EXPLORING “NANO FILLER” BASED ON OIL PALM ASH IN POLYPROPYLENE COMPOSITES

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This study presents the utilization of oil palm ash (OPA), a siliceous material from the fiber of oil palm biomass, as a nanofiller for the development of polymer nanocomposites. Polypropylene-based polymer nano-composites reinforced with OPA along with a compatibilizer were prepared by a melt-mixing technique, using a double screw extruder. Variations in the mechanical, morphological, and thermal properties with the filler and compatibilizer loading were studied. The best dispersion occurred in the polymer nano-composites for which the interactions between the polymer matrix and nanosized OPA appeared to be the highest. The particle size and the dispersion of the oil palm ash within the matrix were determined by transmission electron microscopy. The as-synthesized composite materials were typically characterized by tensile and impact test methods. The morphology of the composite materials was studied by scanning electron microscopy. The thermal properties determined by thermogravimetric analysis (TGA) showed enhanced thermal stability of a series of composite materials. Also, melting studies were carried out by differential scanning calorimetry.

Keywords: Oil palm ash; Polypropylene; Polymer nanocomposites; Transmission electron microscopy

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INTRODUCTION

Soaring prices are a reminder of the essential role that affordable products play in sustainable economic growth and higher human development. Utilization of bioresource materials, especially from clean indigenous resources, has become more pressing than ever.

Oil Palm Ash (OPA) is an abundant agricultural solid material in Malaysia and Thailand. In Malaysia alone, the potential oil palm ash production has been estimated at four million tonnes/year, a quantity that has prompted a great deal of criticism and complaints, mainly attributed to its persistent, carcinogenic, and bio-accumulative effects (Subramaniam 2008; Foo and Hameed 2009). Increasingly, with the price of the ash disposal cost (either in landfills or ash ponds) hitting as high as $5/tonnes in developing countries and $50/tonnes in developed countries, the urgency of transforming the bioresource residue into a more valuable end products has been promulgated (Foo and Hameed 2009).

The ash is produced after the combustion of oil palm fiber and shell as boiler fuel to produce steam for palm oil mill consumption. Although there are some studies on the utilization of OPA such as a cement replacement material, as an adsorbent for the removal of zinc from aqueous solution (Chu and Hasyim 2002), and for flue gas desulphurization (Zainudin et al. 2005), most of the ash is still disposed of in landfills, an outcome that requires a lot of land area.

The utilization of wood, or more particularly wood waste material, as a reinforcing component in polymer composites has become more attractive, especially in the case of price-driven/high-volume applications (Xanthos 1983; Klason et al. 1985; Dalvag et al. 1985; Raj et al. 1989; Raj et al. 1989; Raja et al.1989; Yam et al. 1990; Myers et al. 1991; Felix and Gatenholm 1991; Joseph et al. 1996)

As the hydrophilic OPA is incompatible with polypropylene, compatibilization between the OPA and PP is necessary to form stable PP nanocomposites. There are two ways to compatibilize the OPA and PP. In the first approach, the agglomeration between the surfactant and the OPA is reduced. In the second approach, to improve interfacial adhesion, maleic anhydride grafted polypropylene (PP-g-MAH) appears to be one of the most suitable strategies (Nygård et al. 2008). This compatibilizer, maleic anhydride grafted PP (PPgMA) or maleated PP (MAPP), can be used in compounding of silicate layered nanocomposites (Manias et al. 2001). In this way, the MAPP-pretreated OPA is dispersed uniformly in the PP matrix. The sheer force during compounding or extruding plays an important role in determining the structure of the nanocomposite. As a result, the properties of the resulting hybrid materials depend strongly on the processing conditions.

A high concentration of MAPP has not been found to enhance the compatibility greatly, while MAPP with excess concentration tends to cause deterioration of the properties of the nanocomposites due to the low molecular weight and plasticizing effect of the MAPP. Generally, to achieve a significant intercalation and improvement in the properties, an optimum value of grafted polymer/nanosilicate ratio is required.

