Mechanical and Thermal Properties of Palm-Based Polyurethane Composites Filled with Fe_3O_4, PANI and PANI/Fe_3O_4
(Sifat-sifat Mekanik dan Terma Komposit Poliuretana Sawit Berpengisi Fe_3O_4, PANI dan PANI/Fe_3O_4)

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ABSTRACT

In-situ polymerization method was used to prepare palm-based polyurethane (PU) composites loading with 15 wt% magnetite (Fe_3O_4), polyaniline (PANI) and Fe_3O_4 coated with PANI labeled as PU15, PP and PPM, respectively. FTIR spectroscopy analysis indicated a shift in the carbonyl, C=O and NH in PP. The shift of the peak indicated that there was hydrogen bonding between the C=O (proton acceptor) of urethane with NH (proton-donator) of PANI. PPM gave the highest impact and flexural strengths at 4875 kJ/ m^2 and 42 MPa, respectively but with the lowest flexural modulus (1050 MPa). Two-stage degradation behavior was observed in the TGA thermogram.

Keywords: Magnetite; mechanical properties; polyaniline; polyurethane; thermal property

ABSTRAK

Kaedah pempolimeran in-situ digunakan untuk menyediakan komposit poliuretana sawit (PU) dengan penambahan 15% bt. magnetit (Fe_3O_4), polianilina (PANI) dan Fe_3O_4 tersalut PANI berlabel masing-masing PU15, PP dan PPM. Analisis spektroskopi FTIR menunjukkan terdapat anjakan pada puncak karbonil C=O dan NH dalam PP. Anjakan puncak ini menunjukkan kehadiran ikatan hidrogen antara C=O (penerima proton) daripada uretana dan NH (penderma proton) daripada PANI. PPM memberikan kekuatan hentaman dan lenturan tertinggi pada masing-masing 4875 kJ/ m^2 dan 42 MPa tetapi dengan modulus lenturan terendah (1050 MPa). Peleraian dua peringkat diperhatikan dalam termogram TGA.

Kata kunci: Magnetit; polianilina; poliuretana; sifat mekanik; sifat terma

INTRODUCTION

Magnetic materials is one of the driving forces in generating advanced materials in the new technology era. Among the magnetic material that exists naturally is magnetite, Fe_3O_4, also known as lodestone. Fe_3O_4 have attracted researchers in various fields such as physics, medicine, biology and material sciences due to its multifunctional properties such as small size, supermagnetism and low toxicity (Li et al. 2008).

However, Fe_3O_4 is incompatible with polymer matrices such as polyurethane, polystyrene and polypropylene (Malinauskas 2001; Weidenfeller et al. 2002), which may deteriorate the mechanical, thermal, magnetic and electrical properties of the composites. These properties are dependent on several factors like weight or volume fraction, particle size, surface treatment and interfacial bonding (Saujanya & Radhakrishnan 2000). Mechanical performance of a polymer composite is significantly dependent upon the interaction between filler and matrices (Sreekala et al. 2002). The interfacial interaction between filler and polymer plays a crucial role in determining the quality and properties of the composites (Judeinstein & Sanchez. 1996). Introducing Fe_3O_4, an inorganic particle into PU, is much expected to create incompatibility between both phases. Therefore, creating a good linkage between inorganic filler and organic polymer matrices has become a great challenge in composite fabrication.

One of the promising alternatives to improve the compatibility between Fe_3O_4 and the matrices PU is by modifying the surface of the Fe_3O_4. Several deposition methods had been used including electrochemical and chemical deposition of conducting polymer. Electrochemical deposition is not widely used due to difficulty to control the uniform thickening of the polymer over the Fe_3O_4. Therefore, chemical deposition of conducting polymer such as polyaniline is selected for surface treatment of Fe_3O_4 by using in-situ chemical polymerization method, which can overcome the weakness of the previous method (Kazantseva et al. 2004).

