Novel Conducting Polyaniline Blends with Cyanoresin

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ABSTRACT: Novel conducting polyaniline (PANI)/ cyanoresin (Cyan) blends were prepared by the addition of Cyan/dimethylformamide solutions to aniline monomer/dopant solutions and the *in situ* chemical oxidative polymerization of aniline with ammonium persulfate as an oxidant in aqueous *p*-toluene sulfonic acid solutions. The PANI/Cyan blends were prepared with various compositions (5:95, 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, and 70:30), and blend films of PANI/Cyan were obtained with a casting method. The conductivity of the PANI/Cyan blend films was 10^{-7} to 10^{-2} S/cm, which was measured by a four-probe technique. The tensile strength of the blend films was maintained with an increasing amount of PANI (up to 50 wt %), and this was attributed to intermolecular interactions such as hydrogen bonding between PANI and Cyan and a reinforcing effect through blending. This hypothesis was corroborated by Fourier transform infrared spectroscopy. Field emission scanning electron microscopy and thermogravimetric analysis were also used to investigate the morphology and thermal properties of the conducting PANI/Cyan blend films, respectively. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1035–1042, 2005

Key words: conducting polymer; blends; polyaniline; cyanoresin

INTRODUCTION

Polyaniline (PANI) occupies an important position among inherently conducting polymers because of its advantages with respect to synthesis, doping character, cost, environmental stability, and high electrical conductivity.[1] However, the utilization of this material has been limited because of its poor solubility, fusibility, mechanical properties, and processability.

The emeraldine base form of PANI is soluble in aqueous acetic acid, formic acid, dimethyl sulfoxide, dimethylformamide (DMF), *N*-methylpyrrolidinone, concentrated sulfuric acid, and other strong acids,[2–4] but the solubility is very low. Thus, there have been several efforts to make PANI more soluble and processable. To this end, most research efforts have been concentrated on the chemical functionalization of PANI and blends or composites of PANI with commercial polymers. For example, Cao and coworkers[5–7] reported that PANI doped with a protonic acid such as camphor sulfonic acid (CSA), dodecyl benzene sulfonic acid (DBSA), or *p*-toluene sulfonic acid (TSA) could be dissolved in common nonpolar or weakly polar organic solvents in which most commercial polymers could be codissolved.

The processing method for conducting polymers in the forms of blends and composites with commercial polymers exploits many applications and increases the technological potential of these materials because they can be combined synergistically. These composite materials can be used in practical applications such as energy storage,[8] electro-optical devices,[9] electromagnetic shielding,[10] and microwave absorption,[11–14] heating elements,[15,16] static electricity dissipation,[17–19] conducting glues,[20] paint coatings for anticorrosion protection,[21] conducting membrane materials,[22,23] and sensor materials.[24,25]

Cyanoresin (Cyan) is among the most promising materials for the field of electricity because of its high dielectric constant. It is classified into four grades (CR-S, CR-M, CR-V, and CR-U) according to its chemical composition (Fig. 1). CR-S and CR-V are the commercial names of cyanoethyl pullulan and cyanoethyl PVA, respectively. CR-M is a copolymer of CR-S and CR-V with a ratio of 50:50. CR-U is a commercial name of cyanoethyl sucrose used as a plasticizer of Cyan. Generally, Cyan has excellent solubility in organic solvents and ease of film fabrication. Furthermore, it is highly transparent and exhibits good mechanical properties when it is made into a film. Therefore, poor mechanical properties of PANI can be overcome through blending with Cyan.
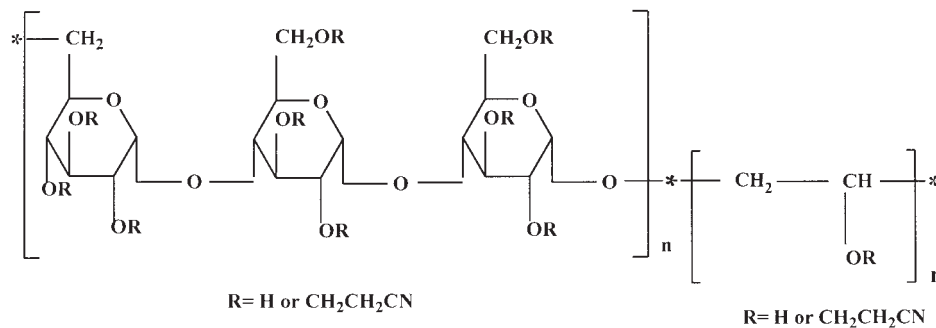
Figure 1 Chemical structures of Cyan (CR-M).