There are several reports on the utilization of OPA as absorbents for toxic gas removal (sulfur dioxide, SOx). The active compound (silica, alumina, potassium, calcium, and hydrated water) in the absorbent prepared from OPA is believed to be responsible for the high absorption capacity of SOx (Foo and Hameed 2009). However, there is no report available on the utilization of OPA as a nanofiller in the polymer matrix. Prospects towards utilization of oil palm ash as a renewable source have been highlighted and outlined, to help overcome a deficiency in knowledge related to the oil palm ash industry.

EXPERIMENTAL

Materials and Methods

Oil Palm Ash (OPA) was provided by the Palm Oil Mill at Ulu Keratong, Segamat, Johor. Polypropylene (PP) and maleated anhydrate polypropylene (MAPP) or Epolene as compatibilizer was procured from Titan Pro Company.

The tensile strength was performed according to ASTM D638 using an Instron Model 1114 Universal Testing Machine. The Charpy impact test was performed by using a Model CS-1370 Impact Pendulum Tester (Zwick).

Thermogravimetric analysis (TG) was performed on a Pyris diamond TGA/ DTA thermal analyser, operating in a dynamic mode at a heating rate of 20^{o}C/min. Differential Scanning Calorimetry analysis (DSC) was performed on a Pyris diamond thermal analyser, operating in isothermal mode at a heating rate of 10 ^{o}C/min.

Scanning electron microscopy (Leica, S360) was carried out to analyze the morphology of the samples that were gold-coated to allow electrical conduction.

The dispersion of the filler within the matrix was examined by a Phillips CM12 transmission electron microscope (TEM).

Preparation of Material

Oil palm ash (OPA) from oil palm mill was sieved through a 60 mesh size sieve to exclude macro-sized particles such as stones, sand, and macro-particles from the incinerator of the oil palm mill. Fine OPA powder was collected and was further ground by using a Grinder/Refiner machine. OPA samples were poured into the grinder/refiner gradually in practicable amounts and kept under the high temperature condition of 250°C in a drying oven for 24 hours in order to prevent the OPA from agglomerating.

Mixing and Manufacturing Polypropylene-OPA Composites

The PP/OPA was compounded using a double screw extruder. Pellets of PP/OPA were moulded under hot press and cold press.

Pre-mixing of PP, OPA, and the coupling agent were carried out initially in a plastic bag in order to mix all the materials together. This compounding was not applicable to achieve a homogenous compound from PP and OPA because of the different densities of PP and OPA. PP has a higher density as compared to OPA. This experiment was carried out by varying the loading percentage of OPA and MAPP, and the samples were designated as shown in Table 1.

Table 1. Sample Designation

Sample	Polypropylene (g)	Oil palm ash (%)	MAPP (%)
SP1	100	0	0
SP2	100	1	0
SP3	100	3	0
SP4	100	5	0
SP5	100	7	0
SP6	100	1	3
SP7	100	3	6
SP8	100	5	10
SP9	100	7	12

RESULTS AND DISCUSSION

Reaction Scheme

The reaction scheme is shown in Fig. 1.

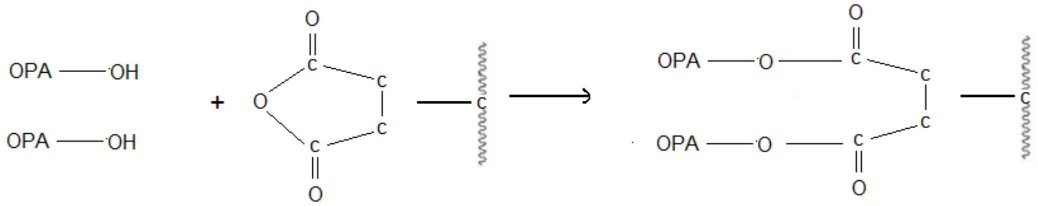

Fig. 1. Reaction scheme involving MAPP treated OPA-PP composites

The grafting is important because it provides interactive sites for increased interaction between the filler and polyolefin matrix. The better interaction between the filler and the matrix material can be expected to favorably affect the results

