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Electrical Conductivity, Thermal, Rheological and Morphological Characteristics of Grafted Blend of Polypyrole and Polypropylene

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Grafted blends of polypyrole (PPy) and polypropylene (PP) were prepared by melt mixing in assisted sonicator twin screw extruder. Dicumyl peroxide (DCP) was used as grafting agent. Electrical conductivity, thermal, rheological and morphological properties of the blend were investigated as a function of PPy composition. Electrical conductivity of PPy-g-PP increased with increasing PPy content. Thermal analysis shows a decrease in melting temperature and crystallinity values as the PPy content increased. This indicates a strong interaction between PPy and PP phase while DCP has successfully acted as crosslinking and grafting agent. Scanning electron microscopy observations on tensile fracture shows an agglomeration behaviour become obvious as PPy content was increased. Despite of that, PPy particles were highly dispersed in the PP matrix indicating a good interaction between the component polymers.

1. Introduction

During the last several decades, conducting polymers such as polyaniline (PANI) and polypyrrole (PPy) have been the subject of numerous investigations due to their excellent physical and chemical properties originating from their unique π-conjugated system (Bhattacharya and De, 1996). Apart from excellent physical and chemical properties PANI and PPy have found applications in various areas like sensors, capacitors (De Melo et al., 2005) and battery recharging materials (Gurunathan et al., 2003) etc. In comparison to the numerous research that's carried out on PANI and PPy, copolymers of aniline and pyrrole are still far from enough. The research on copolymerization of aniline and pyrrole is gradually attracting researchers attention as the copolymers may overcome the shortcomings of a single π-electron in the homopolymer and resulting in a composite with excellent properties (Segal et al., 2005). Figure 1, shows the range of surface resistivity for various materials and their corresponding electrical applications. According to the electronic industries association (EIA) standard 541, a plastic material would be classified as conductive one if it has got the ability to protect against electrostatic discharge (ESD; surface resistivity between 105 and 1,012 ohms sq^{-1}) or electromagnetic interference/radio frequency interference (EMI/RFI; surface resistivity of < 105 ohm sq^{-1}) (Janata and Josowicz, 2003).

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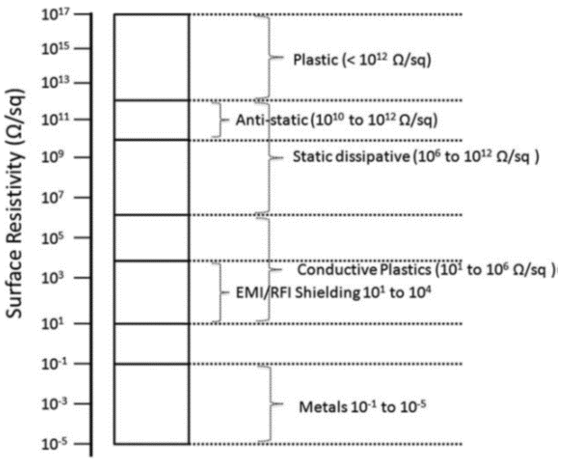

Figure 1: Materials, their surface resistivity and application ranges

Polypyrrole is one of the conducting polymers which have main chain π-conjugation. The electrons are delocalised through the conjugated system and can be switched or jumped between neighbouring redox in redox polymer in order to create the current of electricity. This condition holds the conductive polymer to exhibit the combination of electronic properties of metals and insulation properties of conventional polymer (Saurin and Armes, 1995). Conducting polymers are frequently insoluble and have poor process ability due to its stiffness in the backbone. It is important to incorporate PPy with another polymer or resin. Polypropylene is always the preferred choice as the base resin as it is abundantly available, ease of processing and economical (Yang et al., 1996). The main objective for the preparation of polymer blends or composites is to prepare new polymeric materials with interesting combinations of physical. There are different ways for processing or synthesising of conductive polymers such as electrochemical synthesis or chemical polymerisation (Genies et al., 1983) and (Katsumi et al., 1993). However, electrochemical synthesis technique was found to be not much effective as the resulted polymer blends or composites were of poor quality and low in electro-conductivity. Whereas, chemically polymerisation has become a popular choice of many industries due to simple preparation, short reaction time and can produce in bulk (Omastova et al., 1999) and (Zhang et al., 1993).

The study attempts to present a facile method for the synthesis of PPy-g-PP nanocomposite by single ultrasonic compounding extruder. On the basis of a previous work, the advantage of DCP as grafting agent was evaluated. Further, Electrical conductivity, thermal, rheological and morphological properties of the blend system have been investigated as a function of PPy composition.

