Research Article

Study on the Miscibility of Polypyrrole and Polyaniline Polymer Blends

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We report on the miscibility and phase behaviour of polypyrrole-polyaniline (PPy/PANI) as a function of blend composition. The PPy/PANI blends were prepared by solution processing method, using dimethyl sulfoxide (DMSO) solvent. Characterization of the polymer blends was carried out based on the data analysis from Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and differential scanning calorimetry (DSC). The PPy/PANI system was successfully formed blends in DMSO solvent. The polymer blends showed almost amorphous nature in XRD spectra because of intermolecular interaction between PPy and PANI macromolecules, which was confirmed by FT-IR data. Specifically, the DSC result for the PPy : PANI = 50 : 50 wt.% blend showed only one glass transition temperature (T_g), which indicates that the two polymers are well miscible without undergoing any phase separation.

1. Introduction

Recently, polymer blends have attracted many scientists to devote their lives to study the polymer-polymer system in order to develop new functional plastics with technologically attractive properties [1]. Hence, the polymer blend has been one of the hot research areas for material scientists and engineers because of its versatile applications [2]. Specifically, conjugated polymer blend system is not an exception for this trend of attraction. So far, conjugated polymers showing metallic or semiconducting properties have been commonly synthesized through electrochemical and chemical oxidative polymerization [3]. Between these two methods, the former electrochemical methods produce a film with brittle and not processable property [4]. However, the latter method, that is, chemical oxidative polymerization provides a better opportunity for producing significantly a solution processable polymer, compared to

the electrochemical methods. Thus, many efforts have been made to further improve the processability by preparing soluble conducting polymer through chemical oxidative method, for example, grafting alky side chains to polymeric backbone, and so on. [5]. The other approach to improve the processability of conducting polymer is to blend it with another material such as saturated hydrocarbon or π -conjugated semiconducting polymer [6]. Since mid-1980s, the blending of polyaniline (PANI) with other soluble insulating polymers has received great attention for its potential application to a wide variety of optical and electronic devices [7]. For example, the blending of PANI with polypyrrole (PPy) has enhanced the performance of materials, based on improved mechanical, thermal, electrical, and other processing properties [8]. The recent approaches for preparing polymer semiconductors are through solution processing methods. This method is advantageous from various points of view, such as cost minimization, scale-up, and roll-to-roll

FIGURE 1: Chemical structure of polyaniline (PANI) and polypyrrole (PPy).

processing [9]. The variety of functional chain molecules can be blended with other materials for fine-tuning device performance. Specifically, this blending approach is extremely common in organic photovoltaics (OPV) or organic field-effect transistor (FET) when they prepare active layer or semiconducting channel layer, respectively [10]. In line with this blend approach, the conjugated polymer such as PPy or PANI also has been compounded with various nanomaterials, nanoparticles, and other organic materials for improving materials' properties for advanced applications. Figure 1 shows their chemical structures.

To date, some amounts of researches have been carried out for characterizing the PANI/PPy composites and/or blends. Xing et al. prepared PANI/PPy composite from a PANI dispersion using sodium dedocylbenzene sulfonate (SDBS) as both dopant and surfactant in HCl acid. And they reported that the PANI/PPy system has exhibited some specific interactions between PANI and PPy macromolecules. Also, they pointed out that their PANI/PPy composite has high conductivity based on excellent sponge-like morphologies [11]. According to another research using copolymer such as poly(aniline-co-pyrrole) (PAP), some nanostructures were constructed for application to chemiresistive ammonia sensor, in which the copolymer PAP sensor showed improved sensing ability towards low concentration of ammonia, as compared to its homopolymer PANI or PPy sensors at room temperature. The PAP sensor was reported to be very reliable in terms of cost, recovery time, selectivity, reproducibility, detection range, and stability [12]. The next work indicated that highly conductive PAP copolymer was synthesized by properly controlling prepolymerization time, which showed improved conductivity without any significant change of morphologies of a film [13]. Akundy et al. used electrochemical deposition technique for synthesis of a PANI/PPy composite on the aluminium substrates in the aqueous oxalic acid solution. They reported that some morphology changes were observed in their PANI/PPy composite [14]. The aforementioned results are some background works for studying on the PANI/PPy blend or nanocomposite systems.

