Conductive Blends of Polyaniline with Plasticized Poly(methyl methacrylate)

PASCAL JUVIN,[1] MAGDALENA HASIK,[1] JÉRÔME FRAYSSE,[1] JÉRÔME PLANÈS,[1] ADAM PRON,[1] IRENA KULSZEWICZ-BAJER[2]

[1] Laboratoire de Physique des Métaux Synthétiques, UMR 5819, DRFMC/SI3M, CEA Grenoble 38 054 Grenoble, France

[2] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00 664 Warszawa, Poland

ABSTRACT: Polyaniline (PANI) protonated with camphorsulfonic acid (CSA) and three different poly(alkylene phosphates) (PAPs) (where alkylene = pentylene, hexylene, or nonylene) was used in the fabrication of conductive polyaniline–poly(methyl methacrylate) (PMMA) blends. The lowest percolation threshold (f_p = 0.041 wt %) was obtained for the PANI(CSA)$_{0.5}$–PMMA blend plasticized with 35 wt % of dibutyl phtalate (DBPh). This blend is also very resistant against the deprotonation of its conductive phase in basic solutions of pH = 9. In the case of blends prepared with the use of PAPs as PANI dopants, the percolation threshold strongly depends on the length of the hydrophobic spacer (alkylene group) in the dopant. The percolation threshold decreases in the order PPP > PHP > PNP, whereas the resistance against deprotonation in basic solutions decreases in the following inverse order: PNP > PHP > PPP. This last observation can be rationalized by increasing contribution of hydrophobic segments in the polymeric dopant, when going from PPP to PNP, which renders polyaniline more resistance toward the penetration by aqueous basic solutions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 471–479, 1999

Key words: PANI; CSA; PAPs; PMMA

INTRODUCTION

The progress in the processibility of polyaniline (PANI) observed since 1992[1] has resulted in the fabrication of several types of conductive polyaniline blends with such industrial polymers as poly(vinyl chloride),[2,3] polystyrene,[4,5] and polyamides[6] to name a few. In modern technology, there exists a strong demand for materials that combine flexibility of plastics with high transparency in the visible part of the spectrum and high electronic conductivity.[7] In our previous article,[8]

we have reported the preparation of flexible and highly transparent, conductive blends of polyaniline with plasticized cellulose acetate.

Plastification is a convenient method for improving the flexibility of blends. In addition to cellulose derivatives, several industrial polymers can be used in the plasticized state, among them poly(methyl methacrylate) (PMMA). Poly(methyl methacrylate) is very well suited for the preparation of transparent conductors by blending with polyaniline due to its low extinction coefficient in the visible. Blends of PANI with nonplasticized PMMA have been prepared by several authors.[9–12] Some of them report, for these materials, a very low percolation threshold, significantly below 1 wt %.[2,12] In view of the transparency of the conductive blends, the value of the percolation

threshold is of crucial importance. Because of a high value of the extinction coefficients in the visible measured for the conductive form of polyaniline, the transparency of its blends with conventional polymers can be assured only for extremely low values of the percolation threshold.

In this article, we demonstrate that the use of an appropriate plasticizer does not only improve the flexibility of PANI–PMMA blends but also leads to a significant increase of their conductivity and to much lower percolation thresholds as compared to nonplasticized blends.

In addition to the studies of the preparation of extremely low percolation threshold PANI–PMMA blends, we have investigated their resistance against deprotonation. The weakest point of PANI is its tendency to deprotonate in basic media. Of course, this deprotonation reaction has a disastrous effect on the conductivity of PANI-based blends because only the protonated form of PANI is conductive. In the majority of potential applications, improved resistance against deprotonation is required for PANI blends since such materials can be exposed to basic media and, despite this exposure, they should retain their high conductivity.