In this study, the mechanical properties and thermal behavior of the palm-based PU filled with magnetite and PANI were investigated. The magnetite was then coated with PANI and was added to the PU to form the composites. The effect of this coating on the interfacial bonding between Fe_3O_4 and PU was studied.

MATERIALS AND METHODS

MATERIALS

RBD (refined, bleached and deodorised) palm kernel oil-based monoester was prepared using a method described by Badri et al. (2001). 2,4'-diphenylmethane diisocyanate (MDI) was obtained from Cosmopolyurethane (Port Klang, Malaysia), with NCO content of 31 % while the catalyst 2,2'-dimorpholino diethyl ether (Dabco DMDEE) was purchased from Suka Chemicals Sdn Bhd(Shah Alam, Malaysia). Aniline as monomer was purchased from Riedel-De Haen and distilled under reduced pressure before use and was stored below 0°C. Ammonium persulfate (APS) and hydrochloric acid (HCl) were obtained from Systerm Sdn. Bhd., Malaysia. Ammonium hydroxide (NH_4OH) was supplied by Merck. Fe_3O_4 was provided by Systerm Sdn. Bhd.

SAMPLES PREPARATION

PU15, PU-PANI (PP) and PU-PANI/ Fe_3O_4 (PPM) were prepared with the addition of 15 wt% of each Fe_3O_4, PANI and PANI/Fe_3O_4 as fillers respectively. PANI-coated Fe_3O_4 were prepared by the oxidation of aniline hydrochloride with APS according to the method described by Kazantseva et al. (2004). The resin was prepared by mixing both palm-based monoester and DMDEE. Then the filler was added into the resin. This mixture was stirred homogenously. The PU composite was prepared by adding MDI with a ratio of 1:1 to the mixture and stirred at 1000 rpm for 10 seconds. The mixture was instantaneously poured into a cavity plate with dimensions of 130 mm × 130 mm × 3 mm (length × width × thickness) and compressed for 5 min at 50°C with a pressure of 760 MPa. The composites were conditioned at 23±2°C for 16 h before further characterization.

FOURIER-TRANSFORM INRARED (FTIR) SPECTROSCOPY

A Perkin Elmer FT-IR spectrophotometer was used to analyze the composites. The scanning was carried out at wave numbers ranged from 4000 to 510 cm⁻¹ using DATR (Diamond Attenuation Total Reflectance) technique. The presence of amine (NH), carbonyl (C=O), carbamate (CNH) and COC was determined to justify the formation of PU and to detect any possible changes to the chemical structure of PU in the presence of PANI or PANI/ Fe_3O_4.

MECHANICAL TESTING

Three-point-bending technique was used to carry out the flexural test according to ASTM-D 790 using the Universal Testing Machine model Instron. The PU15, PPM and PP composites prepared were cut into dimensions of 120 mm × 12 mm × 3 mm (length × width × thickness). The testing was carried out at a cross-head speed of 3.1 mm/min. The value of the obtained flexural stress and modulus represented the mean of five sample measurements.

The impact test was performed according to ASTM-D 256 using impact tester model Ceast 6546 (Italy). The unnotched samples of PU15, PPM and PP with the dimensions of 63 mm × 13 mm × 3 mm (length × width × thickness) were tested using a pendulum with energy of 2 J. The value of the obtained impact strength represented the mean of five sample measurements. The impact strength was calculated by using:

$$\text{Impact strength} = \frac{\text{Kinetic energy (J)}}{\text{Cross-sectional area (m}^2\text{)}} \qquad (1)$$

TERMOGRAVIMETRIC ANALYSIS (TGA)

The thermal degradation behavior of the samples was evaluated using Mettler Toledo TGA/SDTA 518ᵉ. About 6-11 mg of samples were subjected to TGA scans at a heating rate of 10°C/min in a temperature range from ambient to 600°C in nitrogen gas environment.

The TGA curves obtained were percentage of weight loss as a function of temperature. Two decomposition steps were identified using a derivative of the TG curves.