In general, there are three common categories of synthesis of PANI/PPy blends or composites, which are (a) electrochemical deposition, (b) copolymerization, and (c) solution processing [15]. They are used in drug delivery, encapsulation, supercapacitor, sensor, and other optoelectronic/electronic devices such as solar cells, light emitting diode, and FET [2]. However, the PANI/PPy system has only a limited application because of its partial miscibility or solubility in the common organic solvents. This limitation affects all optical and electrical properties because of unfavourable processability. Hence, the enhancement of processability through

enhanced miscibility of the PANI/PPy system is very desirable [16].

In thermodynamics, miscibility or solubility means mixing of two or more components on the molecular level, which results in a homogeneous structure with equal thermodynamic state variables. For mixing, the Gibbs free energy of mixing (ΔG_{mix}) must be negative for forming a homogeneous system. According to the principles of thermodynamics, when ΔG_{mix} is negative, the thermodynamic miscibility and homogeneity can be reached. This condition can be fulfilled in the case when strong specific intermolecular interactions are located between the components of a polymer blend. Of course, sometimes, we may have a case, in which there is only moderate or poor interaction, inducing a partial miscibility as a function of temperature and composition [17]. At this moment, note that one way to examine the miscibility and preliminary affinity between two polymers is to study the change in the glass transition temperature (T_g) of polymers after mixing. If the mixture exhibits a single T_g , this evidence means that the two homopolymers are usually miscible. However, oppositely, if the mixture displays more than one T_g , the system is believed to be partially miscible or immiscible [18]. Based on these understandings, in this study, we report the miscibility and phase behaviour of the PANI/PPy system as a function of blending composition, for which FT-IR, XRD, and DSC were utilized.

2. Materials and Methods

Polyaniline was synthesized by chemical oxidative polymerization of aniline in the presence of hydrochloric acid and ammonium persulfate. A 1 M of aniline was dissolved in hydrochloride solution. Then, 0.15 M ammonium persulfate (APS) was dissolved in 50 ml of double-distilled water. After that, we added the APS solution dropwise to hydrochloride solution to initiate the polymerization of aniline. The mixture was stirred with magnetic stirrer for 9 h under 5°C temperature. Then, we added methanol to stop further polymerization and let it unagitated until being precipitated. The resulting precipitate was collected by filtration. Then, the product was washed successively by 0.2 M of hydrochloride, double-distilled water, and acetone, sequentially. Through washing the samples with hydrochloride, we can remove any undesirable residual monomer, oxidant, and other decomposed products. And also, we provide uniform protonation to PANI and wash the sample again by acetone for removing low-molecular-weight organic intermediates and oligomers. Then, finally, our product was obtained as a fine powder, which was dried under vacuum at 50°C for 24 h.

Polypyrrole was synthesized by chemical oxidative polymerization of pyrrole. The 1 M of pyrrole was dissolved in

double-distilled water (10 ml). Then, 1.622 g of Fe_2Cl_3 was dissolved into 50 ml of double-distilled water. After that, the reacting monomers were mixed slowly in a dropwise manner under constant stirring for 30 minutes at 5°C . After that, the polymerization was allowed for 6h under stirring. Then, we kept it unagitated for 24 h until PPy powders were settled down. The resulting precipitate was collected by filtration. And the products were washed by double-distilled water many times and then dried in oven for 12 h at 50°C .

The PANI/PPy samples were prepared by the solution processing method. The PPy polymer was blended with PANI in various compositions, such as PPy:PANI = 50:50, 70:30, 80:20, and 90:10 in wt.%, for which the solvent DMSO was used. As a first step, the PPy and PANI solutions were prepared, respectively, in which ca. 20 mg of polymer was dissolved in 10 ml of DMSO, and the mixture was ultrasonicated for 10 min. Then, the two individual solutions were mixed together according to desirable weight ratio and again ultrasonicated for additional 1 h. Finally, the solvent used was evaporated in an oven at 50°C for 12 h for obtaining our PANI/PPy samples.