There have been several types of conducting PANI blends with industrial polymers, such as poly(vinyl alcohol),[26] poly(acrylic acid),[27] poly(ethylene oxide),[28] poly(vinyl pyrrolidone) (PVP),[29] nylon 6,[30] and poly(ethylene oxide).[31] However, Cyan has not previously been used in the field of conducting PANI blends, and it was expected that the adequate selection of the Cyan grade would enable us to make tailor-made PANI/Cyan blend films. Therefore, Cyan (CR-M) was blended with PANI, and its characteristics were investigated in this study.

EXPERIMENTAL

Materials

Aniline monomer ($C_6H_5NH_2$; 99.5%; Aldrich, St. Louis, MO) was purified by double distillation at a reduced pressure before polymerization. Cyan (Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) and other reagents were used as received. The CR-M grade was used as Cyan. PANI was synthesized by the chemical oxidation of aniline with ammonium persulfate [APS or $(NH_4)_2S_2O_8$; 99%; Duksan Pure Chemical Co., Ltd., Ansan, Korea] in a TSA ($C_7H_8O_3S$; 99%; Kanto Chemical Co., Inc., Tokyo, Japan) aqueous solution according to a modified polymerization procedure.[32]

Synthesis of the PANI/Cyan blends

Conductive PANI/Cyan blends were synthesized by *in situ* chemical oxidative polymerization. The aniline monomer was dissolved in a $1M$ TSA aqueous solution that had been precooled to $-2°C$. Then, an aqueous solution of $1M$ TSA containing dissolved APS was added dropwise to this solution over a period of 20 min with stirring to polymerize the aniline and to dope PANI at the same time. The molar ratio of aniline to APS was kept at 1:0.25 for PANI polymerization because the degree of aggregation increased as the oxidant level was increased and the solubility of the polymer and the shelf-life stability of the solution substantially decreased with an increased level of aggregation.[33] Accordingly, a relatively low oxidant level was adopted in this research.

A Cyan/DMF solution was added in the desired proportion to the polymerization solution with vigorous stirring overnight. After the reaction, a green powder was precipitated in the form of PANI/Cyan salt doped with TSA. The precipitate was washed with a dilute aqueous TSA solution to remove unreacted monomers and impurities and was rinsed with an abundant amount of distilled water until the filtrate was colorless. After the washing step, the precipitated PANI/Cyan blends were filtered with a Büchner funnel and then dried for about 48 h at 50°C *in vacuo* to ensure a low moisture level.

Preparation of the PANI/Cyan blend solutions and films

PANI/Cyan blend solutions and blend films were prepared as follows. The synthesized PANI/Cyan powder (0.989 g) was dissolved in 10.0 g of *m*-cresol at room temperature until a homogeneous viscous solution was obtained, and PANI/Cyan blend films were prepared via the casting of the blend solutions onto a glass substrate. Because the slow evaporation of the solvent helped the crosslinking of PANI and improved the mechanical properties,[34] the evaporation of *m*-cresol was carried out at 40°C for about 72 h in a convection oven. After the solvent evaporation step was completed, PANI/Cyan blend films were removed from the glass surface by immersion in purified water for a few hours.