RESULTS AND DISCUSSION

Figure 1 represents the FTIR spectra of the PU15, PP and PPM composites. Since there is no chemical bonding between Fe_3O_4 and PU, the system is treated as control in this study. The FTIR spectrum for PP and PPM are very much identical. Based on the basic chemical structure of PU and PANI, the most possible interaction is H-bonding as displayed in Figure 2.

The free carbonyl and bonded carbonyl stretching of urethane with typical absorption of around 1714 cm⁻¹ and 1604 cm⁻¹ was used to monitor the formation of H-bonding between either the same or different type of molecules (Mythili et al. 2004). The absorption of free carbonyl at 1714 cm⁻¹ for PU15 shifted to 1704 cm⁻¹ in PP and PPM is due to the intermolecular H-bonding between neighboring NH or NH from PANI. Basically, H-bonding is created between H-acceptor in the carbonyl group of PU and H-donator in the imino group of PANI or from neighboring NH group (Ho et al. 1999). The NH peak shifted to lower wave numbers from 3295 cm⁻¹ to 3290 cm⁻¹ and 1520 cm⁻¹ to 1512 cm⁻¹, which were assigned to NH stretching and NH bending of PU and PANI. This indicated that a certain degree of polymerization was achieved. The carbonyl group in PU interacted more strongly with the NH group in PANI. PU was preponderant in the system. Asymmetric CH_2 stretching and symmetric CH_2 stretching were observed at 2917-2921 cm⁻¹ and 2851-2854 cm⁻¹ respectively (Chattopadhyay et al. 2006). Both wave numbers at 1304-1308 cm⁻¹ and 1210-1214 cm⁻¹ were assigned to the CNH peak of urethane (Ravat et al. 2001). Finally, COC peaks were observed around 1061-1064 cm⁻¹.

The impact strengths of the PU15, PP and PPM composites are presented in Figure 3. The impact strength
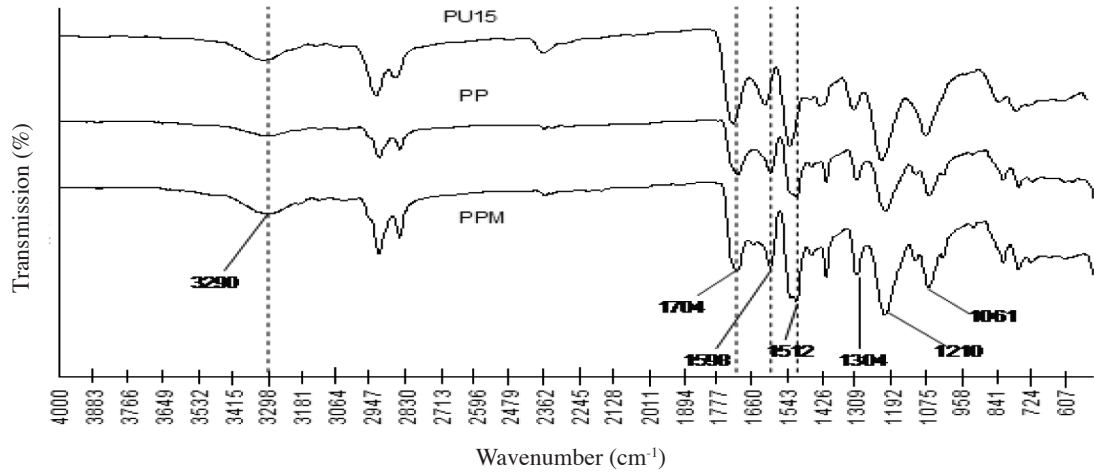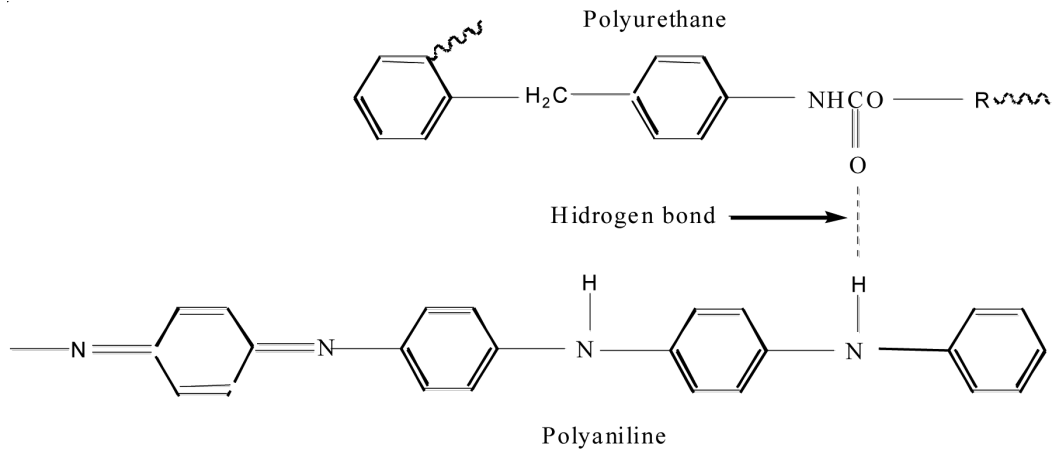
FIGURE 1. FTIR spectra of PU15, PP and PPM