2. Materials and Methods

2.1 Materials

Pyrrole monomer with 0.967 g/mL of density at 20 °C was obtained from Sigma Aldrich, Malaysia. Polypropylene TITANPRO PD855 (MFR230oC=14 g/10 min, density= 0.9 g/cm^3) was obtained from Lotte Chemical Titan Holding Sdn. Bhd, Malaysia. Ferric chloride hexahydrate was supplied by Qrec, Malaysia. Sodium dodecylsulphate (SDS) was purchased from Bendosen, Malaysia and methanol was provided from Merck kGaA, Malaysia.

2.2 PPy Synthesis

2 g of Sodium dodecylsulphate (SDS) was added into 200 mL of distilled water and stirred for about 3 min until it was completely dissolved and a clear aqueous solution was achieved. 25 mL of pyrrole monomer was added drop wise into the solution while stirring. After obtaining the mixture of aqueous SDS solution and the monomer, the mixture of SDS solution and the monomer were placed in the ultrasonic reactor with an adjusted power wave. Then, aqueous solution of Iron (III) chloride hexahydrate, $FeCl_3.6H_2O$ (oxidant) was added drop wise to the mixture. Black PPy precipitate immediately observed right after the addition of oxidant. The polymerisation process was carried out for around 30 min at the temperature of 5 °C. The precipitate was filtered off and washed several times with distilled water and methanol to remove the chemical residue. The obtained powder was dried under vacuum at room temperature for about 10 h.

2.3 Preparation of PPy-g-PP

PP-grafted PPy was prepared by a single ultrasonic compounding extruder. The materials of PP, PPy and DCP (1 %) were placed in the feed hopper before extruded. An ultrasonic power supply of 6 kW was connected to die zone to generate ultrasonic waves at 20 kHz frequency. The barrel surface in the ultrasound treatment zone was streamlined where the compound melt was forced to flow in gaps between the horns and the screw. This was to prevent the creation of a dead zone in the flow domain. The gap opening for the flow of compound in ultrasonic zone will keep at 2.54 mm. The extrudate was pelletized and injection molded into standard tensile test specimens. JSW Model NIOOB II injection-moulding machine was used with the barrel temperatures of 160 °C, 165 °C, 170 °C and 175 °C.

2.4 Characterisation

Electrical conductivity of synthesised PPy was measured by using two probe tests. The current is supplied from Tektronix PS280 DC Power Supply. Morphology of PP-g-PPy after tensile test was studied by using FE SEM JSM-6701F. The high resolution was consisted of 1.0 nm at 15 kV and 2.2 nm at 1 kV. The samples were coated using JFC-1600 Auto Fine Coater before they were scanned by FE SEM JSM-6701F. Thermal analysis was done using the Perkin-Elmer DSC with temperature calibrated by Indium. The samples were first heated at the rate of 10 °C/min from 30 °C to 400 °C in order to avoid possible influence due to the thermal historythe sample. The crystallisation process was then followed as the samples were cooled from 400 °C to 30 °C at the same rate. The samples were heated for the second time with the same parameter as the first heated and melting temperature was determined. Rheological behaviour was analysed by using capillary rheometer Rheograph 75 to get the shear rate and viscosity of PP-g-PPy. The machine used two capillaries with the diameter and the test temperature of 1 mm and 190 °C and the length for each was 20 mm and 10 mm. Pressure and force applied at transducer 1 were 8,936 bar and 50,000 N while at transducer 2 were 10,918 bar and 25,000 N. the diameter of piston used was 15 mm. The rhometer values were corrected and reported.

3. Result and Discussion

3.1 Electrical Conductivity Analysis

Table 1 shows the electrical conductivity of PPy-g-PP blends and it can be observed that with the increasing amount of PPy the conductivity for the subsequent blend increases. This is expected as the conductivity of 100 % PPy is about 1.9 S/m. The higher the amount of PPy means more electrical charge transfer to the blend. Another reason for increasing in the electrical conductivity is the use of DCP as a crosslinking agent, which is explained further along with morphology. DCP has successfully formed a crosslink networking between PPy and PP (Semba et al., 2006) as stated in literature. During processing, DCP initiated a free-radical reaction between PPy and PP forming PPy-g-PP copolymers which subsequently acted as compatibiliser and partially cross-linked networks in the blends as well as grafted PPy onto PP (Wang and Jing, 2005). Increasing amount of PPy subsequently increasing the capability of the PPy-g-PP in conducting electrical charge. Consequently, the conductivity of PPy-g-PP was improved.