Mechanical Properties

Tensile test

The tensile properties of OPA/PP nanocomposites were investigated to reveal the effects of the OPA concentration and compatibilization on the OPA/PP interface and eventually on the tensile behaviour of the materials. Figure 2 showed the tensile strength for neat polypropylene and OPA/PP nanocomposites, along with MAPP.

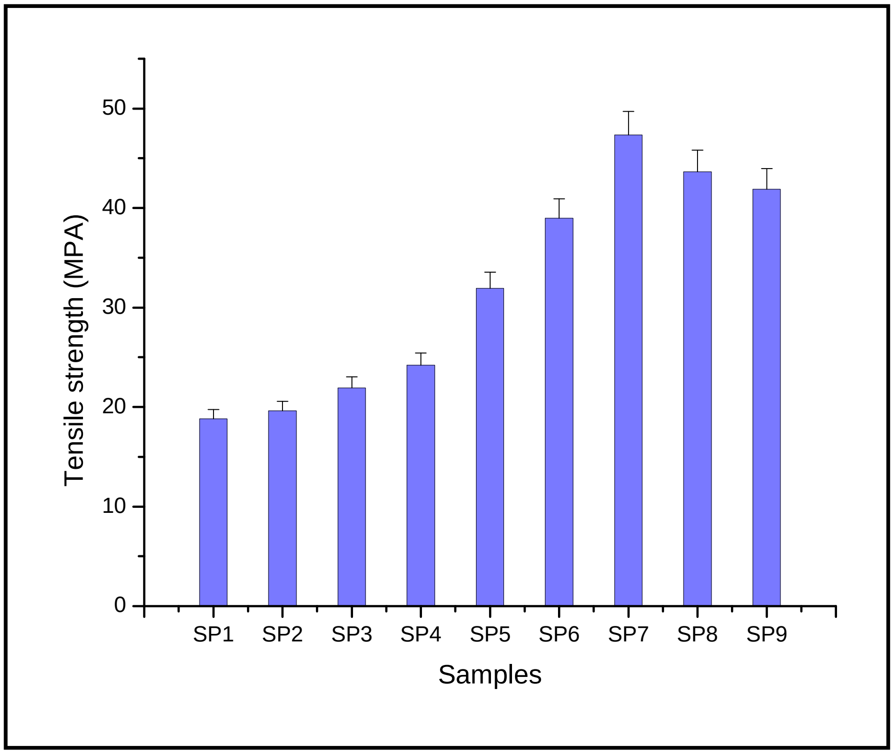

Fig. 2. Tensile strength of neat PP and nanocomposite materials

The composite materials (SP2 through SP9) showed an increasing trend of strength as the filler loading increased as well as with increasing MAPP concentration and showed the highest tensile properties in the case of 3% filler loading and 6% MAPP concentration. The strength is believed to be conferred by the anhydride groups in MAPP, which increase covalent and hydrogen bonding with the OH groups and oxygen from the carboxylic groups (Fig. 1), respectively, improving the adhesion between the filler and the matrix.

Good wetting of the filler by the matrix also resulted in better adhesion of the filler by the matrix whenever stress is applied. Further increase in the filler loading and MAPP concentration showed a decreasing trend. The decreasing trend in the tensile strength could be attributed to agglomeration of the filler within the matrix material, which is supported by the SEM results as well.