Measurements

The electrical conductivity of PANI/Cyan blend films was measured by a four-probe technique with a Keithly 238 high-current-source measuring unit. All conductivity measurements were performed in air and at room temperature by direct contact with the film surface. The electrical conductivity of the samples was calculated as follows:

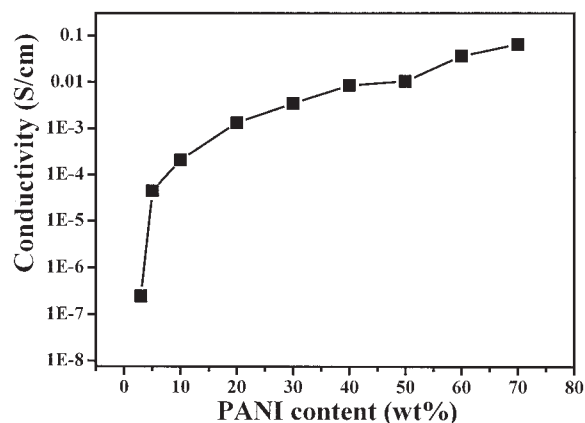$$\sigma(S/cm) = \frac{0.22}{t} \times \frac{i}{V} \qquad (1)$$

Figure 2 Conductivity of PANI/Cyan blends versus the weight percentage of PANI.

where σ is the conductivity, t is the sample thickness, V is the voltage drop across the inner probes, and i is the current passed through the outer probes. Ultraviolet–visible (UV–vis) absorption spectra were recorded at room temperature with a Jasco FP-6500 (Tokyo, Japan), and the spectra were measured in the 300–1000-nm range. To record the spectra of the solutions, we used quartz infrasil cells, with a 1-mm optical path, filled with a 0.01 wt % PANI/Cyan blend solution in m-cresol. Fourier transform infrared (FTIR) spectra of pristine PANI, CR-M, and PANI/Cyan blends were recorded with a Nicolet 760 Magna IR spectrometer with the KBr disc technique. The tensile properties were measured with an Instron 4465 (Canton, MA) universal testing machine. The mechanical properties were tested at room temperature, and at least five specimens were used for each test. The crosshead speed at which the tensile test was carried out was 5 mm/min, and a gauge length of 3 cm was used. The surface and cross-sectional morphology of the PANI/Cyan blend films was investigated with field emission scanning electron microscopy (FESEM) with a JEOL JSM-6330F (Tokyo, Japan) electron microscope operated at 5 and 15 kV on samples containing a thin layer of sputter-coated gold (the magnification is shown in the micrographs of the samples). Thermogravimetric analyses (TGAs) of the PANI/Cyan blends were carried out under a nitrogen atmosphere from 20 to 800°C at a heating rate of 10°C/min with a TA Instrument 2960 (New Castle, DE) thermogravimetric analyzer.

RESULTS AND DISCUSSION

Conductivity

The conductivity measurements of the PANI/Cyan blends were carried out with freestanding films, which were obtained through the casting of the blend

solutions on the glass substrate. Figure 2 presents the conductivity of the PANI/Cyan blend films versus the PANI content. The electrical conductivity of the blend films depended strongly on the weight fraction of PANI in the blends. Also, as shown in Figure 2, the PANI Cyan blends had percolating systems, and the percolation threshold value for the blends was attained when the PANI content was approximately 5 wt %, which was a relatively low value of the percolation threshold in comparison with the value (ca. 20 wt %) of polystyrene (PS)/PANI blends prepared by the same *in situ* polymerization.[35]

With spherical rigid fillers, the percolation threshold takes place at a volume fraction of approximately 16 vol % in a composite.[36] Mixing solid fillers, however, stiffens the material and may cause undue brittleness and processing difficulties at the same time. Thus, *in situ* polymerization is an effective method for making more electrically conducting blends and lower percolation thresholds than the use of conducting polymers with fillers.

Several authors have reported preparing PANI/ poly(methyl methacrylate) (PMMA) blends with extremely low percolation thresholds. Cao and Heeger[37] showed that PANI had conducting paths in PMMA. Pron et al.[38] reported that the dispersion of aggregated PANI grains in the matrix was a key factor in obtaining very low percolation thresholds. Therefore, the electrical conductivity and percolating system could be interpreted on the basis of a hopping mechanism between polaron clusters. It is known that a high percolation threshold ($\approx 50\%$ PANI) leads to severe phase separation and has a negative effect on the mechanical properties.[39] In this study, however, phase separation was not observed for the PANI/Cyan blends under investigation for all compositions; this is discussed later in the FESEM analysis. Therefore, the relatively low percolation threshold indicated that the two classes of polymers (PANI and Cyan) had interactions and miscibility.
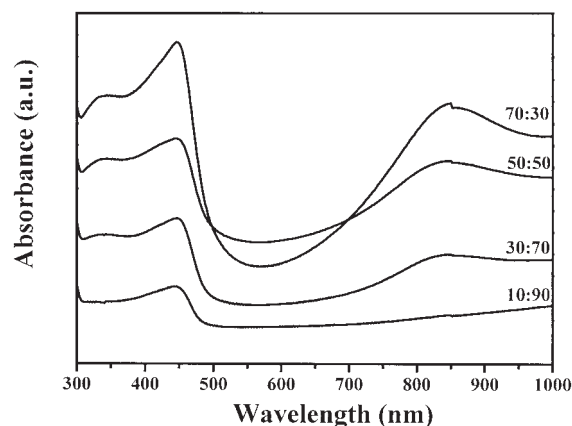