3. Results and Discussion

3.1. The FT-IR Characteristics. In Figure 2(a), the FT-IR spectra of PANI samples, the peak observed at 3433.75 cm^{-1} is due to N-H stretching. The absorption bands at 2923.21 and 2825.55 cm^{-1} are due to asymmetric C-H stretching and symmetric C-H stretching vibrations, respectively. The absorption peaks observed at 1637.68 cm^{-1} were attributed to C=C stretching in aromatic nuclei. The band obtained at $1600\text{--}1500\text{ cm}^{-1}$ corresponds to C-H stretching in aromatic compounds. In Figure 2(b), the spectra of PPy, the strong peak observed at 3447 cm^{-1} is related to N-H stretching. The peak at 2915 cm^{-1} is related to CH_2 , and the peak observed at 1536 cm^{-1} is due to C-C and C=C stretching in the ring. The peak of C-N stretching can be found at 1483 cm^{-1} . The peak 1169 cm^{-1} refers to C-C PPy ring, while the peaks of 786 cm^{-1} and 1036 cm^{-1} can be related to C-H out-of-plane bending and in-plane deformation, respectively. The FT-IR spectra for the PPy/PANI system in various compositions are shown in Figures 2(c)–2(f). The spectra of PPy:PANI = 70:30 and PPy:PANI = 90:10 on Figures 2(f) and 2(e), respectively, indicated that there is a change of spectra due to the different composition in the PPy/PANI system. The PPy:PANI = 50:50 and PPy:PANI = 80:20 spectra on Figures 2(c) and 2(d) showed nearly very trivial change. Overall, the FT-IR spectra showed that there is the change of intermolecular interactions between PPy and PANI with composition, resulting in the change of spectral shape. Specifically, we notice that the specific interactions between PPy and PANI macromolecule were confirmed not only by the change of intensity and shape observed in the range of spectra at $1645\text{--}1130\text{ cm}^{-1}$ for the samples of PANI, PPy, and PPy:PANI = 50:50, but also by the peak shift observed around the spectra at $980\text{--}786\text{ cm}^{-1}$. Furthermore, the peak's broadening and shift was observed around $793\text{--}648\text{ cm}^{-1}$. Therefore, we may expect that these intermolecular interactions might allow the PPy/PANI mixture to form blends.

FIGURE 2: FT-IR spectra of PANI, PPy, the mixture of PPy:PANI = 50:50, PPy:PANI = 70:30, PPy:PANI = 80:20, and PPy:PANI = 90:10 (wt.%).

3.2. The XRD Characteristics. Figure 3(a) displays the PANI's XRD pattern, in which a broad peak was observed at about $2\theta = 20^\circ$ and sharp peak at about $2\theta = 26^\circ$. The peak at 26° is more intensive than the peak at 20° . The peak around 26° indicates that PANI is a semicrystalline polymer, and the peak around 20° displays that PANI has an amorphous character also. Figure 3(b) describes pure PPy spectra, in which the broad peaks at around $2\theta = 24^\circ$ indicate that PPy has significant amorphous nature compared to PANI. The other two small peaks are observed at 33° and 35° , indicating chain ordering in PPy macromolecules in spite of major amorphous nature of PPy. Figures 3(c)–3(f) show the XRD spectra of the PPy/PANI system as a function of composition, in which we studied the miscibility and crystallinity of the PPy/PANI system. If phase separation occurs in the PPy/PANI system, X-ray diffraction peaks from both PPy and PANI are expected to be observed in the compound. However, if not, the absence of XRD peaks from pure polymer, PANI or PPy, indicates that the PPy/PANI system is in a single phase, confirming a blend system. Figures 3(c) to 3(f) show that the weight percent of PANI in the PPy/PANI system is 50, 30, 20, and 10, respectively. The result pointed out that the XRD spectra of PPy:PANI = 50:50 in Figure 3(c) are very distinguished from the other compositions, 70:30, 80:20, and 90:10, of the system in Figures 3(d)–3(f). In Figures 3(d)–3(f), the diffraction peaks of both pure PPy and PANI are observed, indicating they are composite rather than blend. This result showed that the PPy:PANI systems with 70:30, 80:20, and 90:10 mixing ratio showed a phase separation; that is, they might be nanocomposites. In contrast, the spectrum of the PPy:PANI = 50:50 system in Figure 3(c) shows that the peaks at $2\theta = 26^\circ$ (from PANI) and the peaks at $2\theta = 26^\circ$ (from PPy) are disappeared. This XRD results indicated that in the PPy:PANI = 50:50 system, the crystallinity was disappeared through well miscibility (i.e., no phase separation). This observation means that the interactions between PPy and PANI are very high to allow each polymer to mix in a molecular level. Therefore, we confirm that the PPy:PANI = 50:50 (wt.%) is a polymer

