



Fourier Transforms Infrared Spectroscopy and X-ray Diffraction Investigation of Recycled Polypropylene/Polyaniline Blends

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The main objective in this paper is to characterise rPP/PANI blends chemical composition, structure and crystalline phases. This study investigates the synthesis and characterisation of recycled polypropylene/polyaniline (rPP/PANI) blends, prepared by single screw extrusion. Blends with 0 to 10 wt% PANI loading were prepared. The rPP/PANI blends were characterised by Fourier transforms infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The FTIR spectra show the PANI nanofiber in emeraldine salt form and show the grafting and strong interaction between PANI and rPP in the blends. The FTIR results for pure PANI and the blends with varying contents of PANI are consistently related to the structure of the pure PANI and blends discussed in the XRD analysis. XRD results confirmed the formation of PANI nanofiber in the blends and the presence of PANI nanofiber changes in crystallinity of rPP matrix.

1. Introduction

Polypropylene (PP) is a thermoplastic polymer belongs to polyolefin family, having a linear structure that can be melted and remoulded a few times. The PP is also available abundantly as a waste material, causing environmental problems. In order to mitigate this problem, PP can be recycled at their end life phase, producing new value added product with lower production costs. Recycling has been continually improved and new technology have been developed which enables wastes to be reused (Miles and Briston, 1986). Recycled PP as a matrix material in various composites has enabled wider applications of rPP especially in high value applications. The PP has a higher softening point, better resistance to flexing, a higher hardness, a higher tensile strength and elongation and cycle become faster (Whelan, 1982). rPP alone is criticised for the lack of sufficient strength and stiffness which hinder the use in some engineering applications. rPP need to be mixed with other materials such as PE (Vaccaro et al., 1997), nylon (La Mantia et al., 2001) and epoxidised natural rubber (Nakason et al., 2008) by many researchers to improve its drawbacks.

Polyaniline (PANI) is a unique conducting synthetic polymer with good chemical, electrical, and optical properties. The most important properties of PANI include their controllable electrical conductivity, lower density than metals, good environmental stability, and ease of preparation from common chemicals (Castillo-Ortega et al., 2002). However the main problem of PANI in technological application of PANI has been limited by its lack of processability, poor infusibility, poor solubility and poor mechanical strength (Castillo-Castro et al., 2007). To overcome this problem, conventional thermoplastics such as PP (Husin et al., 2015), polyethylene (Greabin et al., 2015), Polymethyl methacrylate (Yang and Ruckenstein, 1993) and polystyrene (Ruckenstein and Yang, 1993) is processed together with PANI resulting in the fabrication of polymer films, which exhibit balanced properties of electrical conductivity, mechanical properties, and processing characteristics. However, a normal blend of PANI and PP ended with poor interaction and resulting inferior properties. Dicumyl peroxide (DCP) can

be used to act as compatibiliser of rPP-PANI and promote coupling through grafting between PANI and rPP matrix (Husin et al., 2015). The blend of rPP-PANI was shown to have good processing properties, and can be processed thermally below the temperature at which the grafting side reaction of PANI took place (Fryczkowski et al., 2004). In this paper, PANI nanofibers were synthesised using ultrasonic sonochemical reaction and rPP/PANI was blended with different loading from 0 to 10 wt% of PANI nanofibers. PANI was successfully grafted onto rPP by using a single screw extrusion in the presence of dicumyl peroxide (DCP). The crystallisation, melt behaviours and morphology structure were also changed because of the graft reaction. The main objective in this paper is to characterise rPP/PANI blends chemical composition, structure and crystalline phases between synthesised PANI nanofibers and rPP/PANI blends in the presence of DCP as a grafting agent using Fourier transforms infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

2. Experimental

2.1 Materials

Recycled polypropylene (rPP) resin was purchased from Titan Petrochemical, Malaysia, Dicumyl peroxide 99 % were purchased from Acros Organics, Thermo Fisher Scientific, New Jersey, USA. Aniline (ANI) (99 %) and ammonium persulfate (APS) were purchased from Sigma-Aldrich and hydrochloric acid 37 % (HCl) were obtained from Tosla. Doped PANI-HCl was chemically synthesised using ANI and APS as oxidant. Nanosised PANI was synthesised using emulsion polymerisation method as describe in our previous work (Husin et al., 2014) in the presence of APS and HCl at 0 °C using ultrasonic reactor.

2.2 Preparation of rPP-PANI blends

rPP and PANI were melt blended using an ultrasound single screw extruder at processing temperature 150 - 160 °C. The rPP containing 0 - 10 wt% PANI and DCP was kept constant at 1 part per hundred (phr) and extruded through a water bath, and then pelletised. The extruded rPP/PANI with DCP grafting was injection moulded into the test specimens for analysis with a temperature profile between 170 to 190 °C.

