angle close to around 22.5 and 16.8 , respectively. The higher crystallinity index was observed for pure PTFE filler which could be due to the regular arrangements of atom existence in the structure. Similar results have been reported, where the crystallinity index of virgin PTFE ranged from 85% to 95% (D'Amorin et

al., 2013). In addition, the other peaks of PTFE have low intense and occurred between 31° and 42° . The superimposed on an amorphous halo (broad peak under crystalline) was measured at 37° (D'Amorin et al., 2013). The lowest crystallinity index was obtained with pure ABS. The PTFE filled ABS polymer materials has more crystallinity index than pure ABS. XRD curve for pure ABS and PTFE filled ABS materials has two major peaks at 19.8° and 27.5° , the sharp peaks indicate a semi-crystalline nature of polymers. Importantly, the addition of PTFE into ABS did not affect the crystal nature of the materials (Zhang et al., 2012 and Mrinal et al., 2008).

3.3 Thermogravimetric analysis

In order to investigate the thermal stability of the ABS/PTFE composites, the thermogravimetric analysis was carried out and the results are presented in the Fig. 3. From the primary thermograms it can be clearly understood that the PTFE filler possessed the maximum thermal stability followed by the ABS/20 wt.% PTFE composites. It is evident that the incorporation of PTFE filler improved the thermal stability of the composites. The inflection temperature corresponding to the maximum degradation of the polymers was found at 598°C for the PTFE filler and 418°C for the ABS matrix. Similarly, the inflection temperature of the composites with 10 and 20 wt.% PTFE filler were found at 419°C and 570°C , respectively. This can be attributed to the incorporation of highly stable PTFE filler (Sawyer et al., 2003).

3.4 Dynamic mechanical analysis

The temperature dependence of the storage modulus (E') and the mechanical loss factor ($\text{Tan } \delta$) of the ABS/PTFE composites were determined using dynamic mechanical analysis and the results are presented in Fig. 4.

Figure 4(a) shows the E' with respect to temperature, and it is evident that the ABS matrix and the ABS/PTFE composites exhibited higher E' values up to a temperature of 75 °C. Furthermore, it can be observed that there was an enhancement in the E' of the composites when compared to pure ABS. The reinforcing effect of PTFE filler and its rigid nature due to high strength of the CF bonds compared to CH bonds enabled the composites to store more energy. In the temperature range of 75 to 120 °C the drop in the E' for pure ABS and the composites was noticed. This could be due to the movement of the macromolecule chains in the free volume (He et al., 2016). The mechanical loss factor ($\tan \delta$) of the ABS/PTFE composites is presented in Fig. 3(b). From the Fig. 4(b), it is evident that the composites exhibited α -relaxation peaks, which relates to the motion of the main chain molecules associated with its glass transition (T_g). The peak position of the $\tan \delta$ is generally considered as the T_g of the material. The $\tan \delta$ values were found at 121.9 °C, 119.8 °C and 120.8 °C for pure ABS, ABS/10 wt.% PTFE and ABS/20 wt.% PTFE composites respectively. The $\tan \delta$ values showed the shift of T_g to a slightly lower value. At temperatures (130 to 150 °C) where the molecular chains are free to move the damping is very low due to the lesser interaction and friction between the molecules (Guo, 2002).

4. Conclusions

To design a light weight material with improved thermal properties, a new combination of polymer composite was synthesized using thermoplastic ABS and crystalline PTFE with injection molding method. The effect of crystalline PTFE filler with varying wt. % showed significant changes on the structural and thermal characterization properties of the ABS. Moreover, in all the cases the composite performance (ABS + PTFE with 10 and 20 wt. %) lies between the pure ABS and PTFE. Both TGA and DMA results show that the improvement of properties varied, based on the wt. % of the PTFE filler. The addition of 20 wt. % PTFE filler

exhibited maximum thermal resistance as well as highest storage and damping factor compared to pure thermoplastic ABS matrix. Due to this enhanced thermal performance, these composites can be used in polymer tribology applications in various composite-based industries. Studies on dispersibility of filler and their blending mechanisms are hereby recommended to further explore the dynamism of these materials, based on their inherent properties.