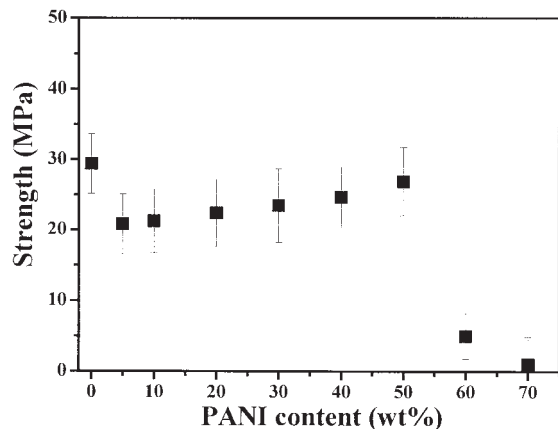**Figure 3** UV–vis spectra of PANI/Cyan blends.

Figure 4 Tensile strength of PANI/Cyan blends versus the weight percentage of PANI.

UV–vis spectroscopy

The UV–vis samples of the PANI/Cyan blends were prepared in *m*-cresol as clear green solutions. The absorption characteristics of the protonated PANI became predominant with an increase in the PANI content, as shown in Figure 3. There were three major absorption peaks, with the π–π^* transition on the polymer chain, polaron band, and localized polaron of electrons at about 320, 440, and 850 nm, respectively. This indicated that the PANI/Cyan blends had a localized conformation.

Xia et al.[40] and Juvin et al.[41] discussed the relationship between the UV–vis spectra of protonated PANI and the conformation of its chain. They pointed out that the emeraldine adopts an extended coil conformation that promotes the delocalization of polarons in particular solvent-protonating acid systems, such as *m*-cresol/CSA. This delocalization is manifested in the UV–vis spectra by an intense broad band extending far in the near-IR region. Moreover, it is well known that the delocalized conformation is more desirable than the localized conformation for higher conductivity and that the types of dopants and solvents greatly affect the conformation of conducting polymers. Therefore, localized conformation observed in this study was attributed to the use of TSA as a dopant. Further studies with other dopants (hydrochloric acid, CSA, DBSA, etc.) are now proceeding.

Tensile properties

The tensile properties of the blend films were investigated. Generally, PANI is known as a very rigid material, and the tensile strength of most PANI blends or composites has a decreasing tendency as the concentration of PANI increases.[42,43] Moreover, because PANI is not completely dissolved or is dis-

solved at a very low concentration, it acts as defects in blends or composites, such as carbon-black-filled or metal-powder-filled composites. However, as shown in Figure 4, the tensile strength of the PANI/Cyan blend films was maintained as the concentration of PANI was increased up to 50 wt % in this study. These results can be explained by the fact that PANI had sufficient solubility and there were some interactions such as hydrogen bonding (Scheme 1) or molecular-level miscibility between PANI and Cyan in the PANI/Cyan blends.[44,45] With more than 50 wt % PANI, however, the rigid or brittle characteristics of pristine PANI became dominant, and so the tensile strength of the PANI/Cyan blends substantially decreased.

Figure 5 presents the elongation at break versus the PANI content of the PANI/Cyan blend films. The elongation of the PANI/Cyan blend films steadily decreased with increasing PANI because pristine PANI had comparatively rigid or brittle properties. Consequently, we thought that the extremely poor tensile strength of pristine PANI could be overcome by blending with Cyan, which presumably would make PANI processable.