3. Characterisation

3.1 Fourier Transform Infra-red Spectroscopy (FTIR)

FTIR were used to detect the existence of functional groups in the rPP/PANI blends. Neat rPP, PANI nanofibers and rPP/PANI blends were characterised using Perkin-Elmer 2000 with a resolution of 4 cm⁻¹ for 16 scans over wave number range of 370 - 4,000 cm⁻¹.

3.2 X-Ray Diffraction (XRD)

XRD were used to obtain information about the crystalline properties of neat rPP, PANI nanofibers and rPP/PANI blends. X-ray powder diffraction (XRD) analysis was conducted on a Rigaku SmartLab Diffractometer operated at 40 kV and 35 mA using Cu Ka radiation.

4. Results and Discussion

4.1 Fourier Transform Infra-red Spectroscopy (FTIR)

The molecular structure of PANI nanofibers was synthesised via the ultrasonic sonochemical method and characterised by using the FTIR spectroscopy. The details IR adsorption of PANI nanofibers are given in Table 1. Based on Figure 1, the IR spectrum of the synthesis PANI nanofibers salts occurred at 1,561, 1,493, 1,400, 1,306, 1,247, 1,115, 822 and 743 cm⁻¹. The absorption peaks of 1,561 and 1,493 cm⁻¹ are attributed to the C=N and C=C stretching mode of vibration for quinone and benzenoid units of PANI. The absorption peak around 1400 cm⁻¹ is attributed to the N=N stretching. The finding is similar with a study by Pretsch et al. (2000). The bands of 1,306 and 1,247 cm⁻¹ correspond to the C-N stretching of the secondary aromatic amine as presented in two different C-N bonds links in composites. The bands at 1,115 and 743 cm⁻¹ are assigned to the in-plane and out-of-plane aromatic C-H bending modes. The strong band and became more intense around 1,115 cm⁻¹ proving that the PANI is conductive and presents in the form of emeraldine salt. The adsorption peak at 822 cm⁻¹ is due to the out-of-plane C-H bonding of benzene ring. This synthesised PANI IR adsorptions have similar trends in the Bedre et al. (2012) work which band at 822 cm⁻¹ originates out of plane C-H bending vibration. Out-of-plane deformations of C-H on 1,4-disubstituted rings are located in the region of 800 – 880 cm⁻¹ (Cochet et al., 2001). The peak at about 684 cm⁻¹ (out-of-plane deformation of C-H) indicates the formation of the 1,3-disubstituted benzene ring (Sayyah et al., 2001).

The IR spectrum of PANI salts also exhibits bands at the range $3,500$ to $2,900\text{ cm}^{-1}$. The medium absorption of $3,400$ and $3,110\text{ cm}^{-1}$ corresponds to the stretching (N-H) vibrations of the secondary amine of the synthesised PANI salt. The spectrum bands observed at $3,400\text{ cm}^{-1}$ are originated from the free and hydrogen bonded N-H (stretching (N-H) vibrations of secondary amine) (Rao et al., 2002). This is as expected as the resultant synthesised PANI nanofibers is identical to the emeraldine salt form of standard PANI as previous literature reports. The FTIR spectra of rPP/PANI blends exhibit characteristic peaks for both of PANI and rPP as shown in Figure 2. FTIR spectroscopy was used as a complementary technique to monitor a functional group of rPP/PANI blends. Before addition of DCP content, the band absorption spectra has only PP characteristic band, mainly produced by group such as C-C, CH, CH_2 and CH_3 as well as by various type of vibration (Karger-Kocsis, 1989).

No PANI related band can be seen without the presence of the PANI peaks as well. After addition of DCP, the chemical structure of rPP/PANI blends were obviously changed. The different characteristics peaks occurred due to the presence of DCP as can be seen in Figure 2. This is suggesting that the addition of DCP grafting agent influenced the chemical structure of rPP/PANI blends, its characteristic is as appear in the diagram. Based on Figure 2, the characteristic peaks of rPP/PANI is clearly consistently alike even with an increase of PANI contents. The broad band of transmittance spectra at approximately $2,950$, $2,920$ and $2,840\text{ cm}^{-1}$ is due to transmittance peak at rPP ($2,950\text{ cm}^{-1}$) and PANI $2,916\text{ cm}^{-1}$ of the band. The band at $2,950$, $2,920$ and $2,840\text{ cm}^{-1}$ corresponds to aromatic C-H stretching vibration. This suggests a strong interaction between polyaniline and the rPP matrix.