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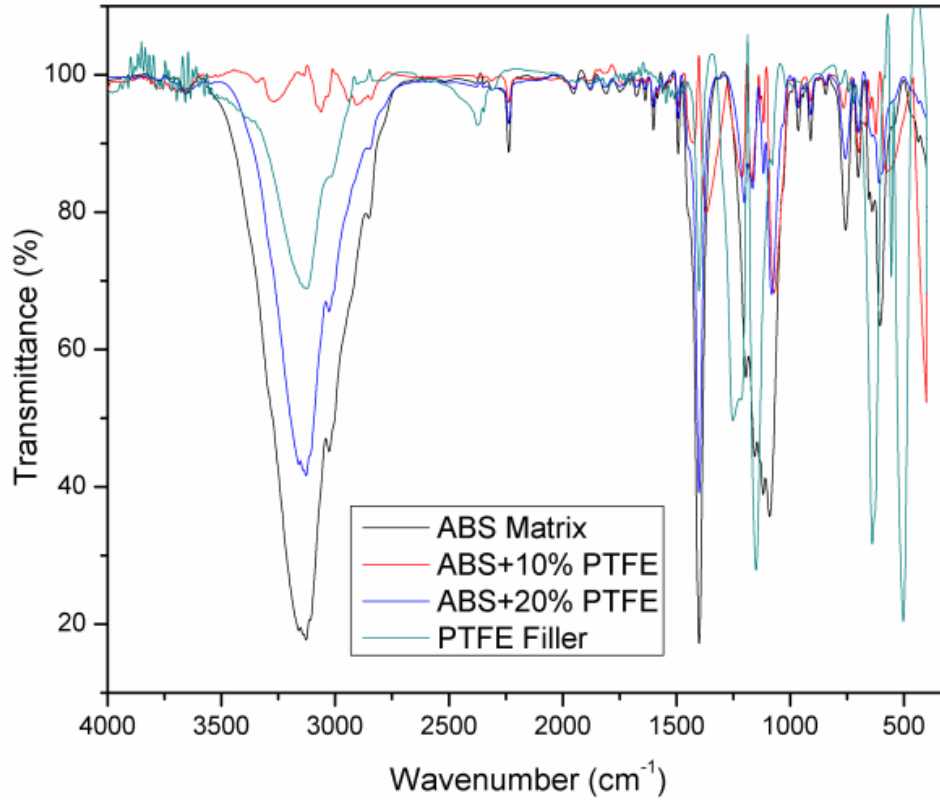


Figure 1 FTIR spectra of ABS matrix, PTFE Filler, ABS/10 wt.% PTFE and ABS/20 wt.% PTFE composites

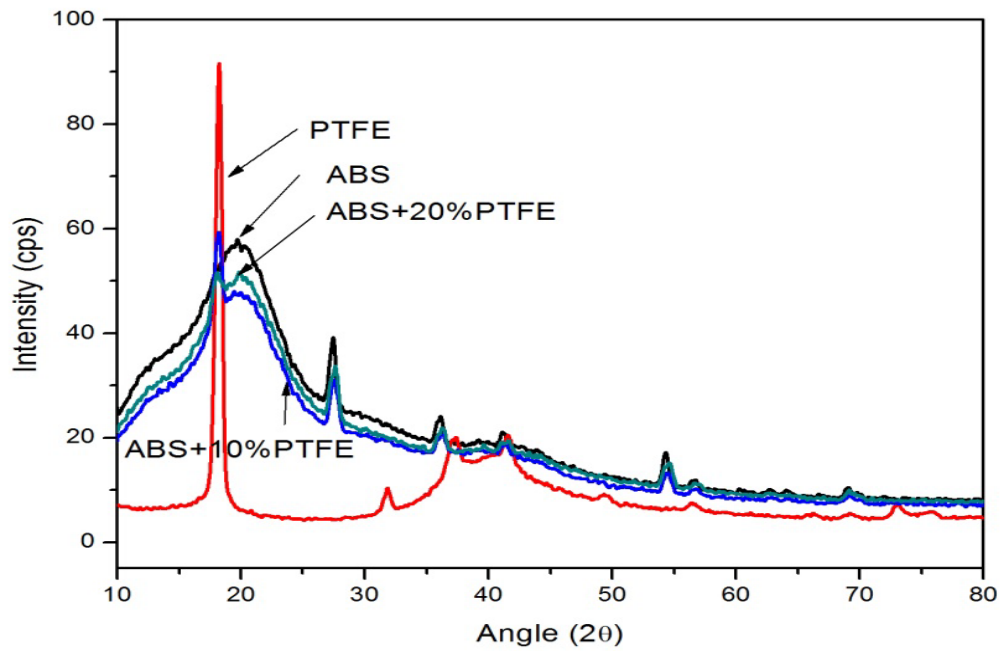


Figure 2 XRD spectra of ABS matrix, PTFE Filler, ABS/10 wt.% PTFE and ABS/20 wt.% PTFE composites