Impact strength

According to ASTM A370, a standard specimen for Charpy impact test is 10 mm × 2.5 mm × 55 mm. The Charpy impact test, also known as the Charpy v-notch test, is a standardized high strain-rate test that determines the amount of energy absorbed by a material during fracture. Fracture and failure of composites occurs due to many reasons, such as uncertainties in the loading or environment, defects in the composites material, inadequacies in design, or deficiencies in construction or maintenance. Figure 3 shows the results of impact test to rupture the specimens of OPA/PP nanocomposites.

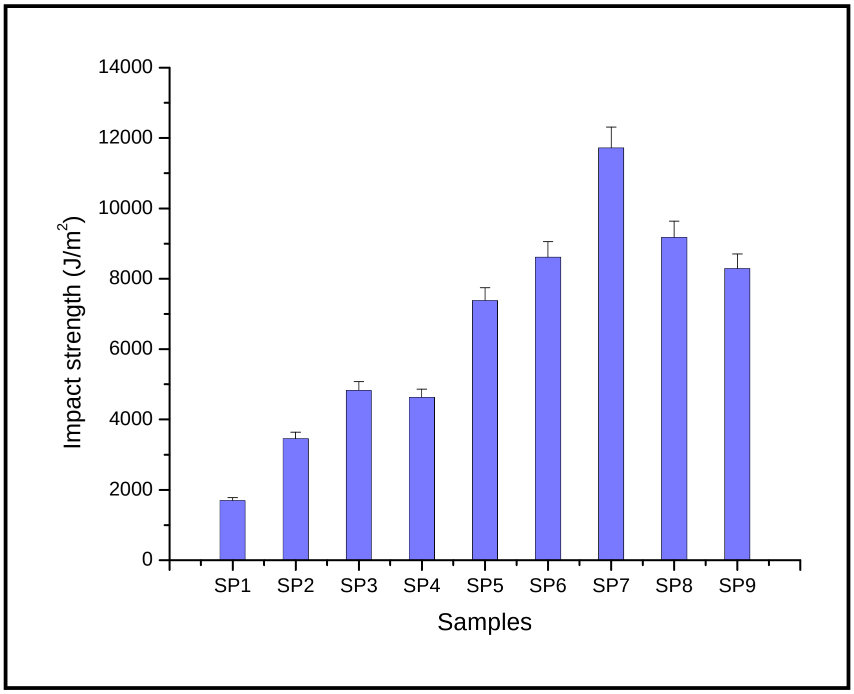

Fig. 3. Impact strength of virgin PP and nanocomposites materials

The composite materials showed an increasing trend of impact strength as the filler loading as well as the MAPP concentration increased. Remarkably enhanced impact properties were observed at 3% filler loading and 6% MAPP concentration. Hence, SP7 was found to be critical loading percentage showing efficient properties in comparison to other compositions. A higher concentration of filler and compatibilizer in the polypropylene matrix leads to the formation of a plastic deformation zone around the OPA particles and an improved ductility of polypropylene matrix

Transmission Electron Microscopy (TEM)

This technique provides information about the particle size and nanodispersion of filler within the matrix. TEM supplies information only on a very local scale. However, it is a valuable tool because it enables us to see the polymer and the filler on a nanometer scale. The images (see Fig. 4) provide information regarding likely sizes of particles present in the matrix. The figure shows the polymer nanocomposite system with critical loading of OPA and MAPP concentration. In Fig. 4 the particle sizes on the TEM image are worth noting. Nanoparticles showed agglomeration in some parts of the composite films due to the conformation of the polymer chains adhering to the nanoparticles. The TEM photomicrographs in Figs. 4a and 4b contain a large number of multilayered OPA platelets intercalated with PP. SP7 showed smaller particle sizes of ca. 19 nm, as compared to ca. 34 nm in the case of SP8. Thus, SP7 showed better dispersion.