FESEM analysis

The morphologies of the PANI/Cyan blends were evaluated with FESEM. Figure 6 shows the surface
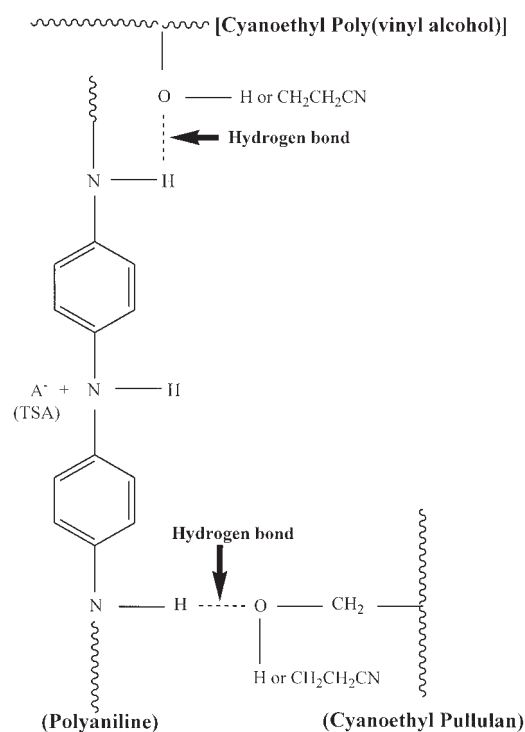
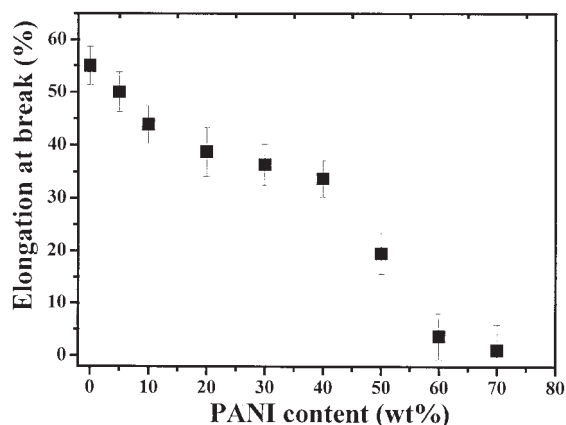**Scheme 1** Schematic of hydrogen-bond formation between PANI and Cyan.

Figure 5 Elongation at break of PANI/Cyan blends versus the weight percentage of PANI.

images of PANI/Cyan blend films. As the concentration of PANI increased in the blend films, a microvoid morphology became dominant. Paul and Pillai[46] pointed out PANI protonated with sulfonic acid of 3-pentadecyl-phenoxyacetic acid, which was blended with ethylene vinyl acetate, showed a microvoid morphology because of PANI aggregates, and the presence of microvoids might also affect the tensile properties adversely. Oh et al.[47] synthesized PANI with various acidic dopants with an electrochemical method and found that the dopants had a great influence on the morphology of PANI. Pud et al.[48] also reported the morphology of poly(ethylene terephthalate) (PET)/PANI composites with atomic force microscopy, and they observed that PET and the

undoped form of the PET/PANI composite exhibited comparatively flat surfaces, whereas doping led to the emergence of mountainous features; they concluded that the dopant size and its nature affected the surface morphology of the composite. Therefore, it was assumed that the microvoids of the surface, in this research, arose from the characteristics of the dopant (TSA).

Figure 7 shows cross-sectional images of PANI/Cyan blend films. PANI is represented by dark, continuous parts, whereas the white spherical regions correspond to the Cyan phase. The microvoid morphologies on the surfaces of the blend films almost disappeared, and homogeneous spherical morphologies appeared. In a study of PS/PANI blend morphologies,[35] it was found that the uniform and nonspherical morphologies yielded higher conductivity than spherical morphologies. Although the PANI/Cyan blends had spherical morphologies, the spheres were very small (ca. 50 nm), and they showed a highly uniform distribution of the two phases. Therefore, we thought that these highly uniform morphologies of the PANI/Cyan blends were obtained as a result of intermolecular interactions between PANI and Cyan, such as hydrogen bonding.