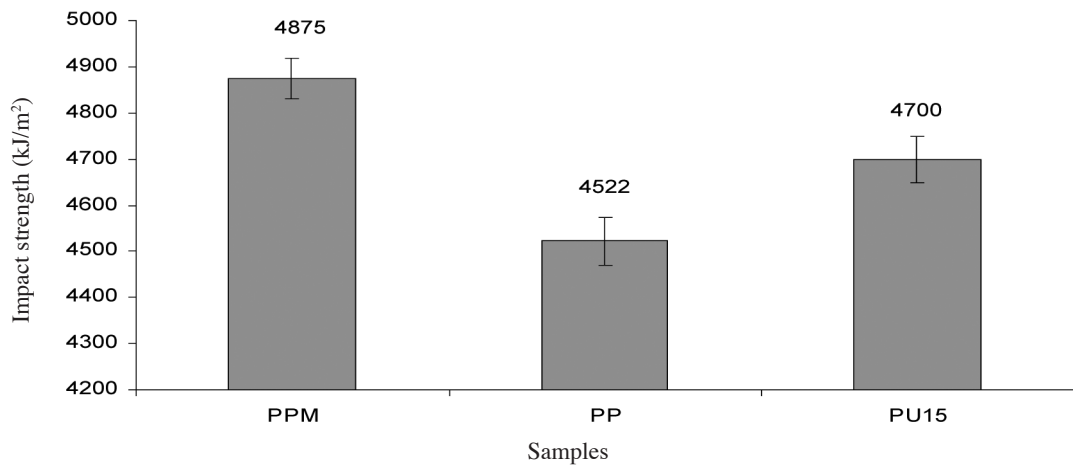FIGURE 2. Probable intermolecular interaction between PU and PANI through hydrogen bond

FIGURE 3. Impact strengths of the PU15, PP and PPM composites

of a sample reflects its ability to resist high-speed stress generation. PPM showed higher impact strength compare to PU15 and PP that is 4875 kJ/ m² compared to 4700 kJ/ m² and 4522 kJ/ m², respectively.

The average size distribution of PANI/Fe$_3$O$_4$ is shown in Figure 4. The agglomeration of the Fe$_3$O$_4$ particle was reduced when coated with PANI, clearly indicated by the size distribution. PANI has the tendency to reduce the