EXPERIMENTAL

Reagents

Polyaniline in the oxidation state of emeraldine was synthesized chemically by oxidation of aniline with ammonium persulfate at $-25°C$. The details of the preparation can be found elsewhere.[13] The resulting emeraldine hydrochloride was then transformed into the free base state by deprotonation with an excess of $0.3M$ aqueous solution of NH_3. The inherent viscosity of the polymer was equal to 1.49 dL/g at 25°C (0.1 wt % of emeraldine in H_2SO_4).

The following four protonating agents were used: poly(pentylene phosphate) (PPP), poly-(hexylene phosphate) (PHP), poly(nonylene phosphate) (PNP), and camphorsulfonic acid (CSA). Poly(alkylene phosphates) of the general formula

$$\left[O-\underset{\underset{O}{\overset{\parallel}{P}}}{\overset{OH}{|}}-O\left(CH_2\right)_n \right]_x$$

where synthesized according to the method described in the literature.[14,15] First poly(phosphonates) were obtained by polycondensation of dimethyl phosphate with corresponding diols and then oxidized with N_2O_4 to poly(alkylene phosphates). The number-average molecular weight M_n varied from 8500 to 14,000. (+−) −10-CSA (98%) was purchased from Aldrich and was vacuum-dried prior to use. Dibutyl phtalate (DBPh) (Aldrich) and m-cresol (MC) (Merck) and PMMA (medium molecular weight, Aldrich) were used without further purification.

Protonation of Emeraldine Base

As already stated, the following four protonating agents were used: three poly(alkylene phosphates) (PPP, PHP, and PNP) and CSA. Prior to the protonation reaction emeraldine base (EB) and the protonating acids were dried in a vacuum line at 80°C for 2 h. The molar ratio of poly(alkylene phosphate) mer to PANI mer or CSA molecule to PANI mer was 0.5. It is assumed here that PANI mer has the formula $C_6H_4NH_{0.5}$. The number 0.5, denoting hydrogen bonded to nitrogen, originates from the fact that in emeraldine imine and amine, nitrogens are in equal numbers, which gives, on the average, 0.5 H per N. EB and the protonating agent were then transferred to m-cresol to give a suspension of 0.5 wt % (calculated with respect to EB). The suspension was then stirred typically for 1 week. During this time, its ultraviolet–visible—near-infrared (UV–vis—NIR) spectrum was periodically registered. The reaction was stopped when two consecutive registrations gave the same spectra. Then, the suspension was centrifuged at 5000 rpm for 15 min. The following two fractions of protonated PANI were separated upon centrifugation: the fraction that sedimented and the one that remained in m-cresol. Only nonsedimented fraction was used for the preparation of PANI–PMMA blends. The concentration of nonsedimented PANI in m-cresol was determined by measuring the difference between the initial EB mass taken for the protonation and the mass of sedimented PANI after its deprotonation. It turned out that in the case of the protonation with CSA, 94% of initial PANI does not sediment upon the centrifugation. In the case of the protonation with PPP, PHP, and PNP, these values are 22, 22, and 44%, respectively. Whether the obtained solutions are real or colloidal solutions is still the matter of a scientific debate.[16] Nevertheless, they can be con-

veniently used in the solution processing of PANI. It should be noted here that the amount of non-sedimented fraction strongly depends on the amount of water in EB, the protonating acid, and the solvent. The amount of this fraction quickly decreases with the increase of water content. For this reason, careful drying of all components is recommended.

Preparation of PANI–PMMA Blends

Three series of blends were prepared with 0, 25, and 35 wt % of plasticizer (DBPh). First, 10 wt % solutions of PMMA in *m*-cresol were prepared (with or without the plasticizer). Then, these solutions were mixed with appropriate amounts of *m*-cresol solutions of protonated PANI and additionally stirred for 2 h. From this homogeneous, by eye solution, freestanding films were cast by slow evaporation of *m*-cresol at 40°C. Typical thickness of the samples was between 60 and 100 μm.