Pron et al.[38] reported that significant numbers of grain clusters or agglomeration led to an increase in the value of the percolation threshold and that the good dispersion of aggregated grains was a key factor in obtaining a low percolation threshold. In this study, the obtained percolation threshold value was approximately 5 wt % PANI, and this result indicated that
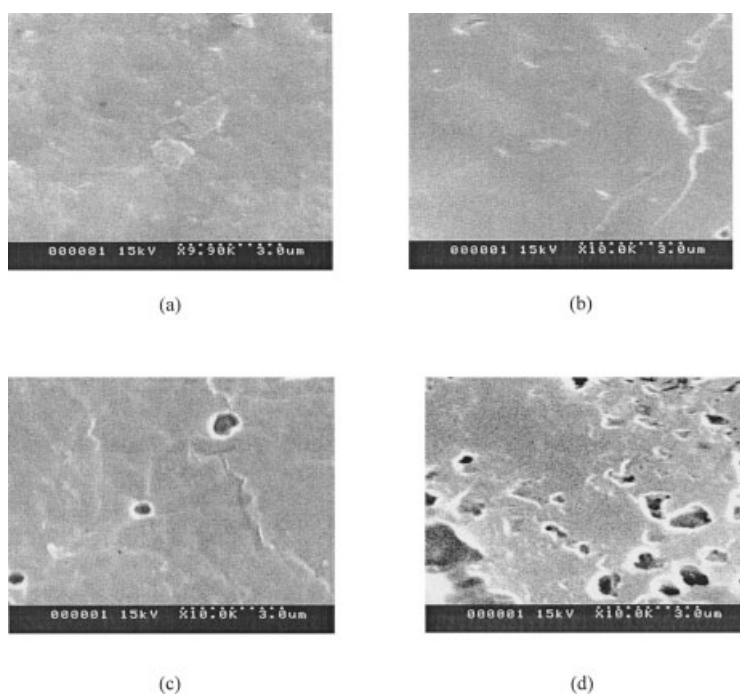

Figure 6 Planar views of PANI/Cyan blends by FESEM: (a) 10:90, (b) 30:70, (c) 50:50, and (d) 70:30.
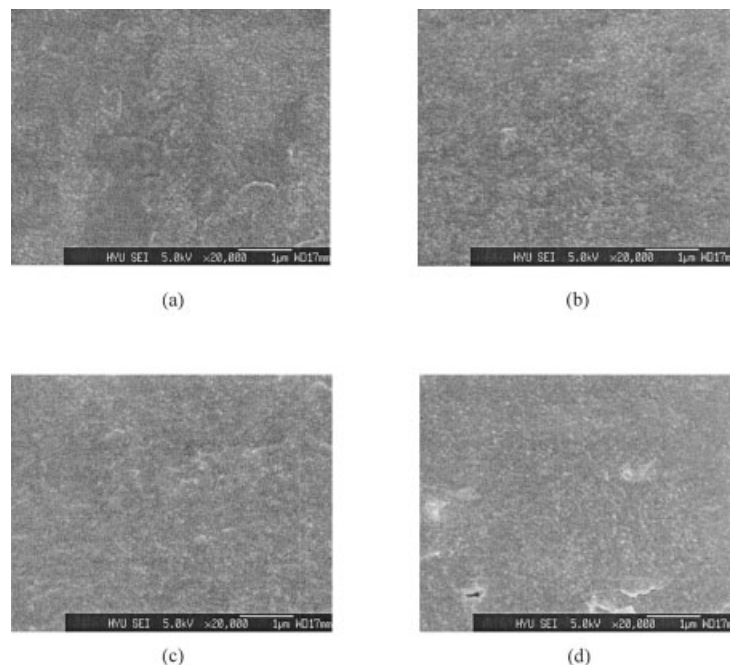
Figure 7　Cross-sectional views of PANI/Cyan blends by FESEM: (a) 10:90, (b) 30:70, (c) 50:50, and (d) 70:30.

both the type of morphology and the sphere size of the polymer were decisive factors for high conductivity or low percolation thresholds because the smaller the spheres were, the easier it was to make conducting paths of PANI.

