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A new route to polyaniline composites

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A novel route to preparation of polyaniline (PANI) composites based on mixing of a solution of host polymer with preliminarily formed colloidal PANI dispersion of very fine particles (lower limit *ca* 5 nm) is reported. This colloidal PANI dispersion was formed by oxidative polymerization of aniline (ANI) in the presence of dodecylbenzenesulfonic acid in aqueous medium, and can be dried and redispersed in an organic solvent, enabling composites of PANI with water-soluble and water-insoluble polymers to be prepared. Besides its simplicity, this route reveals the possibility of easily controlling the design of composites (particle size and particle size distribution). The polymer composites PANI–poly(vinyl alcohol), thus prepared, combined high electrical conductivity (up to 2–3 $\mathrm{S\,cm^{-1}}$) and transparency (between 20 and 50% at film thickness 50 μm) even in a non-oriented state. © 1997 Elsevier Science Ltd. All rights reserved.

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Introduction

Polyaniline (PANI) has attracted considerable attention because of its unique electrical, optical and electrooptical properties and its numerous potential applications[1].

One of the key problems related to the potential application of PANI is its processability. The most promising approach to the solution of this problem is the preparation of PANI composites with processable thermoplastic polymers. Moreover, the application range of these composites depends mainly on their design. Particularly, the design of composite materials of a mixture of conducting and insulating phases in the nanometre range has flourished in the past few years[2].

Two basic approaches to the preparation of PANI-containing composites can be distinguished. In the first one, composites have been prepared by polymerizing aniline (ANI) in the presence of another polymer[3–16]. In the second approach, composites have been obtained by 'dissolving' PANI in solution or in a melt of another polymer[18–24]. Two basic methods can be distinguished in the first approach. In the first method ANI in the gaseous state was polymerized in a polymer film swollen by water[3], or a polymer film was preliminarily swollen in ANI, which was polymerized thereafter[4].

From a technological point of view the second method is more convenient and consists of polymerizing ANI in the presence of a water-soluble polymer in aqueous or aqueous-organic media[5–16]. In this direction were aimed our previous investigations. We first succeeded in preparing stable aqueous colloidal dispersions of PANI using poly(vinyl alcohol) (PVAL) as a steric stabilizer[11–14]. It is not yet clear how to regulate the shape and the size of particles in such colloidal dispersions, thus affecting the design of composites obtained therefrom.

The increasing application of the second approach is related, first of all, to the successful results of Cao and coworkers, suggesting the use of the so called functionalized protonic acids in the protonation of PANI[18–20]. The complex obtained by mixing those acids (mainly dodecylbenzenesulfonic acid, DBSA, and camphorsulfonic acid) with deprotonated PANI, is soluble in common solvents, such as toluene, xylenes, decalin etc., and makes the PANI compatible with polymers soluble in these solvents[18–23]. The complexes can also be dispersed in the melt of polymers, such as poly(vinyl chloride), and poly(caprolactone)[24].

The most characteristic features of the PANI-containing composites obtained by using functionalized acids, are the non-typical percolation behaviour (in respect of both the shape of the dependence 'composition-conductivity' and the low percolation threshold), the possibility of preparation of transparent films, and the possibility of keeping the mechanical properties of the composites at a level essentially equivalent to those of the host bulk polymer. Also, such composites (e.g. with polyethylene or with PVAL) can be stretch-aligned, which allows the electrical conductivity to be increased by one or two orders of magnitude, and even highly oriented PANI with anisotropy on a molecular scale to be prepared[20].

It has to be noted that the question of the role played by functionalized acids in the formation of PANI-containing composites, is still under consideration.

The results obtained recently by Banerjee and Mandal[17] can be regarded as a confirmation of the crucial effect of the design of the composites (irrespective of the preparation method) on the percolation behaviour and other properties of the composites. The authors broke preformed submicronic PANI.HCl particles of oblong shape (250 nm × 190 nm) by sonication in a solution of matrix polymer to sizes less than 20 nm. The design of the composites obtained is analogous to that of PANI-containing composites prepared by using functionalized acids. (The above mentioned submicronic PANI.HCl

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particles were prepared by polymerization of ANI in the presence of poly(vinyl methyl ether) as a steric stabilizer[5].)