Deprotonation Studies

The prepared blends were kept in a large excess of pH = 9 buffer solution (Carlo Erba; boric acid, potassium chloride, and sodium hydroxide), and their UV–vis—NIR spectra were periodically registered. For parallel samples kept in the same buffer solution, direct current (DC) conductivity was measured for increasing exposure time to the basic medium.

Measurements

UV–vis—NIR absorption spectra of solutions and films were measured on a Lambda 900 Perkin–Elmer spectrometer. For the solution, spectra quartz infrasil cells of 1-mm optical path were used.

DC conductivity of the blends was measured under room conditions using a four-probe technique with parallel gold contacts. The ohmic behavior was checked in each case.

RESULTS AND DISCUSSION

Electrical transport properties of protonated PANI films, among other factors, depend strongly on the protonating agent and the processing medium. There exist dopant/solvent couples, which favor high conductivity of PANI films obtained by casting, such as, for example, CSA–*m*-cresol[1] and CSA–hexafluoro-2-propanol.[17] In the case of a three-components system PANI–dopant–*m*-cresol, it is possible to predict electrical transport properties of the processed films by the investigation of UV–vis—NIR spectra of the solution used for casting.[18] If due to specific solvent–dopant interactions,[19,20] a conformation favoring the delocalization of charge carriers (polarons) is achieved, the spectrum shows one localized peak at 440 nm and a monotonically increasing absorption, which starts at approximately 500 nm and extends into NIR. Chain conformation, leading to localized polarons, gives rise to three well-defined absorption peaks at 360, 430, and approximately 900 nm. Of course, upon casting, better conductors are obtained in the former case. In Figure 1, the spectra of PANI protonated with poly(alkylene phosphates) (PAPs) and with CSA are presented. It is clear that the desired conformation is achieved for CSA and PNP-protonated PANI. Protonation with PPP and PHP results in a small contribution of the peaks due to localized polarons, which are superimposed on the increasing NIR absorption. The removal of the solvent worsens the spectra, which is manifested by more pronounced contribution of the localized polarons peaks in the spectra of free standing film of PANI–PMMA blends (compare Figs. 1 and 2). Nevertheless, similarly as previously studied CSA, PAPs seem to be very good protonating agents, suitable for the preparation of highly conductive blends.

In Table I, the results of electrical conductivity measurements of PANI(PAP)$_{0.5}$–PMMA blends are collected. At this point, the role of the plasticizer (DBPh) in the improvement of the electrical properties of the blends should be underlined. For nonplasticized samples, the percolation threshold is well above 4 wt %, and none of the prepared samples was conductive. The addition of 25 wt % of DBPh efficiently lowers the percolation threshold, which is now < 4 wt % for PANI(PPP)$_{0.5}$–PMMA, < 2 wt % for PANI(PHP)$_{0.5}$–PMMA, and < 1 wt % for PANI(PNP)$_{0.5}$–PMMA. A similar effect of the plasticizer was observed for PANI–cellulose acetate blends.[8]

Even lower percolation thresholds are obtained for PANI(CSA)$_{0.5}$–PMMA blends. In Figure 3, the conductivity of the blend versus the PANI content is plotted for different contents of the plasticizer. From the inset of Figure 3, which presents the data obtained for PANI contents below 0.3 wt %, it is clear that the addition of the plasticizer has two effects. First, for a given content of PANI, it causes approximately a two–three-fold increase in the conductivity of the blend. Second, it efficiently lowers the percolation threshold.

Figure 1 UV–vis—NIR spectra of polyaniline protonated with poly(alkylene phosphates) and camphor sulphonic acid registered for m-cresol solutions: (a) PANI(PPP)$_{0.5}$; (b) PANI(PHP)$_{0.5}$; (c) PANI(PNP)$_{0.5}$; (d) PANI(CSA)$_{0.5}$.

