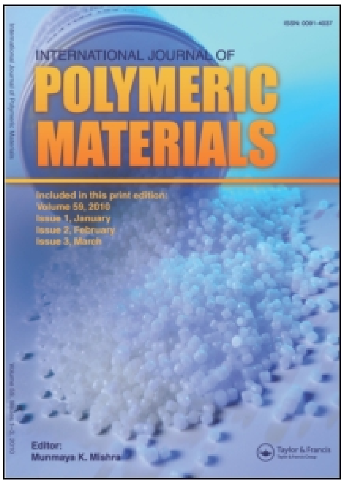

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Electroactive Polymer Blends Prepared *In Situ* Via Bulk Polymerization of Aniline in the Presence of Polyethylene*

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Electroactive polymer blends of high density polyethylene and polyaniline as the conductive constituent are prepared for the first time in situ by oxidative bulk-polymerization of aniline in the presence of polyethylene and dodecylbenzenesulfonic acid. The blends reveal substantially higher electrical conductivity as compared to the data found in literature for analogous blends obtained previously by casting solutions or by melt extrusion of polyethylene and preliminary prepared polyaniline. The conductive constituent does not deteriorate the melt-processing performance of the matrix polymer and the blends are processable without losing conductivity.

Keywords: Polymer blends; Polyaniline; Polyethylene; Bulk-polymerization; Electrical conductivity

INTRODUCTION

Polyaniline (PANI) is an intrinsically conducting polymer which offers very promising opportunities for industrial applications due to its unique electrical, optical and electrooptical properties and its stability [1–3]. One of the key problems related to the potential application of PANI, however, is its poor processability. The most promising

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* Dedicated to Professor Stoiko Fakirov on the occasion of his 65th birthday.

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approach to the solution of this problem is the preparation of PANI blends with processable thermoplastic polymers.

Two basic approaches to the preparation of PANI containing polymer blends can be distinguished.

In the first one, blends have been prepared *in situ* by polymerizing aniline (ANI) in the presence of another polymer [4–17]. In this case either the monomer has been diffused into the matrix polymer and then polymerized in aqueous or organic medium [4, 5], or aniline has been polymerized in the presence of a water-soluble matrix polymer in aqueous (or aqueous-organic) medium, resulting in aqueous colloidal dispersion, the blend being isolated wherefrom [6–13]. In the last direction were also aimed our previous investigations [14–17].

The second approach to PANI blends consists in dispersing *preliminary prepared* PANI in a solution or in a melt of another polymer. Such an approach was described by Wessling [18, 19], Banergee and Mandal [20], Angelopoulos *et al.* [21]. The increasing application of this approach, however, is related, first of all, to the successful results of Cao *et al.* [22–24] suggesting the use of the so called functionalized protonic acids in protonation of preliminary prepared deprotonated PANI. The complex obtained by mixing those acids (mainly dodecylbenzenesulfonic acid, DBSA, and camphorsulfonic acid) with deprotonated PANI, is "soluble" (the precise term should be dispersible) in common solvents, such as toluene, xylene, decalin *etc.*, and makes PANI "compatible" with polymers soluble in this solvents [19–27]. The complex can also be dispersed in the melt of polymers [28–32]. We have reported recently a novel route which consists in simple mechanical mixing of a colloidal aqueous PANI dispersion synthesized by polymerizing ANI in the presence of DBSA with a solution of a host polymer [33].

It has to be noted that in all the studies on PANI up to date the polymer has been prepared by oxidative polymerization (chemical or electrochemical) of ANI in a solvent (mostly aqueous) medium. The only exception was reported by Klavetter [34] who suggested a solvent-free preparation of PANI by chemical oxidative bulk-polymerization of ANI in the presence of DBSA and dibenzoyl peroxide as the oxidant. This work, however, has not been aimed in preparation of PANI blends.

Now, we will report on *in situ* preparation of electroactive PANI blends by oxidative *bulk* polymerization of aniline in the presence of high density polyethylene (PE). The bulk-polymerization method eliminates many of the production steps required in the other polymerization techniques.

EXPERIMENTAL

The composites were prepared *in situ* by adding equimolar amounts of DBSA (Tokyo Kasei), ANI and ammonium peroxydisulfate (both Fluka) into powdered PE (“Neftohim”, Bulgaria), followed by bulk polymerization of ANI at room temperature for 4 hr. with subsequent drying in vacuum at 50°C.

For the sake of comparison, PANI/PE blends were also prepared by dry-blending PE with PANI-DBSA complex preliminary synthesized according to the procedure described previously [33].