A similar explanation reported by Xia and Wang (2002), which indicates that the peaks spectra modes at $1,456\text{ cm}^{-1}$ (due to C=C stretching vibration of benzenoid rings), at $1,252\text{ cm}^{-1}$ (due to C-N stretching) and for the quinonoid units at $1,380$ and $1,306\text{ cm}^{-1}$ corresponding to quinoid ring. Earlier studies by Tang et al. (1988) also suggested that the IR transmittance modes at about $1,500$ and $1,600\text{ cm}^{-1}$ are associated with aromatic ring stretching and the band at $1,564\text{ cm}^{-1}$ peak to the quinonoid ring and the $1,456\text{ cm}^{-1}$ peak to the benzenoid ring. The IR transmittance spectrum of band at $1,564\text{ cm}^{-1}$ exhibits a very low intensity ratio peaks, consistent with the presence of predominantly benzenoid units. The informative peak in the IR transmittance spectra of rPP/PANI blends is the C-N stretching transmittance in Quinoid Benzenoid Quinoid (QBQ) units at about $1,380\text{ cm}^{-1}$.

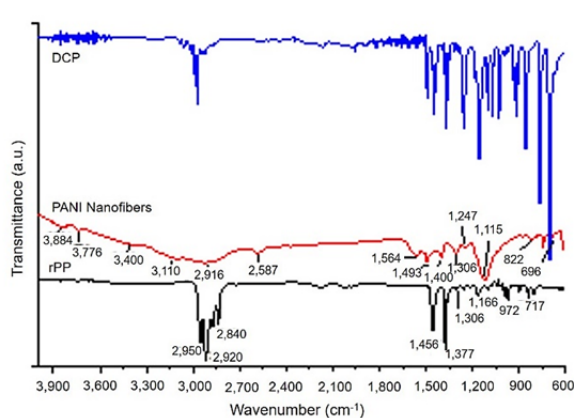


Figure 1: FTIR spectra of neat rPP, DCP and PANI

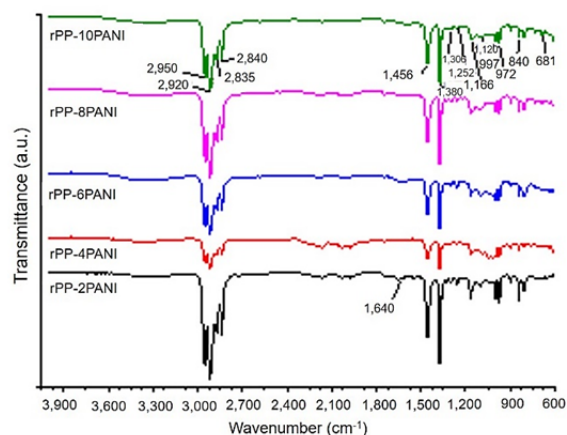


Figure 2: FTIR spectra of rPP/PANI blends nanofibers.

The transmittance band at $1,120\text{ cm}^{-1}$ was assigned to $\text{N}=\text{C}=\text{N}$ bending vibration shift towards the lower wave number corresponds to the PANI. The shift of $1,120\text{ cm}^{-1}$ band to lower wave number could be attributed to the hydrogen bonding between rPP and imine group of the grafted chain of PANI. The transmittance band at 841 cm^{-1} was assigned to aromatic C-H out of plane bending vibration of two adjacent hydrogen atoms on a 1,4-disubstituted benzene ring. Tang and co-workers (1988) summarised the assignment of IR adsorption band of PANI. FTIR analysis above show significant grafting between PANI and PP which indicate by the modification peaks that are visible at $3,400$, $3,937$, $1,166$ and 681 proved the formation of grafting between PANI and PP. The IR transmittance studies clearly suggested the graph polymerisation of rPP on to PANI.

4.2 X-ray diffraction (XRD)

The X-ray diffraction patterns of neat rPP, PANI nanofibers and rPP/PANI blends with different PANI loading are shown in Figure 3 and 4. Figure 3 shows the X-ray diffraction confirms the formation of PANI nanofiber, three

characteristic peaks around $2\theta = 6.0^\circ$, 19.09° and 26.26° presented in the XRD pattern of the PANI nanofiber. Yangyong and Xinli (2007) also reported the same XRD pattern. According to the studies reported by Chaudhari and Kelkar (1996), Banka and Lunzy (1999) and Lunzy and Banka (2000), the nanofibers are in partial crystallinity. The partial crystallinity of polyaniline nanofiber may be due to the amine and imine groups in the structure of doped PANI, which can form stronger intermolecular and intramolecular hydrogen bonds. Figure 4 shows the XRD patterns changes in the crystallinity of rPP, upon addition of PANI nanofibers. The Bragg reflections at 14.02° , 16.74° , 18.5° and 21.6° correspond to the indexed planes of the monoclinic crystals of neat rPP showed typical crystalline peaks at $2\theta = 14.02^\circ$ and 16.74° . In the XRD pattern of rPP/PANI blends diffraction peaks at $2\theta = 6.0^\circ$, 15.94° , 16.74° and 18.5° correspond to the PANI emeraldine salt. The peak at $2\theta = 6.0^\circ$ is characteristic of an interlayer repeat distance of alkyl tails of counterions that function as spacers between parallel planes of stacked PANI backbones (Morgan et al., 2001). The peaks centred at $2\theta = 15.94^\circ$ and 25.24° are ascribed to the periodicity parallel and perpendicular to the PANI chains. As reported by Wang et al. (2008), the main peaks at $2\theta = 9$, 16.2 , 20.84 and 25.05 for the XRD pattern are attributed to the structure of parallel, periodically intercalated with vertical in polymer chains.