In order to determine the percolation threshold more precisely, we have fitted the data presented in Figure 3 to the scaling law of percolation theory,[21] as follows:

$$\sigma(f) = c(f - f_p)^t \qquad (1)$$

where c is a constant, t is the critical exponent, f is the volume fraction of the conductive phase, and f_p is the volume fraction at the percolation threshold.

In our calculations, for practical reasons, we have used the mass fraction instead of the volume

a) **PANI(PPP)$_{0.5}$/PMMA/DBPh film**
4 wt % PANI-EB, 25 wt % DBPh

b) **PANI(PHP)$_{0.5}$/PMMA/DBPh film**
4 wt % PANI-EB, 25 wt % DBPh

c) **PANI(PNP)$_{0.5}$/PMMA/DBPh film**
4 wt % PANI, 25 wt % DBPh

d) **PANI(CSA)$_{0.5}$/PMMA/DBPh film**
1 wt % PANI-EB, 25 wt % DBPh

Figure 2 UV–vis—NIR spectra of free standing films of polyaniline–poly(methyl methacrylate) blends: (a) PANI(PPP)$_{0.5}$–PMMA; (b) PANI(PHP)$_{0.5}$–PMMA; (c) PANI(PNP)$_{0.5}$–PMMA; (d) PANI(CSA)$_{0.5}$–PMMA.

fraction. Since the densities of all components of the blend are very close, this change is of minimal significance. Also, for comparative reasons, we expressed the PANI content as EB wt % to make it independent of the mass of the dopant, which varies depending on its type. In all three series of studies (0, 25, and 35 wt % of the plasticizer), we get an excellent fit to the scaling law of percola-

Table I   Conductivities of Nonplasticized and DBPh Plasticized Blends of Poly(alkylene phosphate)-Doped Polyaniline with Poly(methyl methacrylate), Expressed in S/cm

	% PANI Base			
Dopant	4 Wt %	2 Wt %	1 Wt %	% DBPh
PPP	$9.0 * 10^{-8}$	$5.7 * 10^{-9}$	$1.3 * 10^{-9}$	0 wt %
PHP	$2.4 * 10^{-7}$	$1.7 * 10^{-7}$	$6.7 * 10^{-8}$	0 wt %
PNP	$2.8 * 10^{-7}$	$3.6 * 10^{-8}$	$1.0 * 10^{-8}$	0 wt %
PPP	$2.8 * 10^{-4}$	$9.9 * 10^{-7}$	$3.0 * 10^{-8}$	25 wt %
PHP	$1.1 * 10^{-2}$	$1.0 * 10^{-3}$	$4.1 * 10^{-8}$	25 wt %
PNP	$6.7 * 10^{-2}$	$2.6 * 10^{-2}$	$3.5 * 10^{-3}$	25 wt %

tion. The calculated parameters of eq. (1) are listed in Table II. For nonplasticized samples, we get the critical exponent = 1.6, which is slightly higher than reported in Reghu et al.[12] for the same blend. These authors give the value of 1.33, which is smaller than the value predicted by the universal law (t = 2.0) and attribute it to thermally induced hopping between disconnected (or weakly connected) part of the percolating network. Upon lowering of the temperature, t approaches the theoretical value. Our f_p value is also lower than reported in Reghu et al.[12] It should be noted that in Reghu et al.,[12] the f_p is expressed as $PANI(CSA)_{0.5}$ wt % fraction. For correct comparison, it should be expressed as EB wt % fraction, as in our article. The recalculation gives f_p = 0.13 for the blend studied in Reghu et al.[12] and 0.054 in our nonplasticized samples.

The addition of the plasticizer does not only lower the f_p value but also increases the value of t. For 35 wt % of DBPh, the percolation threshold is as low as 0.041, and the t value reaches, within the experimental error, the universal value predicted by the percolation theory. The interpretation of the variation of these two parameters is very difficult unless clearly resolved transmission electron microscopy (TEM) micrographs are available. However, one is tempted to propose the following interpretation. The increase of the t value from 1.6 to 2 upon addition of the plasticizer can be treated as a manifestation of the increasing ramification of the conducting network; t = 2 corresponds to the exponent obtained for the incipient percolation cluster, whereas t = 1 is obtained for the effective medium approximation; the decrease of f_p indicates that an infinite cluster

Figure 3   Conductivity versus PANI content in PANI-$(CSA)_{0.5}$–PMMA blends containing varying amounts of DBPh plasticizer. The inset shows, in detail, the results for PANI content < 0.3 wt %.