anisotropic dipolar interaction of the Fe_3O_4 and as a result reduce the agglomeration. The size of the PANI coated Fe_3O_4 at 50% percentile was 1.3 µm. A smaller particle is possible to reduce the porosity created by larger PANI/Fe_3O_4 particles. As a result, a packed composite like the PPM is obtained. In addition, good interfacial adhesion due to the presence of hydrogen bond between urethane and PANI improved the energy transfer from the PU to the filler. Thus, higher impact strength is achieved compared to PU15. Besides that, PANI form a film that coated the Fe_3O_4 surface instead of forming a rod like porous material (Sapurina et al. 2002). In this case, porosity was greatly reduced in PANI/Fe_3O_4 composite, led to better stress transfer between the PU and Fe_3O_4 in PPM. The impact strength for PP is 7.2% lower than PPM, and stand the lowest impact strength as PANI exist in the form of porous rod-like solid (Ding et al. 2008; Kong et al. 2008). This results in discontinuity in the matrix, hence producing stress concentration points in the composite (Badri et al. 2006). The ability to absorb or distribute stress is decreased.

The flexural strength and modulus of the PU15, PP and PPM composites are presented in Figure 5. They showed a similar trend as the impact strength. The results obtained were referred to the composites when they started to fracture (Khairul Anuar & Badri 2007). Flexural strength of PPM was 7.1% (39 MPa) and 2.3% (41 MPa) higher than PP and PU15, respectively. An improvement in the interfacial bonding and reduced porosity for PPM as compared to both PU15 and PP helped in the absorption of stress loaded on the composites.

However, PU15 showed the highest flexural modulus that is at 1090 MPa. This is followed by the PP which is 0.3% lower than PU15 and PPM by 3.7%. Flexural modulus indicates stiffness of a material (Khalid et al.
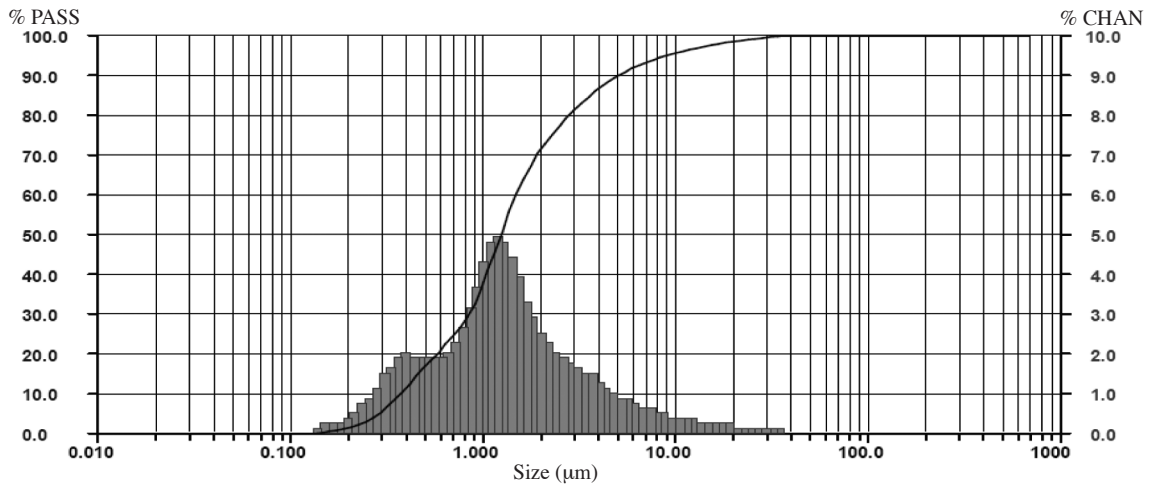