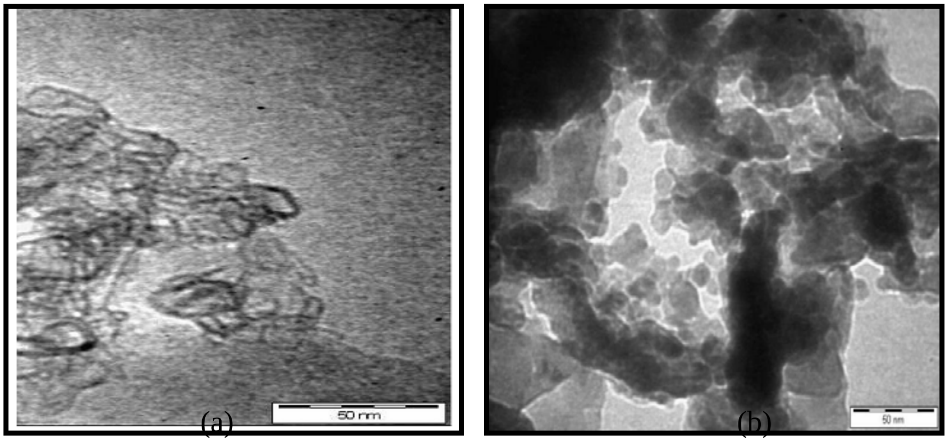

Fig. 4. TEM images of (a) SP8 and (b) SP7

Scanning Electron Microscopy

The primary goal of using SEM was to determine particle dispersion. SEM images of the surfaces of virgin polypropylene, oil palm ash and that of polymer nanocomposite materials were taken (Fig. 5).

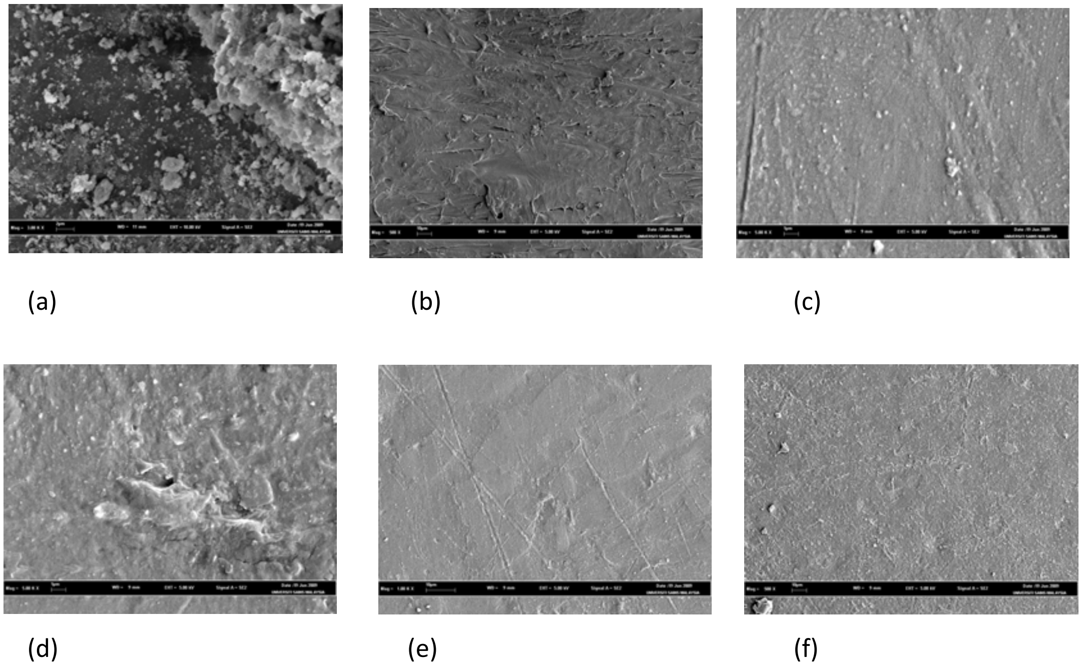

Fig. 5. SEM micrographs of (a) oil palm ash, (b) pure polypropylene, (c) SP3, (d) SP4, (e) SP7, and (f) SP8

Typically, oil palm ash is characterized by a spongy and porous structure, of which its main components are in irregular form, with a sizable fraction showing cellular textures.