Table II   Scaling Law Parameters Calculated for PANI(CSA)$_{0.5}$–PMMA Blends Containing Different Amounts of DBPh Plasticizer

Amount	p_c	t	R (Correlation Coefficient)
0 wt % DBPh	0.054 ± 0.005	1.6 ± 0.2	0.997
25 wt % DBPh	0.046 ± 0.001	1.9 ± 0.1	0.996
35 wt % DBPh	0.041 ± 0.001	2.0 ± 0.1	0.997

PANI(PHP)$_{0.5}$/PMMA/DBPh - pH=9.

Figure 4 Evolution of the UV–vis—NIR spectrum of PANI(PHP)$_{0.5}$–PMMA blend upon exposure to a pH = 9 buffer solution (plasticizer content 25 wt %).

spans over the entire sample for even lower PANI contents. Based on the above arguments, it may be postulated that the plasticizer plays the role of an interphase builder (compatibilizer). Morphological studies of the PANI–PMMA–plasticizer system are not totally conclusive at the present time; however, TEM observations of a similar system of PANI–cellulose acetate–plasticizer unequivocally show ramified morphology.[22]

The weakest point of conductive polyaniline is its tendency to deprotonate. Since only the protonated form of PANI is conductive, its deprotonation results in a significant conductivity drop. Polyaniline used in the fabrication of blends should therefore exhibit improved resistance against deprotonation because these materials are sometimes exposed to basic media. The idea of the use of macromolecular dopants (polyalkylene phosphates) for the improvement of PANI resistance against deprotonation was based on the assumption that this reaction may be inhibited due to kinetic reasons. Since the deprotonation product is polymeric (polyalkylene phosphate in a form of a salt), it cannot easily diffuse out from the PANI matrix, and, for this reason, the deprotonation process can be slowed down.

For the studies of the deprotonation reaction of PANI in four types of blends prepared in this

research, we have used UV–vis—NIR spectroscopy and conductivity measurements. Blends containing 4 wt % of PANI were kept in a large excess of a buffer solution of pH = 9, and their spectra and conductivity were periodically measured. In Figure 4, the evolution of the spectrum for PANI(PHP)$_{0.5}$–PMMA blend, with increasing time of the exposure to the solution of pH = 9, is presented. The spectrum significantly changes, even for very short exposure times. Initially, the intensity of the broad absorption tail, associated with the presence of delocalized polarons, quickly decreases; and the peak at approximately 800–850 nm due to localized polarons becomes more pronounced. For longer exposure times, a new peak, characteristic of the totally deprotonated PANI–emeraldine base, appears at 630 nm. Such evolution implies strong heterogeneity of the deprotonation process with zones of localized and delocalized polarons coexisting with zones of totally deprotonated PANI (i.e., emeraldine base). For two other macromolecular dopants, PPP and PNP, the behavior is qualitatively the same. However, as judged from the evolution of the spectra, the deprotonation rate decreases in the following order: PPP > PHP > PNP.

The above results are confirmed by the conductivity measurements. In Figures 5 and 6, the normalized conductivity σ/σ_0 (where σ_0 is the conductivity for the time of exposure = 0) is plotted versus

Figure 5 Evolution of the electrical conductivity of PANI–PMMA blends upon exposure to a pH = 9 buffer solution for short exposure times (plasticizer content 25 wt %).

