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Electrically conductive polymer blends comprising polyaniline

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SUMMARY

Electroactive polymer blends comprising polyaniline (PANI) as conductive constituent and poly(methyl methacrylate) (PMMA), polystyrene (PS) and methyl methacrylate-butadiene-styrene (MBS) copolymer as a thermoplastic constituent (TC) were prepared by using various techniques: *in situ* by oxidative polymerization of aniline in aqueous dispersions of the TC; by coagulating of latex of TC in the acidic dispersions wherein PANI has been preliminary obtained; and by dry blending. It was shown that highest conductivity values revealed *in situ* prepared PANI/PMMA blends, where the intermolecular interactions between the constituents were suggested to be stronger than in the other systems studied.

INTRODUCTION

Inherent problem with intrinsically conductive polymers like polyacetylene, polypyrrole and polyaniline (PANI), is the inability to process them by conventional techniques. An useful approach to the production of processable materials consists in the combination of a thermoplastic polymer (TP) with a conductive polymer such as PANI.

It is known (1, 2) that polymerization of a monomer in polymer matrix is a promising route to the preparation of new materials *in situ*. Electrically conductive polymer blends have been prepared *in situ* by chemical or electrochemical oxidation of aniline in films of TP: poly(vinyl chloride) (3), polyolefins (4), poly(methyl methacrylate), poly(acrylic acid) (5).

A new procedure for processing of powdered conductive polymer blends of intrinsically conductive polymer (polyacetylene, polypyrrole, PANI) and various insulating TP by extrusion or pressing was patented by Zipperling-Kessler (Germany) (6). Melt processed blends (melt of TP) showed a percolation threshold at ca. 10% PANI. Conductivity of neat (100 %) PANI was reached at ca. 50% PANI in the blend (7).

As far as the authors are aware, there are no data in the literature about the *in situ* preparation of electrically conductive polymer blends by chemical oxidation of aniline in aqueous dispersions of TP like poly(methyl methacrylate) (PMMA), polystyrene (PS) and methyl methacrylate-butadiene-styrene (MBS) copolymers.

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EXPERIMENTAL

Aqueous latexes of insulating TP (PMMA, PS, MBS copolymer of composition in mass %: methyl methacrylate-25, butadiene-39 and styrene-36) were obtained by free radical emulsion polymerization using potassium peroxidisulphate as initiator, under argon, at 65°C, as described previously (8,9). After addition of aniline and aqueous HCl to the latex, an oxidation of aniline by using of ammonium peroxidisulphate was carried out at 5°C for 48 h. *In situ* prepared polymer blends were filtered, washed and dried at 60°C under vacuum.

For comparison were prepared:

- dry blends of powdered PANI and TP; powdered PANI was obtained by oxidative polymerization of aniline in 1M HCl at 5°C using ammonium peroxidisulphate as an oxidant (10), followed by filtering, washing and drying; powdered TP (PMMA, PS, MBS) was obtained by coagulating of the corresponding latex by electorlyte with subsequent filtering, washing and drying (8, 9).
- blends obtained by coagulating of TP latex in the acidic suspension wherein PANI has been preliminary prepared by oxidative polymerization of aniline followed by filtering, washing and drying (this method will be hereafter reffered to as "coagulation").

All samples were pressed at 140°C and 0,7 GPa in pellets of thickness 0,5 mm. Electrical resistance of the compressed pellets was measured by the four probe technique. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer 2C; glass transition temperature, T_g, was determined as the mid-point of the transition range.

RESULTS AND DISCUSSION

Dependence of conductivity,σ, of blends comprising PANI and PMMA, PS or MBS vs. composition is shown on Fig.1, a-c. Blends of reasonably high σ (ca.10^{-6} S/cm) were prepared using the three methods at relatively low concentration of PANI (ca.10 mass.%) , the percolation threshold obviously being lower than 10%. On increasing concentration of the conductive constituent up to 30-40 mass.%, σ close to that of the conductive constituent itself (i.e. 100% PANI) were achieved. Polymer blends of the same composition prepared *in situ*, by dry blending or by coagulation revealed conductivities nearly of the same order of magnitude.

However, *in situ* prepared blends comprising lower than 85 mass.% PMMA as a thermoplastic constituent, revealed higher conductivity compared to dry blends and blend obtained by coagulation. Besides, in the whole range of constituents ratios studied, *in situ* prepared blends PANI/PMMA revealed higher conductivity compared to the blends of nearly the same content of the conductive constituent, but comprising PS and MBS.