We now report a novel route to the preparation of PANI-containing composites, which allows the distribution of preformed colloid PANI particles of 5–30 nm size in a host polymer without sonication. The polymer composites thus obtained exhibit a percolation threshold lower than 0.5%, even in a non-oriented state, and represent flexible free-standing films which combine high electrical conductivity and transparency.

According to our new approach, PANI-containing composites can be obtained by simple mechanical mixing of: (a) colloidal PANI dispersion with particle size 5–30 nm synthesized by polymerizing ANI in the presence of an oxidant and DBSA; with (b) a solution of the host polymer. The method is extremely simple, and leads to exceptional properties of the composites obtained.

Experimental

Materials. Reagent-grade ANI, hydrochloric acid, ammonium peroxydisulfate, PVAL (molar mass 72 000, 86 mol% vinyl alcohol units) and xylene were purchased from Fluka. Ethylene–(vinyl acetate) copolymer (EVA), Elvax 210 (Du Pont de Nemours) containing 11 mol% of vinyl acetate units, and DBSA (Tokyo Kasei) were used as received.

Polymerization. In a typical synthesis of colloidal PANI dispersion, to a stirred aqueous solution of DBSA (0.1 M, 100 ml) were successively added 0.01 mol of aniline and a solution of 0.01 mol of ammonium peroxydisulfate in 5 ml deionized water. Polymerization was carried out at 20–22°C for 4 h.

Preparation of composites. The colloidal PANI dispersion thus obtained can be used for preparation of composites with both water-soluble (such as PVAL) and water-insoluble (such as EVA) host polymers. In the first case, the corresponding amount of the dispersion was mixed with 10 wt% PVAL solution. In the second case, two methods of mixing were used. In the first one, the dispersion was mixed with 10 wt% xylene solution of EVA. In the second method, dried (60°C) colloid PANI particles were redispersed in xylene and then mixed with EVA xylene solution. Free-standing films of the composites were prepared by casting the colloidal systems thus obtained on a Teflon support. The composites PANI–PVAL were compared with similar composites synthesized by polymerization of ANI in presence of PVAL and either HCl[11–14] or DBSA.

Characterization of dispersions. The colloidal PANI dispersions prepared in the presence of DBSA, including samples redispersed in xylene, were studied by transmission electron microscopy (TEM) (JEOL-100B). The colloidal systems prepared by mixing of colloidal PANI dispersions with aqueous PVAL solution were also studied by scanning electron microscopy (SEM) (JSM-5300). The concentration of all the colloidal systems prior to evaporation was about 1×10^{-3} g cm^{-3} with respect to PANI.

Characterization of composites. Transmission of the films in the range 400–800 nm was recorded on a SPECORD M42 (Carl Zeiss). Electrical conductivity measurements of the films were performed by the conventional four-probe technique.

Results and discussion

The polymerization of ANI in the presence of DBSA results in the formation of very fine colloidal PANI dispersions of broad particle size distribution (*Figures 1a* and *1b*). As seen from TEM, the basic size of predominantly spherical colloid PANI particles is *ca* 5 nm, the largest particles being 30–35 nm and consisting of smaller particles.

Obviously, in the case at hand, DBSA acts mainly as a surfactant. However, it is also possible for DBSA to supply counteranions for PANI chains, along with HSO_4^- anions formed as a result of the oxidant reduction. The ability of DBSA to form micelles at concentrations higher than the critical micelle concentration (CMC) (in the case at hand the polymerization of ANI takes place at DBSA concentrations substantially higher than the CMC) determines the possibility for the polymerization to proceed in such micelles, resulting in the formation of very fine colloidal PANI dispersions.

Hence, dilution and addition of electrolytes has to result in a gradual enlargement of the colloidal particles and precipitation of dispersion. Such a phenomenon was actually observed on adding of water or saline solution to the dispersions. On the other hand, the dispersions can be diluted without precipitation by adding additional amounts of DBSA, i.e. by keeping its concentration higher than the CMC.