IR spectroscopy

FTIR spectra of PANI/Cyan blends (10:90 and 50:50), pristine PANI (PANI-TSA), and Cyan (CR-M) are displayed in Figure 8. Pristine PANI showed characteristic peaks for C=C of quinoid ring stretching, C=C of benzenoid ring stretching, aromatic C—N stretching, secondary C—N stretching, C—H aromatic in-
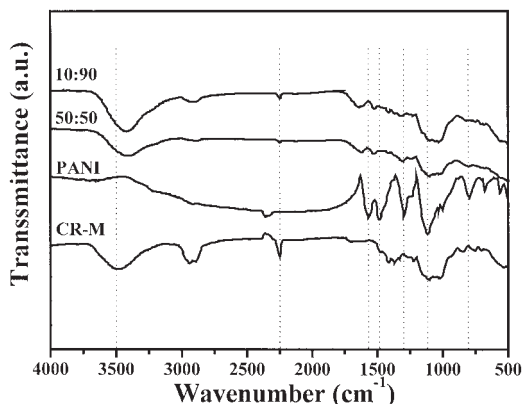

Figure 8　FTIR spectra of pristine PANI, CR-M, and PANI/Cyan blends.

plane bending vibrations, and C—H aromatic out-of-plane bending vibrations at about 1560, 1500, 1310, 1290, 1110, and 810 cm^{-1}, respectively. These peaks in PANI were modified in position or intensity with the blend formation. Obviously, these modifications indicated the structural changes of PANI in its blends. There were no features in the spectra between 1700 and 2800 cm^{-1} because no functional groups of PANI showed vibration absorption peaks in this region. These results indicated that the doping agent was sulfonic acid with benzene rings.[49-51]

The peak of CR-M corresponding to 3500 cm^{-1} was assigned to the hydroxyl (O—H) moiety. For pristine PANI, there was no peak at the point, but the PANI/Cyan blends showed shifted peaks at about 3400 cm^{-1}. Generally, a free (non-hydrogen-bonding) O—H stretching band appeared at about 3600 cm^{-1}, and a broad O—H stretching vibration was obtained for intermolecular hydrogen bonding from 3400 to 3300 cm^{-1}. Thus, the hydroxyl peak was thought to shift to a lower frequency of 3400 cm^{-1} for PANI/Cyan blends because of intermolecular hydrogen bonding between PANI and Cyan. According to Ikkala et al.,[52] interacting pairs for hydrogen bonding in PANI complexes are composed of two groups: donor (—OH) and acceptor (—NH, —SO$_3^-$, C=O, etc.).

Another possible interpretation is the formation of amine (N—H) bonds between PANI and Cyan. Because the amine band appeared at about 3500–3300 cm^{-1}, the amine band, which was overlapped
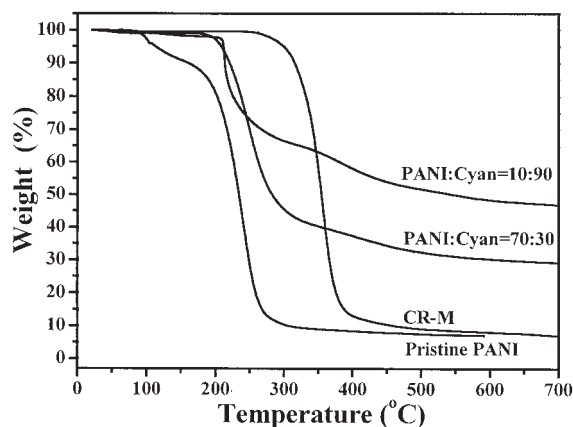
Figure 9 TGA thermograms of pristine PANI, CR-M, and PANI/Cyan blends.

by the O—H band, could influence O—H peak shifting. Moreover, the cyanide (C≡N) peak of CR-M at 2250 cm^{-1} and the C—N stretching band of PANI at 1310 cm^{-1} almost disappeared for the blends, and this meant that C≡N in the cyanoethyl (CH$_2$CH$_2$CN) group of CR-M and C—N of PANI interacted with the hydrogen molecules in PANI and CR-M, respectively.