Generally, the particles are not consistently dispersed. Flocculants of varying sizes, some very large, were found at the surface.

The presence of rough morphology as shown in Fig. 5(b) may create stress concentration points, which in turn reduce the strength of the samples. It can also be seen that the surface of SP7 composites was relatively smooth compared to SP7 composites, which indicates that the former is less ductile than the latter. From Fig. 5(e) it is clear that good interfacial adhesion is formed between the PP matrix and OPA. This may be attributed to the treatment of OPA and PP with MAPP, which produces some degree of compatibility with polar groups of OPA. These observations support the results of tensile strength tests, where OPA-PP composites displayed higher strength in case of 3% OPA and 6% MAPP loading percentage than the rest of the composites. Figures 5(c) and 5(d) showed poor morphology as compared to the rest of the composite materials. This might be due to nonhomogeneous dispersion and poor wettability of the filler by polypropylene matrix in the absence of compatibilizer. Also, the bigger sizes of the palm ash agglomerates contribute to the poor dispersion and wettability by the PP matrix.

Thermogravimetric analysis

Figure 6 shows the TGA thermograms of the composites with different concentration of compatibilizer. The addition of 6% compatibilizer to the hybrids increased the onset decomposition temperature by about 40 °C compared to that of pure polymer. This increase was probably due to the physico-chemical adsorption of the volatile products on the OPA, which indicates that the dispersion of OPA was improved by the addition of compatibilizer in the polymer matrix.

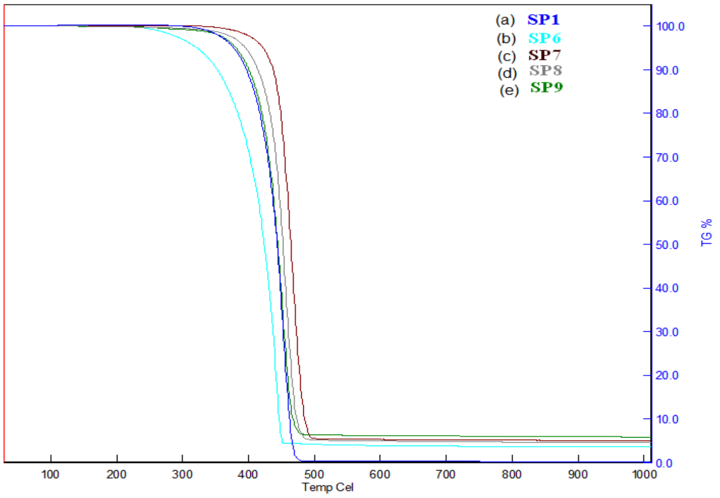

Fig. 6. Thermograms of (a) SP1, (b) SP6, (c) SP7, (d) SP8, and (e) SP9

At 50% weight loss level, the addition of 1 to 3% filler increased the decomposition by 30 °C, whereas the decomposition temperature decreased slightly at the level of 5% filler loading, as shown in Table 2.

The increase in decomposition temperature could be attributed to hindered diffusion (i.e., a barrier effect) of volatile decomposition products caused by the dispersed oil palm ash nanoparticles in the PP matrix (Qin et al. 2004).

Table 2. Thermal Degradation Temperatures and Residue Weight of Various Composite Samples

Specimen	Moisture (%)	T_{on} (°C)	T_{50} (°C)	Res. wt % 600°C
SP1	1.1	361	461	0.8
SP6	1.7	341	458	5.3
SP7	1.9	401	489	7.2
SP8	2.0	388	473	6.8
SP9	2.2	365	464	7.7

Differential Scanning Calorimetry

Figure 7 shows representative DSC curves of melt-crystallized PP/OPA powder thermoplastic composite materials. The endothermic thermal transitions centered in the vicinity of 161 °C and 168 °C provide evidence of melting of PP crystals with different degrees of perfection.