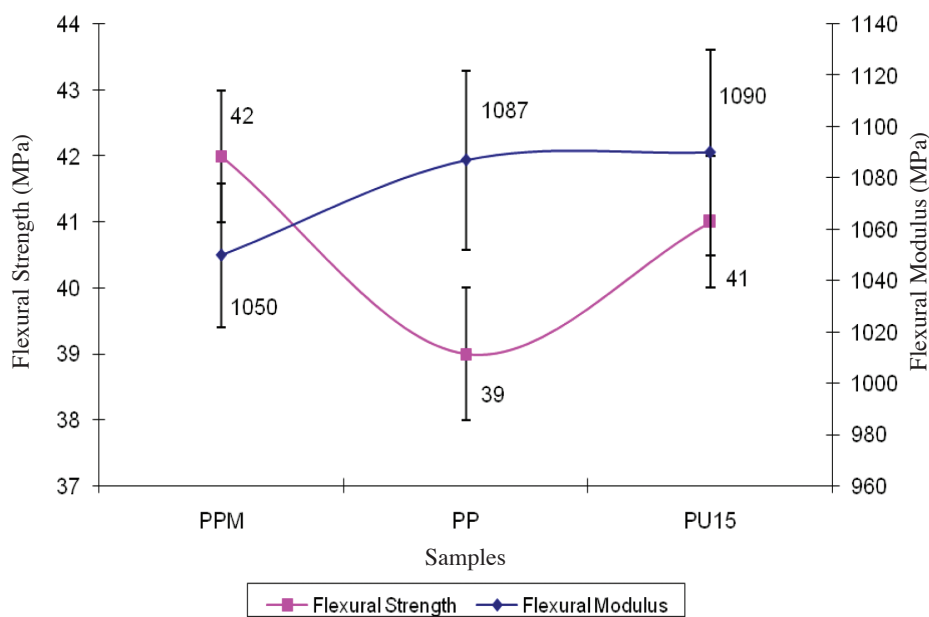FIGURE 4. Particle size distribution of the PANI- Fe_3O_4

FIGURE 5. Flexural strength and modulus for PU15, PP and PPM composites

2008). Fe_3O_4 is naturally occurred as a hard material. Same goes with the rod shape PANI (0.1-2 GPa) (Wilson et al. 2007). As a result, the modulus of PP and PU15 increased significantly. On the other hand, being a light density material at 1.1 g/ cm^3 (Tsotra & Friedrich 2004), PANI contributed higher volume fraction in PP compare to volume fraction of PANI/Fe_3O_4 in PPM with the same loading percentage. Therefore, PP showed more characteristic of PANI compared to PPM and resulted in higher flexural modulus in PP compare to PPM .

Figure 6 represents the TGA thermogram of PU15, PP and PPM composites. Based on the TGA, increasing the loading of Fe_3O_4 has significantly increased the percentage of weight loss in the composites, that is 92%, 88% and 75% weight loss for PP, PPM and PU15, respectively. Inorganic material such as Fe_3O_4 has higher stability and do not easily decompose at a lower temperature range.

The analysis using the differential curve, DTG indicated two degradation stages. The onset temperature in the first step degradation related to the hard segment (isocyanate) and the second step degradation corresponded to the soft segment (polyol) of the PU (Zhang et al. 2009). PU15 has the highest first thermal degradation onset (165°C) compared to PP (161°C) and PPM (161°C). Although there is interaction between PANI and PU in both PP and PPM, the thermal stability was lower than PU15. The hydrogen bonding formed between PANI and PU created a distance between the soft and the hard segment in PU. Thus, the PU chain in PP and PPM was easily in motion than in PU15. This reduced the thermal stability of the PP and PPM.