Figure 6 Evolution of electrical conductivity of PANI–PMMA blends upon exposure to a pH = 9 buffer solution for long exposure times (plasticizer content 25 wt %).

the time of exposure. From the evolution of the conductivity, it is clear that $PANI(PPP)_{0.5}$ and $PANI(PHP)_{0.5}$ deprotonate quicker than PANI $(PNP)_{0.5}$ and $PANI(CSA)_{0.5}$. Up to 24 h of exposure to the buffer solution of pH = 9 PANI $(PNP)_{0.5}$ and $PANI(CSA)_{0.5}$ deprotonate with a similar rate, then the deprotonation of PANI $(PNP)_{0.5}$ is more accelerated (compare Figures 5 and 6). Evidently, $PANI(CSA)_{0.5}$ is the most resistant against deprotonation and shows a relatively small conductivity drop, even after 10 days of exposure to solutions of pH = 9.

For three dopants of the macromolecular nature, PPP, PHP, and PNP, one can notice that the deprotonation rate measured by the decrease of the conductivity depends on the length of the hydrophobic spacer between the phosphate hydrophilic groups. In agreement with spectroscopic studies, the deprotonation rate decreases in the following order: PPP > PHP > PNP. Thus, the deprotonation rate can be correlated with the hydrophobicity of poly(alkylene phosphate) anion created upon the protonation of PANI. In the polyanion originating from PNP, the contribution of the hydrophobic segments is larger than in the case of the polyanion originating from PHP, which, in turn, is more hydrophobic than the polyanion formed from PPP. Thus, more hydrophobic dopant anions prevent more efficiently polyaniline matrix from the penetration of aque-

ous deprotonation solution, and the deprotonation reaction is slowed down. A similar effect of the length of hydrophobic spacer on the ability to absorb water or aqueous solutions is well known for polyamides of the following formula:

$$-[CO-NH-(CH_2)_n]-_x$$

In this case, the maximum amount of absorbed water decreases with increasing n. The analogy with polyaniline doped with poly(alkylene phosphates) is evident in this case.

As demonstrated in this research, the macromolecular nature of the dopant does not prevent polyaniline from deprotonation. Since, in the case of poly(alkylene phosphate)-protonated polyaniline, the deprotonation must create polyalkylene phosphate salt, which is of limited mobility due to its macromolecular nature, the deprotonation must proceed via microphase separation. This microphase separation is indirectly confirmed by UV–vis—NIR spectra, which indicate the coexistence of the zones of undoped PANI together with two types of zones of protonated PANI. Thus, a dopant that improves PANI stability against deprotonation does not need to be of polymeric type; but, in addition to strong Bronsted acid centers, it should possess hydrophobic groups built, which assure sufficient hydrophobicity of the doped PANI.

At the end, it should be noted that the Brönsted acidity of the dopant molecule also plays an important role in PANI resistance against the deprotonation. $PANI(CSA)_{0.5}$ deprotonates much slower at pH = 9 than $PANI(PNP)_{0.5}$ does, despite the fact that PNP is more hydrophobic than CSA. However, CSA is a stronger Brönsted acid than PNP and, for this reason, forms stronger adduct with the polymer.

CONCLUSIONS

To summarize, we have prepared polyaniline–poly(methyl methacrylate) blends using four different PANI protonating agents. In all cases, we have demonstrated that the addition of a plasticizer–dibutyl phtalate (DBPh) improves the conductivity of the blend and lowers the percolation threshold. For $PANI(CSA)_{0.5}$–PMMA blends containing 35 wt % of DBPh, we obtained the percolation threshold as low as 0.041 wt %. In addition, the deprotonation reaction at pH = 9, responsible

for the conductivity drop, is extremely slow in this material.

In the case of the use of macromolecular PANI dopants of the poly(alkylene phosphate) type, we observe a clear correlation between the length of the hydrophobic spacer, the value of the percolation threshold, and the resistance against deprotonation. With increasing length of the alkylene spacer, the value of the percolation threshold decreases, and the resistance against deprotonation increases.

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