The colloidal PANI dispersions obtained can be dried and redispersed in an organic solvent. For that purpose we used xylene, since the composites of PANI with EVA copolymer were prepared with this solvent. As seen from TEM, the size of colloid PANI particles redispersed in xylene is also in the range 5–20 nm, however they are less dense, and besides spherical particles there are also particles of irregular shape.

It is worth noting that we have first obtained a stable fine colloidal PANI dispersion in the presence of DBSA. To the best of our knowledge there is only one paper dealing with polymerization of aniline in the presence of DBSA. Österholm *et al.*[25] have prepared a PANI–DBSA complex by emulsion polymerization of ANI in an aqueous–xylene system. However, data about the characteristics of the dispersions obtained are not available.

Our approach consists of the preparation of composites containing PANI which has been preliminarily formed as very fine colloid particles. Besides its simplicity, this approach allows control of the design of composites (particle size and size distribution) with regard both to PANI and to the host polymer. The first can be attained to a great extent by controlling the DBSA concentration in the system, as described above. Concerning the host polymer, controlled design could be attained in 'organized' systems (e.g. polymer dispersions and networks); this will be a subject of our further investigations.

The design of composites has to affect, first of all, the percolation behaviour and the transparency. It can be supposed that the smaller the PANI particles the lower

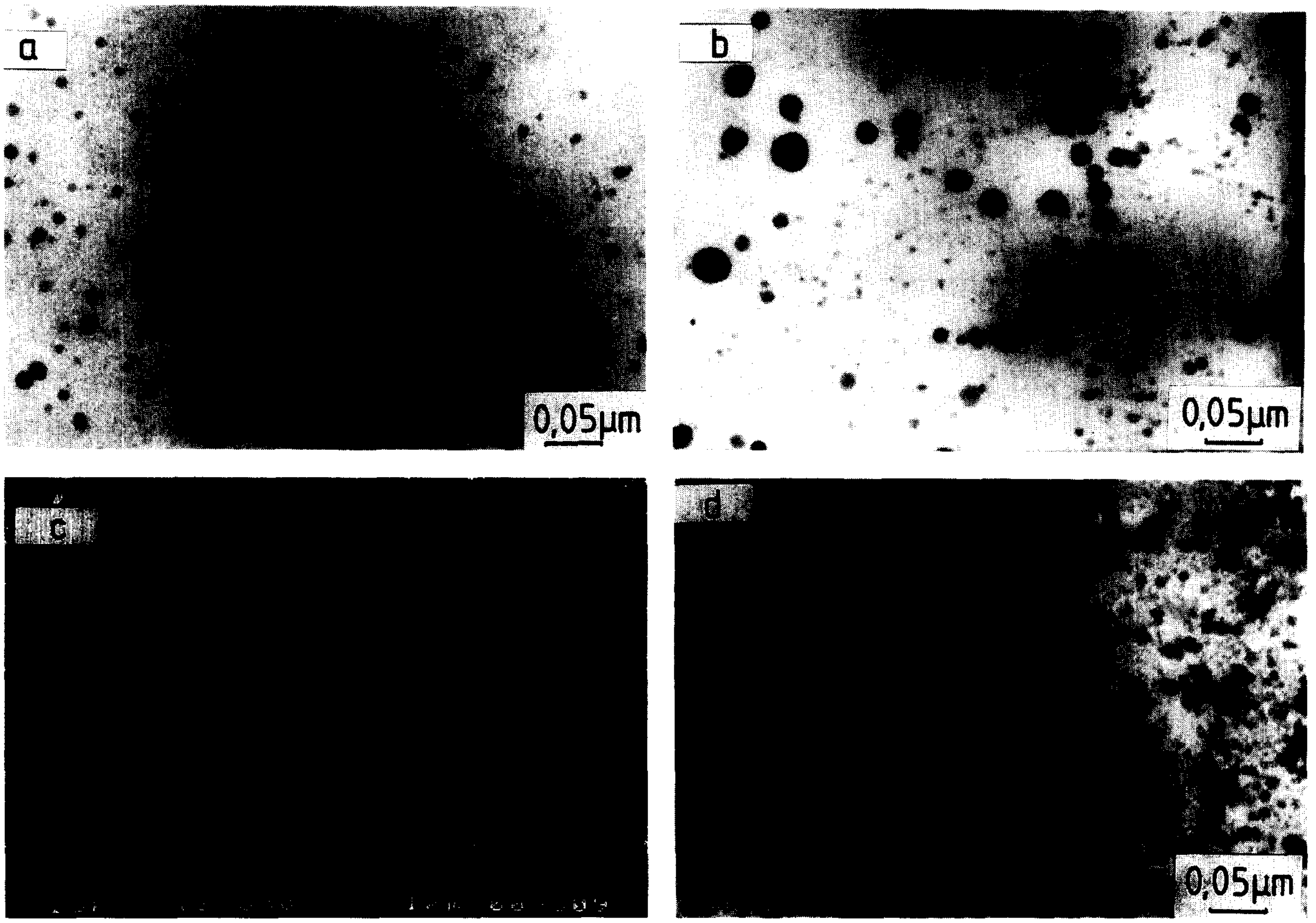

Figure 1 TEM (a, b and d) and SEM (c) micrographs of colloidal PANI dispersions obtained by: (a) and (b) polymerizing ANI in presence of DBSA (different areas of the same sample are given); (c) and (d) mixing of preformed PANI dispersion stabilized by DBSA with PVAL solution up to PANI content of 2.5 wt% (c) and 16 wt% (d)