Table 1: Electrical conductivities calculated and determined by using guarded 2-probe method

Sample	Electrical conductivity (S/cm)
100 % PPy	1.9
100 % PP	3.5×10^{-14}
PP/PPy 5 % Ppy	6.8×10^{-11}
PP/PPy 10 % Ppy	7.3×10^{-9}
PP/PPy 15 % Ppy	6.5×10^{-8}
PP/PPy 20 % Ppy	3.7×10^{-7}

3.2 Thermal analysis

The DSC heating scan of the grafted blend system and the extracted data of melting temperature, heat of melting and crystallinity are shown in Figure 2 and Table 2. The melting temperature of pure PP is around 164.95 °C. The addition of 5 wt% of PPy into the system reduced the melting temperature to 162.68 °C. This implies that grafting and crosslinking affects the crystallinity of the blend, thus melting it at relatively low temperatures. Further increment of PPy does not have much effect on the melting temperatarure of the blend but, the crystallinity continues to decrease. Overall, the thermal properties of PPy-g-PP are not much different than the properties of PP especially properties related to crystalline behaviour. Thus, the processing properties of PPy-g-PP are very similar to that of P as also reported by Wang et al. (2001).

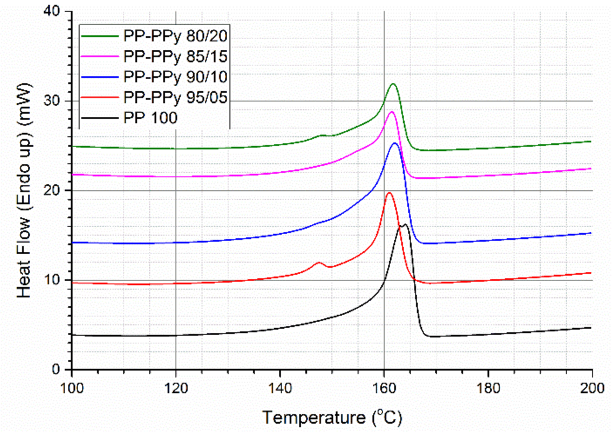

Figure 2: Thermodynamic curves of neat PP resin and PPy-g-PP blends

Table 2: Thermodynamic properties of neat PP resin and PPy-g-PP blends

Specimen	T_m (1^{st} Heating) (°C)	T_m (2^{nd} Heating) (°C)	ΔH(J/g)	Xc (%)
PP 100	164.95	164.05	85.7952	41.4
PP-Ppy 95/05	162.68	161.10	78.3532	39.8
PP-PPy 90/10	163.61	162.04	73.5827	39.5
PP-Ppy 85/15	162.25	161.47	69.1856	39.3
PP-Ppy 80/20	162.71	161.74	63.6563	38.4

*100% crystalline of PP is 207 J/g (Vander, et al., 1998)

3.3 Rheological Analysis

Figure 3 shows the storage modulus of PP and its grafted blend with PPy as a function of temperature. Results indicates that the viscosity increased with increase in incorporation content of PPy into PP. This behaviour can be attributed to the fact that higher degree of PP-PPy interactions requires higher shear stress and longer relaxation times to flow. As can be seen also from the Figure 3, the processability of PP-g-PPy is affected by the addition of PPy to the polymer blends. Increasing amount PPy into the system increased the ability of PPy-g-PP to be obviously non-Newtonian material, which attributes to the difficulty in processing because of higher viscosity (Shumigin et al., 2011). At the beginning, addition of 5 wt% of PPy decreased the viscosity at low shear rate (below 100 /s) and remained same beyond that. The reduction is attributed to the good processibility due to PPy acting as a plasticiser. It can be seen from SEM micrograph (Figure 4 (a)), PPy has localised and distributed evenly in the system and helping molten PP to flow. Addition of 10 wt% and more of PPy increased the viscosity and the increment is more prominent at 20 wt% of PPy. This is attributed to the agglomeration of PPy has restricted the molten PP to flow (Van der wal et al., 1998).