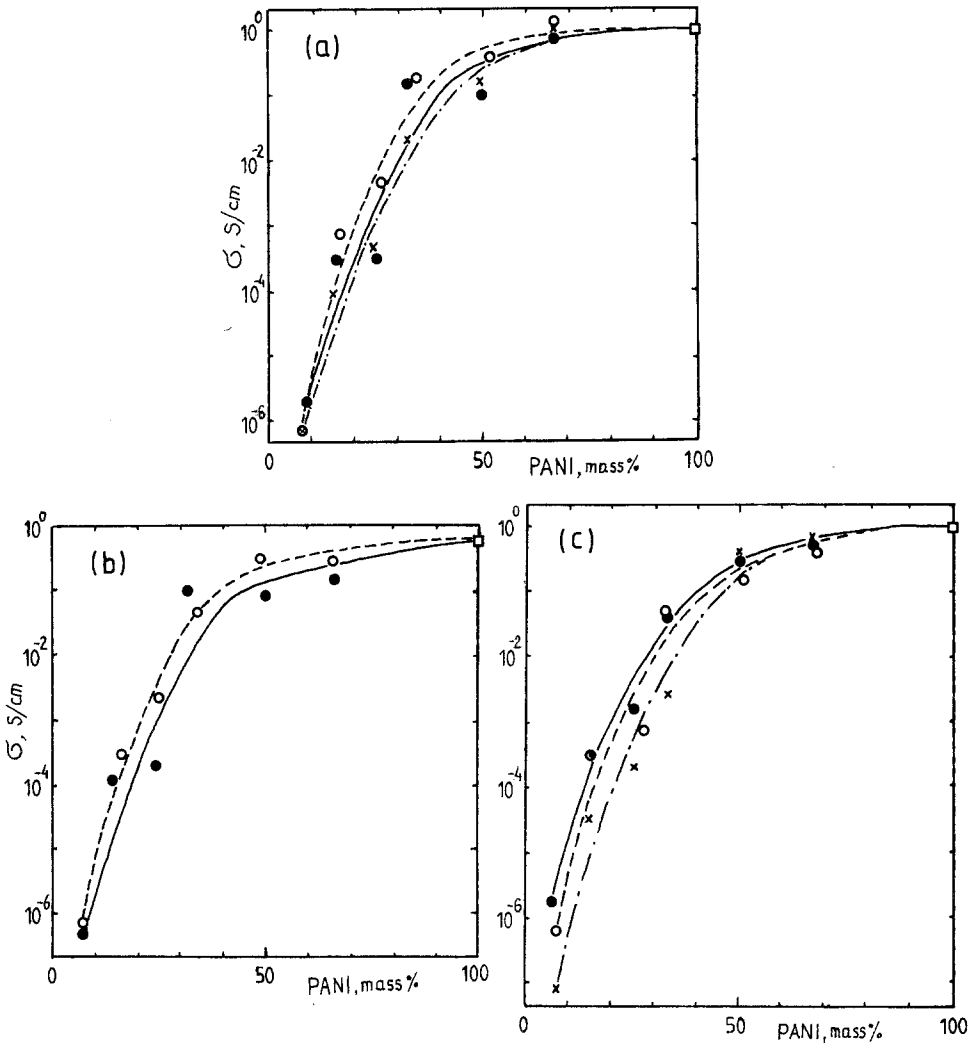

Fig. 1. Electrical conductivity vs. composition of polymer blends comprising PANI and PMMA (a), PS (b) or MBS copolymer (c).

o -blends prepared *in situ* by oxidative polymerization of aniline in aqueous dispersions of the thermoplastic polymer; (--------)

● -dry blends (————)

x -blends prepared by coagulating the latex of the thermoplastic polymer in the acidic dispersion wherein PANI has been preliminary obtained (—·—·—·)

TABLE 1. Glass transition temperature of PMMA, PS and their blends with PANI in mass ratio 1:1

Polymers and their blends	T_g,°C	ΔT_g,°C
PMMA	99,8	-
PANI/PMMA - *in situ*	117,0	17,2
PANI/PMMA -dry blend	108,7	8,9
PANI/PMMA - coagulation	113,0	13,2
PS	100,0	-
PANI/PS - *in situ*	105,5	5,5
PANI/PS - dry blend	102,9	2,2
PANI/PS - coagulation	100,0	0,0

These facts showed that the conductive constituent was dispersed better in the polymer blends PANI/PMMA prepared *in situ* than in the corresponding blends obtained by coagulation or dry blending, and all kind of blends comprising PS and MBS.

It is known (6) that intrinsically conductive polymers like polyacetylene, polyaniline and polypyrrole could form more homogeneous blends with thermoplastic polymers which solubility parameter, δ, is higher than 8,6 $(cal/cm^3)^{1/2}$. Taking into account that δ value of PMMA, PS and polybutadiene is 9,3, 8,8 and 8,4 $(cal/cm^3)^{1/2}$, respectively (11), it could be supposed that compatibility of PANI with PMMA should be better compared to that with PS and MBS.

Compatibility of a pair of polymers or more precisely the presence of specific interactions between their macromolecules, could be estimated by the changes in the glass transition temperature, T_g, of the two constituents in the blends. DSC data on T_g of PMMA, PS and their blends with PANI (in ratio 1:1) prepared *in situ*, by coagulation or by dry blending are presented in Table 1. As seen, the shift of T_g

$$\Delta T_g = T_g^{blend} - T_g^{PMMA(PS)}$$

toward higher values is substantially larger in the blends PANI/PMMA, compared to the blends PANI/PS. Besides, ΔT_g of the *in situ* blends PANI/PMMA is considerably larger compared to the blends, prepared by coagulation or by dry

blending of the constituents.

These results showed that the interaction between the macromolecules of PANI and PMMA in their blends, particularly those prepared *in situ*, are stronger than in blends PANI/PS, thus resulting in a better compatibility and higher electrical conductivity, respectively. This is most pronounced in the blends prepared *in situ*.

However, it could be supposed that, beside the influence of the intermolecular interactions, the increase of T_g of PMMA constituent could be presumably affected also by chemical interactions between the constituents. This supposition, however, was not confirmed by the extraction results of PANI/PMMA blends prepared *in situ*; PMMA was completely extracted from the blends.

In conclusion it could be stated that electroactive polymer blends comprising PANI could be prepared without preliminary isolation of the thermoplastic constituent (PMMA, PS, MBS) from the latex, both *in situ* by oxidative polymerization of aniline or by coagulating the latex in the acidic dispersion wherein PANI has been previously obtained. Among the polymer blends studied, the highest electrical conductivity values revealed *in situ* prepared PANI/PMMA blends where the intermolecular interactions between the constituents are stronger or compatibility is better than in the other systems studied.

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