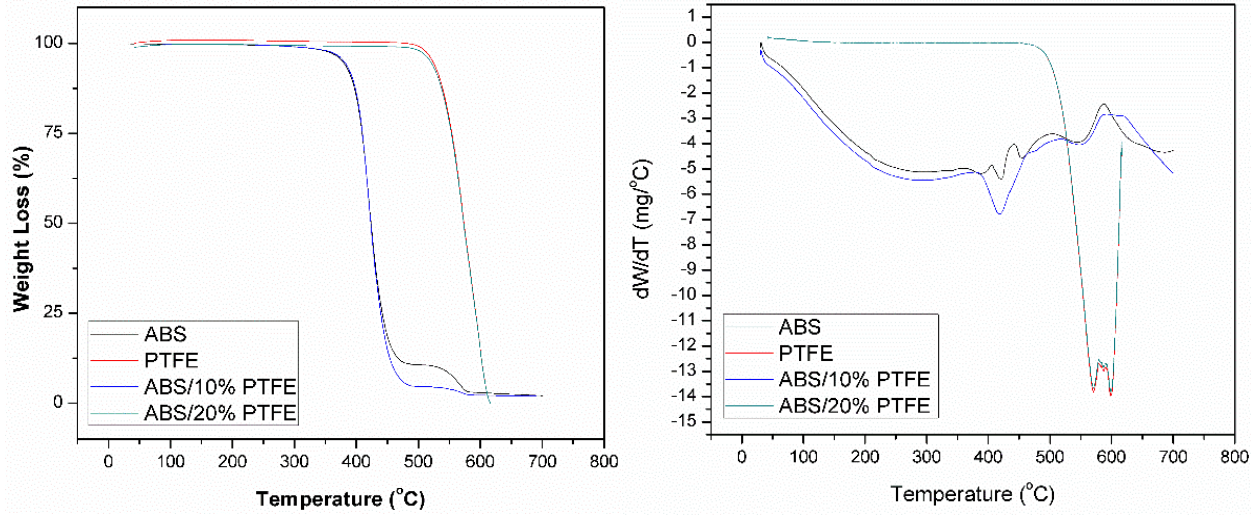


Figure 3 (a) Primary and (b) Derivative thermograms of ABS matrix, PTFE filler, ABS/10 wt.% PTFE and ABS/20 wt.% PTFE composites

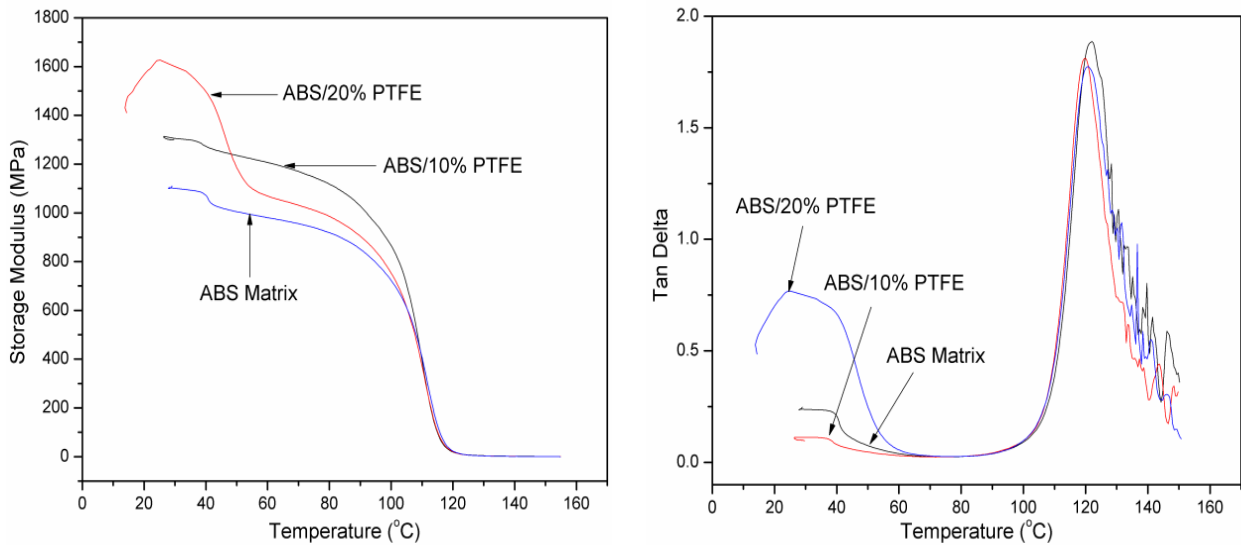


Figure 4 (a) Storage modulus and (b) Mechanical loss factor (Tan δ) of ABS matrix, ABS/10 wt.% PTFE and ABS/20 wt.% PTFE composites