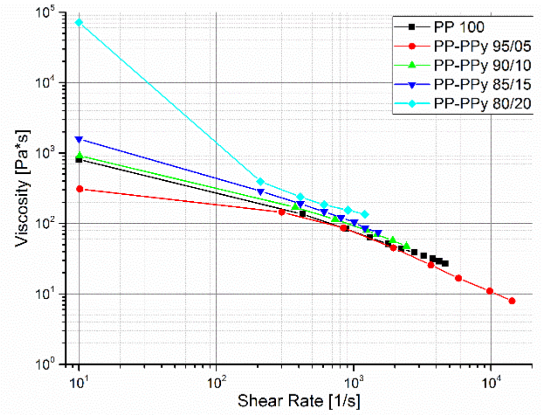

Figure 3: Rheological curves of neat PP resin and PPy-g-PP blends

In comparison with PP, PPy has higher melt viscosity, especially, at low shear rate, where contribution of PPy phase becomes more apparent. Further, when small quantity (0.2 part per hundred (phr)) of DCP was introduced to the system, it was good enough to initiate the grafting reaction. This proves that DCP was successfully incorporated onto the PPy-PP blend system. This result is agreement with the study done by Ma et al. (2012). Consequently, viscosity of PPy-g-PP increased as amount of PPy increased. Generally, the increase in viscosity depends on the concentration, particle size, particle size distribution and shape of the filler (Shumigin et al., 2011). PPy particle shapes are almost sphere and with uniform size. The presence of PPy particles perturbs normal polymer flow and hinders the mobility of chain segments. The higher the amount of the PPy, the worse is the dispersion of the minor phase in the melt and the higher is the viscosity of the polymer blends.

3.4 Morphological Analysis

Figure 4 shows the effect of the PPy (5 to 20 wt%) on the morphology of PPy-g-PP. SDS is an anionic surfactant and its molecules will self-assemble into aggregates such as micelles, vesicles and lamellar structures in an aqueous solution above the critical micelle concentration (CMC), and the morphology of micelles is closely related with the surfactant. A series of PPy with different morphologies were obtained by changing the content of pyrrole and the results are shown in Figure 4. PPy showed globular morphology with the diameter ranging from 100 to 500 nm and considerable agglomeration like cauliflower could be observed. The results show the morphology of the PPy was decided by not only SDS concentration but also the concentration of the monomer. When the concentration of the monomer was low with fixed SDS concentration, PPy nanowires occurred and their diameters became thicker gradually with the increasing of the monomer concentration. Also, it can be seen as the concentration of PPy is increased, the tendency of uniform dispersion of PPy also increases, thus resulting in increased electrical conductivity as reported in Table 1. Similar phenomenon was reported by Massoumi et al., (2012).

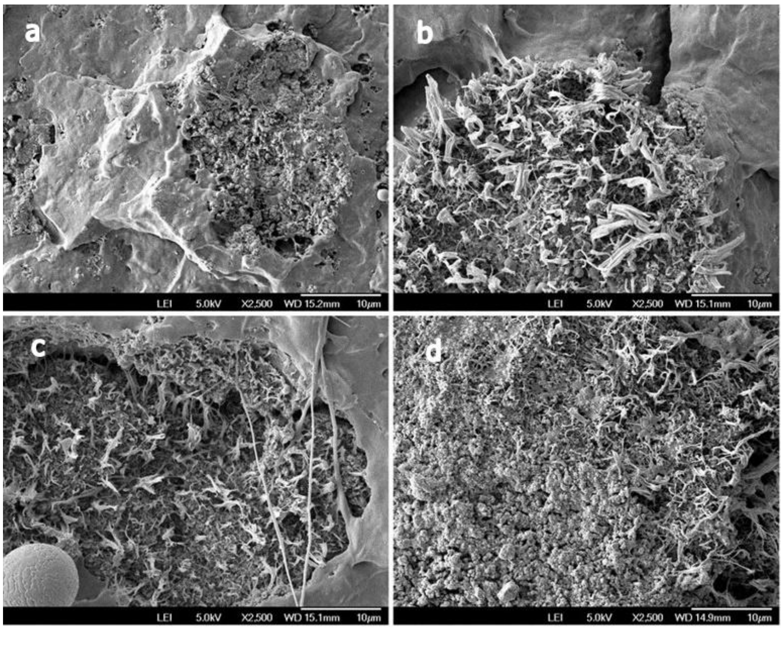

Figure 4: FESEM images of PPy-g-PP blends (a) 5 wt% of PPy (b) 10 wt% of PPy (c) 15 wt% of PPy and (d) 20 wt% of PPy.

4. Conclusion

PPy-g-PP blends were successfully synthesised in SDS solutions by changing the PPy concentration. The characteristics of products such as conductivity, morphology and structure were studied. Results show the content of PPy have a considerable effect on the conductivity, morphology and structure of resultant products. The electrical conductivity values increases with increase in PPy content and for 20 wt% PPy the electrical conductivity was in the range of static dissipative. Results shows the addition of PPy into the PP matrix introduces interfaces between them and effecting the crystallisation rate. The interfacial area is dependent on the components and the distribution of the additional components in the semi-crystalline matrix. Morphological analysis shows PPy had a globular morphology with the diameter ranging from 100 to 500 nm and considerable agglomeration like cauliflower. A change in surfactant or change in concentration of surfactant will help in enhancing the morphology. Therefore, it can be concluded that with a further improvement in properties (specially electrical conductivity), PPy-g-PP can find application for EMI/RFI shielding.

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