Table 1: Peak absorbance of synthesised PANI samples

Frequency (cm^{-1})	Observed band due to
3,200 - 3,500	(N-H) vibrations of secondary amine
3,400	hydrogen bonded N-H (stretching (N-H) vibrations of secondary amine
1,561	C=N stretching mode of vibration for the quinonoid and benzenoid units of PANI
1,493	C=C stretching mode of vibration for the quinonoid and benzenoid units of PANI
1,400	N=N stretching
1,306 and 1,247	C–N stretching of secondary aromatic amine
1115	aromatic C-H in-plane bending in the 1,4-disubstituted benzene ring
822	out-of-plane deformation of C-H in the 1,4-disubstituted benzene ring
696	aromatic C-H out-of-plane bending vibrations

The rPP/PANI blends showed characteristic peaks of neat rPP together with the $2\theta = 6.0^\circ$ PANI nanofibers peak. While the intensity of the peak at $2\theta = 6.0^\circ$ increased with PANI nanofibers loading in the blend samples, the intensities of all of the other peaks decreases, signifying a lowering in rPP crystallinity upon blending with PANI nanofibers. The same results are also reported elsewhere (Ashveen et al. 2012). The presence of the $2\theta = 6.0^\circ$ peak in the blend samples showed that PANI nanofibers had maintained its microstructure upon blending with rPP. From the XRD pattern of PANI nanofibers in Figure 3, the PANI nanofiber has highly ordered crystal structure which is expected to exhibit high electrical conductivity. Comparing with the XRD pattern of the rPP/PANI blends in Figure 4, is showed that the crystalline structure has improved by the XRD pattern of PANI nanofibers.

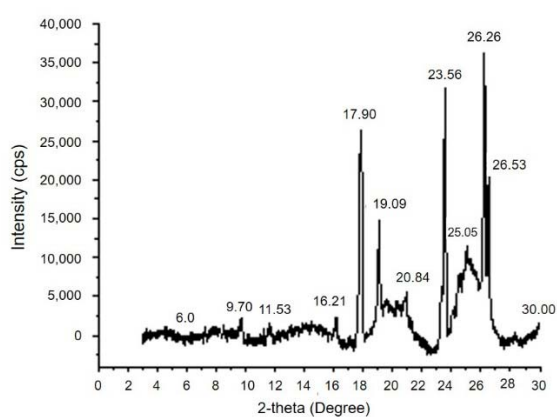


Figure 3: XRD spectra of PANI nanofibers

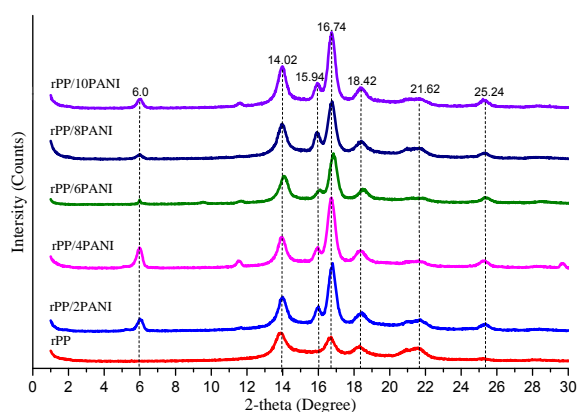


Figure 4: X-ray diffraction pattern of rPP/PANI blends

5. Conclusions

In this work, PANI nanofibers and rPP/PANI blends had been successfully prepared. FTIR analysis confirms that a PANI nanofiber has been obtained in the emeraldine salt form. FTIR analysis also showed strong interaction between PANI and rPP matrix to confirm that the occurred grafting in rPP/PANI blends. From XRD analysis we found that the diffraction peak at $2\theta = 6.0^\circ$, 15.94° , 16.74° and 18.5° correspond to the PANI emeraldine salt, and $2\theta = 6.0^\circ$, 19.09° and 26.26° presented in the XRD pattern of the PANI nanofiber. The XRD pattern in rPP/PANI blend showed the presence of PANI nanofiber changes in crystallinity of rPP matrix. The intensity of the peak at $2\theta = 6.0^\circ$ increased with PANI nanofibers loading in the rPP/PANI blends however the intensities of all of the other peaks decreases, signifying a lowering in rPP crystallinity upon blending with PANI nanofibers.

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