Powdered composites were processed in a melt index apparatus (Priborstroi, Russia) at 140°C, 5 kg. The processing temperature was chosen to be ca. 10°C higher than the melting peak of PE (129,3°C) and also several degrees higher than the end of PE melting (132°C) measured on Perkin Elmer DSC 7 differential scanning calorimeter in an argon atmosphere at heating rate of 10°C/min. The strands obtained were cooled to ambient temperature in air and then compressed at 60°C, 12000 kg/cm^2 into pellets, the electrical conductivity, σ, of which was measured by conventional four-probe technique.

RESULTS AND DISCUSSION

As is evident from Figure 1, PANI/PE blends prepared *in situ* by polymerizing ANI in bulk in the presence of DBSA (curve 1) revealed substantially higher conductivity as compared to the data found in literature for PANI/PE blends obtained by casting “solutions” (curve 3 [22]) or by melt extrusion (curves 2 [31] and 5 [32]). Electrical conductivity of the blends prepared in this work by dry blending PE with preliminary synthesized PANI.DBSA complex (Fig. 1, curve 4)

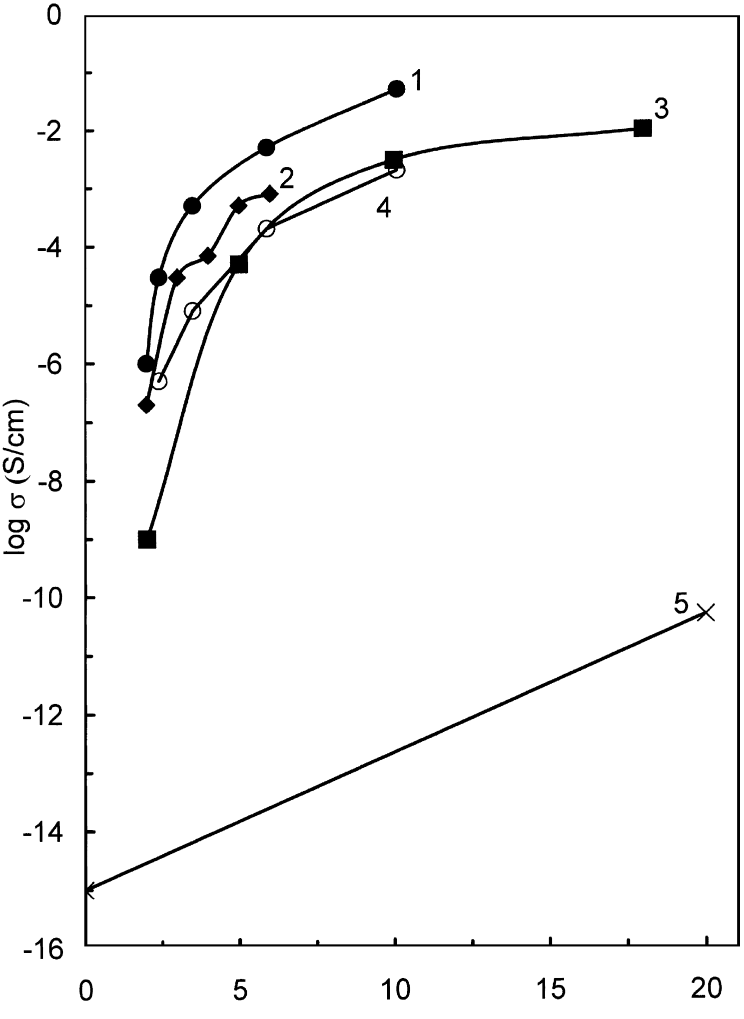

FIGURE 1 Electrical conductivity, σ, *vs*. content of PANI-complex in polyblends with polyethylene: 1(●): *in situ* prepared blends by polymerizing aniline in bulk in the presence of PE and DBSA according to the present work; 2(◆): blends obtained by melt extrusion of PE, PANI doped with bis(2-ethylhexyl hydrogen phosphate), and lauryl gallate [31]; 3(■): blends obtained by casting "solution" of PE and PANI doped with DBSA [22]; 4(○): blends obtained in this work by dry-blending PE with preliminary prepared PANI.DBSA complex; 5(X): blends obtained by melt extrusion of PE and PANI doped with p-toluenesulfonic acid [32].

was also measured to be at least one order of magnitude lower as compared to *in situ* prepared blends (Fig. 1, curve 1).

The lowest percolation threshold for PANI/PE blends prepared previously has been found to be below ca. 3 mass% of PANI complex in melt processed PE blends containing PANI doped with phosphoric acid esters as an electroactive constituent and gallic acid esters as compatibilizers [31]. For bulk-polymerized blends in the present work the percolation threshold appeared to be lower than ca. 2 mass% of PANI complex.