The second degradation stage involved breaking of PANI chain and the soft segment in the PU chains. Reduction in the second stage temperature for PANI was due to the presence of hydrogen bond between PANI and PU (435°C to 395°C in PP and 410°C to 370°C in PPM).
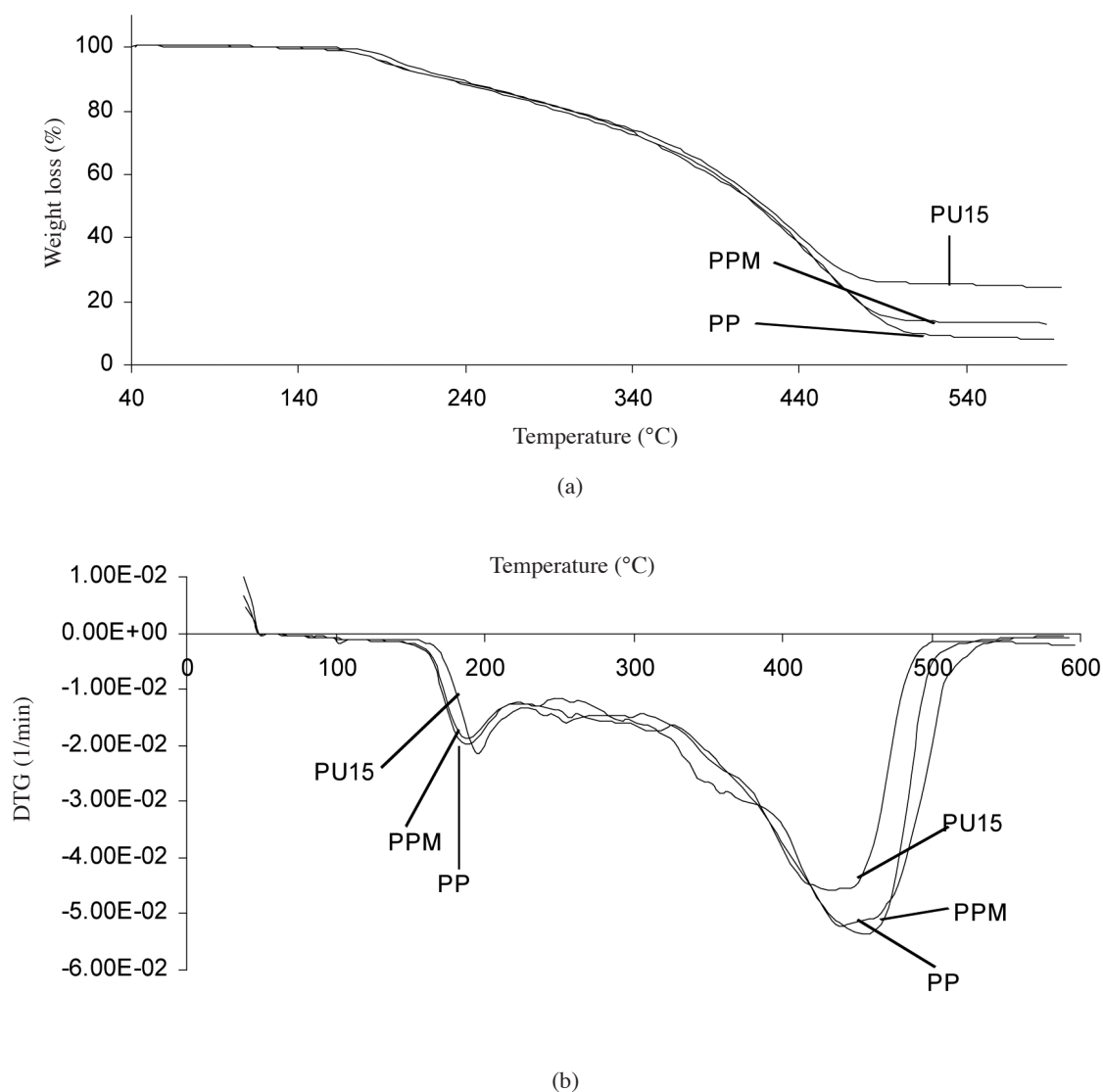

(a)

(b)

FIGURE 6. The (a) TGA and (b) DTG thermograms of the PU15, PP and PPM composites

Conclusions

This study has successfully produced PU composites utilizing PANI treated and untreated Fe_3O_4 as well as PANI itself to be the filler. Hydrogen bonding was formed between carbonyl (PU) and NH (PANI), which increased the intermolecular interaction between PANI and PU. This was observed in the chemical shifting in both NH and C=O group in the PP and PPM through FTIR spectroscopy analysis. Improved intermolecular interaction between the filler and PU in PPM, which is one of the driving factors that result in highest impact and flexural strengths than PP and PU15. However, PPM showed the lowest flexural modulus than both PP and PU15. TGA and DTG analyses, onset temperature of PU15 was higher than PP and PPM in the first degradation whereas the onset temperature was higher than PU15 and dependence on PANI content in the composite.

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