FIGURE 3: XRD of (a) PANI, (b) PPy, and (c–f) PPy/PANI mixture.

blend instead of composite. Finally, we double-checked its blending/miscibility/single-phase possibility through thermal properties, for example, DSC results.

3.3. The DSC Characteristics. The DSC analysis was done to assess the thermal effect on phase behaviour. In polymer science, the glass transition temperature is significantly important to determine whether a polymer-polymer mixture is miscible or immiscible or partly miscible. In the DSC thermogram, if a single T_g was observed for a mixture, we would say that it is a blend with miscibility. However, if the two T_g were observed in a mixture, we would decide that the components are an immiscible system, that is, a composite. Figures 4(a)–4(c) show the glass transition temperatures of pure PANI, pure PPy, and the PPy:PANI = 50 : 50 mixture, respectively. The DSC curve of PANI and PPy shows broad endothermic peaks at 359.95 K and 384.85 K, respectively. In literatures, PANI's T_g was observed at 385.15 K [19], and PPy's T_g was displayed at 371.15 K [20], indicating that our measured T_g is close to the literature's reports within ~ 10 – 20°C error. When evaluating the PPy:PANI = 50 : 50 system in Figure 4(c), we observed that there is only single glass transition temperature. This key result indicated that the two polymers, PPy and PANI, are a miscible system when we are blending them with 50 : 50 weight ratios. The glass transition temperatures of each pure polymer and their PPy:PANI = 50 : 50 mixture are summarized in Table 1. Note that the T_g of the PPy:PANI = 50 : 50 system is falling between the pure component polymers.

4. Conclusion

The PPy/PANI system was successfully obtained by the solution processing method using DMSO solvent. In the XRD spectrum, the PPy:PANI = 50 : 50 system showed that the peaks originated from pure PPy or PANI disappeared, which indicates that the characteristic of crystallinity disappeared and resultantly the PPy:PANI = 50 : 50 system has amorphous nature. In the FT-IR analysis, the blending of

FIGURE 4: The DSC analysis to examine the miscibility of the PPy/PANI system.

TABLE 1: Glass transition of PPy, PANI, and PPy:PANI = 50 : 50.

Polymer mixture (wt.%)	T_g (K)
PPy:PANI = 0 : 100	359.95
PPy:PANI = 100 : 0	384.85
PPy:PANI = 50 : 50	375.78

PPy and PANI makes the FT-IR spectra's intensity and shape be changed. The broadening and shift of peaks was also observed. These phenomena confirm that there are specific interactions between PPy and PANI macromolecules when blended together. Finally, the DSC thermogram indicated that there is only single glass transition temperature for the PPy:PANI = 50 : 50 system. Therefore, we conclude that the PPy:PANI = 50 : 50 system is a miscible polymer blend.

Data Availability

The data that support the findings of this study are available from the corresponding author upon the reasonable request. The data are not publicly due to confidentiality and privacy research participants.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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