In PANI/PVP blends,[53] IR peaks of quinoid and benzenoid are much subdued as a result of structural modification, primarily because of intermolecular hydrogen bonding between —NH of PANI and the carbonyl group of PVP. Also, for PANI/PVA composites,[54] benzenoid and quinoid absorption bands of PANI are significantly shifted to higher wave numbers for blends as a result of hydrogen bonding. In this research, the quinoid ring stretching at about 1560 cm^{-1} shifted to 1630 cm^{-1}, and the benzenoid ring stretching at about 1500 cm^{-1} also shifted to 1530 cm^{-1} in PANI/Cyan blends. The band corresponding to C—H in-plane bending at 1110 cm^{-1} for PANI was also much subdued for PANI/Cyan blends, and this was another proof of interaction between PANI and Cyan.

Therefore, there were obvious interactions between PANI and Cyan, and those results support the fact that PANI and Cyan were miscible. The miscibility made the PANI/Cyan blends combine in a synergistic matter, and so the mechanical properties of PANI increased via blending with Cyan.

TGA

The thermal properties of pristine PANI, Cyan, and PANI/Cyan blends were evaluated by TGA, and the TGA thermograms are shown in Figure 9. In the thermogram of PANI-TSA, the initial weight loss was observed between 60 and 200°C and was attributed to the loss of moisture and unbound dopant;[55] major

weight loss was observed from 200 to 300°C (ca. 70%) and was due to TSA degradation. Above 350°C, the weight loss was related to main-chain degradation of PANI.[56] For Cyan (CR-M), almost a one-step weight loss of the main chain was observed between 300 and 400°C. The PANI/Cyan blends showed the initial weight loss of moisture and unbound dopant in the range of 60–200°C and the second weight loss of TSA in the range of 200–300°C. Finally, weight losses of the PANI and Cyan main chain were observed above 350°C.

Doyle's method[57] was used to analyze the thermal degradation stability, and the integral procedural decomposition temperature (IPDT) was calculated as follows:

$$IPDT(°C) = A*K*(T_f - T_i) + T_i \qquad (2)$$

where $A*$ is the area ratio of the total experiment curve divided by the total TGA thermogram, $K*$ is the coefficient of $A*$, T_i is the initial experimental temperature, and T_f is the final experimental temperature. The values of the IPDT parameters ($A*$, $K*$, and $A*K*$) and IPDT are listed in Table I. As shown in Table I, PANI-TSA had the lowest IPDT value (233.8°C), and Cyan had a somewhat higher IPDT value (313.5°C) than PANI-TSA. This indicated that Cyan had more thermal stability than PANI-TSA. Therefore, it was possible to enhance the thermal stability of PANI through blending with Cyan. Moreover, as shown in Table I, the PANI/Cyan blends had higher IPDT values (697.3 and 541.5°C for 10:90 and 70:30, respectively) than the pristine PANI or Cyan. These results are more evidence of the hydrogen bonding between PANI and Cyan.[44] Consequently, the poor mechanical properties and thermal stability of PANI were overcome by synergistic combination with Cyan.

CONCLUSIONS

PANI/Cyan conducting blends were prepared by *in situ* chemical oxidative polymerization. The conductivity of the blends had a range of 10^{-7}–10^{-2} S/cm, and the percolation threshold was about 5 wt % PANI. The tensile strength was well maintained at 26.89 MPa

TABLE I
Thermal Stability Parameters for the Pristine PANI, CR-M, and PANI/Cyan Blends

Sample	$A*$	$K*$	$A*K*$	IPDT (°C)
Pristine PANI	0.305	1.183	0.361	233.8
CR-M	0.344	1.129	0.388	313.5
PANI/cyan 10:90	0.520	1.687	0.877	697.3
PANI/cyan 70:30	0.442	1.529	0.676	541.5

with the addition of up to 50 wt % PANI, whereas the blends became dramatically brittle with more than 50 wt % PANI because the characteristics of pristine PANI were becoming dominant. FTIR spectroscopy and FESEM analysis revealed that PANI and Cyan had mutual interactions such as hydrogen bonding and miscibility. Thus, the enhanced mechanical properties were attributed to the mutual interactions between the two classes of polymers. Moreover, TGA results proved that the thermal stability of PANI was enhanced through blending with Cyan.

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