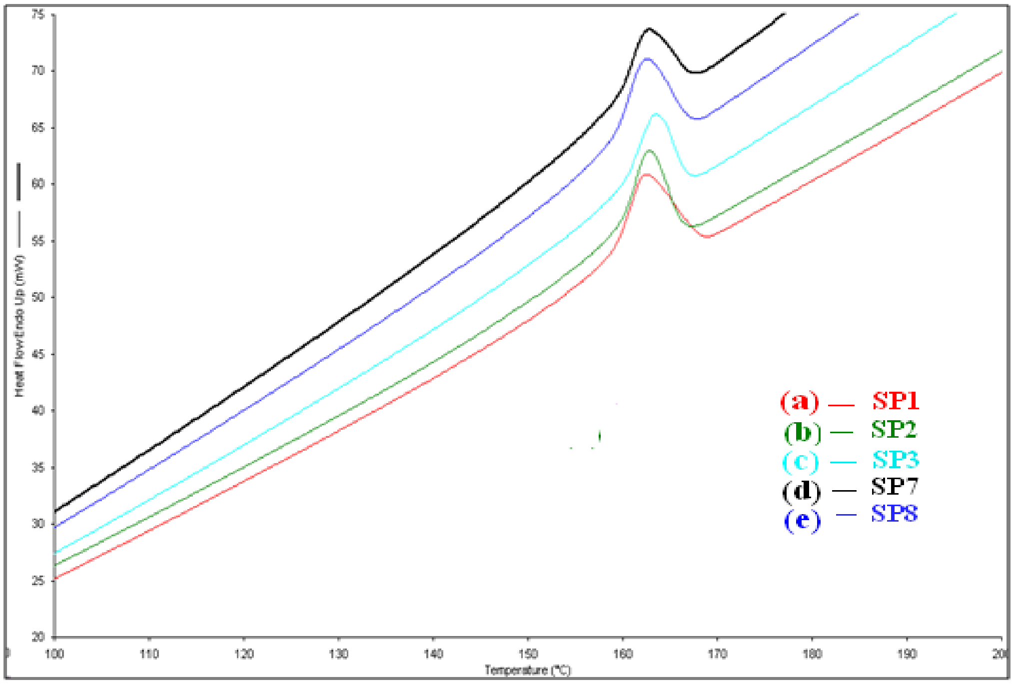

Fig. 7. DSC results of (a) SP1, (b) SP2, (c) SP3, (d) SP7, and (e) SP8

All the composite systems had a higher melting temperature (*Tm*), compared to neat PP. Neat PP had the lowest *Tm* (161.3 °C), while composite material with OPA (3%)/ MAPP (6%) had the highest value of *Tm* (168.1°C). This increment in melting temperature might be attributed to the formation of different crystalline phases in PP matrix, which implies the occurrence of nucleation within the matrix material.

CONCLUSIONS

1. The effects of filler material and compatibilizer on the thermal decomposition behaviour, mechanical properties and morphology of PP/OPA nanocomposites were optimized.
2. The addition of OPA (1 to 7%) and compatibilizer (3 to 12%) increased the decomposition temperature.
3. Also, the addition of OPA and MAPP to neat PP increased the tensile strength, compared to the virgin PP.
4. Favorable interfacial properties and the lack of agglomeration at low OPA concentration in PP explained the high values of the mechanical properties.
5. The TEM micrographs illustrated that the average particle size in case of SP8 was 34 nm, while the particle size of SP7 was 19 nm.
6. Thermal stability of the composite materials has ameliorated due to the addition of coupling agent and filler loading percentage as compared to the neat polypropylene.
7. The melting studies by DSC analysis showed increment in the melting temperatures of the composite materials as compared to the neat polypropylene.

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