As suggested by Cao *et al.* [22], the morphology of blends obtained by using PANI complexes with functionalized protonic acids as conductive constituent must be bi-continuous, perhaps analogous to an interpenetrating network. Presumably, in bulk-polymerized blends the conductive pathways in the phase-separated continuous conductive PANI network should be more perfect (ordered), as compared to solution or melt blending, since they have been formed by polymerizing small monomer (aniline) molecules in the PE matrix rather, than by interpenetrating of PANI and PE chains. This has to result in lower percolation threshold and higher conductivity of PANI/PE blends obtained. Unfortunately, we were not able to measure directly electrical conductivity of compressed pellets of the nascent powdery blends without thermal treatment since the pellets were too brittle. That is why we have measured conductivity of samples thermally treated in the melt-index-apparatus as described above.

It can be suggested that PANI/PE blends prepared by bulk-polymerization of ANI exhibit a “memory” in respect to the conductive pathways after melting of PE at relatively low temperature (140°C) and resolidification upon cooling to ambient temperature. Thus, they revealed lower percolation threshold and higher conductivity as compared to solution or melt blending (Fig. 1). Moreover, they possess remarkable stability of electrical conductivity upon thermal treatment under the processing conditions. Upon second and third heating cycle in the melt-index-apparatus the conductivity did not decrease, but even increased substantially for some of the blends (Tab. I). Thus, σ of the blend containing 3.5 mass.% of PANI complex enhanced from 5.10^{-4} S/cm after the first treatment up to 5.10^{-3} S/cm after the third cycle of thermal treatment, *i.e.*, by one order of

TABLE I Melt index and electrical conductivity of bulk prepared PANI/PE blends

	PANI.DBSA		*Conductivity*		
Sample no.	*Complex in the blends, mass%*	*Melt index (140°C, 5 kg), g/10 min*	*After first heating cycle, S/cm*	*After second heating cycle, S/cm*	*After third heating cycle, S/cm*
1	0.0	1.7	–	–	–
2	2.0	2.1	10^{-6}	10^{-6}	10^{-6}
3	2.4	2.2	3.10^{-5}	4.10^{-5}	3.10^{-5}
4	3.5	2.3	5.10^{-4}	9.10^{-4}	5.10^{-3}
5	5.9	2.5	5.10^{-3}	7.10^{-3}	6.10^{-3}
6	10.1	2.8	5.10^{-2}	4.10^{-2}	5.10^{-2}

magnitude. Perhaps, in the case at hand the conducting network became more perfect as a result of microphase separation of the constituents [35], the system being revealed a "memory" upon each following processing cycle.

Therefore, it can be stated that PANI/PE blends prepared in bulk are processable without losing conductivity, which appeared to be one of the main drawbacks of previously *in situ* prepared blends [36]. Moreover, the processing performance of PE did not decay in the presence of non-fusible conductive constituent, as inferred from the melt-index values increasing from 1.7 g/10 min. for the net PE up to 2.8 g/10 min. for the blend containing 10.1 mass.% PANI complex (Tab. I). This is obviously due to the plasticizing effect of DBSA, which is acting also as a compatibilizer [32] improving the PE-PANI interactions.

After completion of this work, a publication [37] appeared dealing with polymer blends of PANI protonated with camphorsulfonic acid (CSA) and ultra high molecular weight PE prepared by using the "solution" method from an m-cresol/decaline mixture. According to the authors, besides the solubilization of the two polymers, the solvent mixture also promotes specific interactions that lead to improvement in solubility and conductivity of the blend. The authors claimed that the conductivity achieved ($\sigma \approx 5.10^{-6}$ S/cm and 7.10^{-3} S/cm for blends containing 1% and 5% of PANI, respectively) has been well above those reported by Cao *et al.* [22] and presented in Figure 1 above. Unfortunately, it is not clear whether the percentages reported in [37] are relevant to the net PANI or to the PANI. CSA complex. But obviously, σ of the bulk-prepared PANI/PE blends reported in the present work (Fig. 1, curve 1) are at least close (in case the PANI content in [37] refers to PANI.CSA complex) or even substantially higher (if the net PANI content has been referred in [37]), as compared to the polymer blends prepared from the mixed solvent.

In conclusion, it can be stated that electroactive PANI/PE blends of fairly high electrical conductivity can be prepared in situ by oxidative bulk-polymerization of aniline in the presence of polyethylene. The conductive constituent did not deteriorate the processing performance of the matrix polymer and the blends are processable without losing conductivity.

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