the percolation threshold of the composites. Further increase of concentration of such particles (above the percolation threshold) has to result in improvement of the conducting network, i.e. to enhanced conductivity of the composites. It is also reasonable to expect enhanced transparency of composites on decreasing size of PANI particles.

The experimental data described below confirm these suggestions.

The size of preformed colloid PANI particles could be changed upon 'dilution' of the colloidal PANI dispersion obtained in the presence of DBSA with PVAL solution. As seen from *Figures 1c* and *1d*, when the PANI content in the composite is *ca* 2.5 wt%, the average size of the PANI particles is about 100 nm, which is nearly an order of magnitude higher than the particle size (*ca* 10 nm) in composites containing about 16 wt% PANI.

The low percolation threshold (lower than 0.5 wt%) of PANI–PVAL composites obtained by mixing of colloidal PANI dispersion stabilized by DBSA with PVAL solution, and the monotonic increase of conductivity by more than four orders of magnitude on increasing PANI content from 0.5 to 16 wt% (*Figure 2*, curve 3), confirmed the above mentioned suggestion for the influence of the PANI particle size on the percolation behaviour. As can be seen, the dependence of conductivity on PANI content in PANI–PVAL composites obtained by polymerizing ANI in PVAL solution according to our method[11–14] (*Figure 2*, curve 1), where the size of colloid PANI particles is *ca* 500–600 nm, reveals quite a different shape. It has to be noted, however, that in the last case at least two percolation thresholds exist: the first at PANI content lower than 1 wt% and the second at PANI content between 5 and 10 wt%. This indicated the different type of composite design at low (lower than 5 wt%) and high PANI content.

For PANI–PVAL composites obtained by polymerization of ANI in PVAL solution by use of DBSA

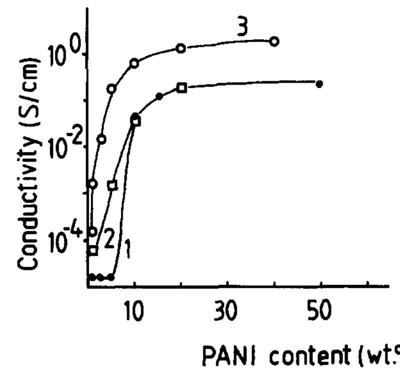

Figure 2 Electrical conductivity vs PANI content of PANI–PVAL compositions obtained by: (1) ANI polymerization in the presence of PVAL and HCl; (2) ANI polymerization in the presence of PVAL and DBSA; (3) mixing of colloidal PANI dispersion synthesized in the presence of DBSA with PVAL solution

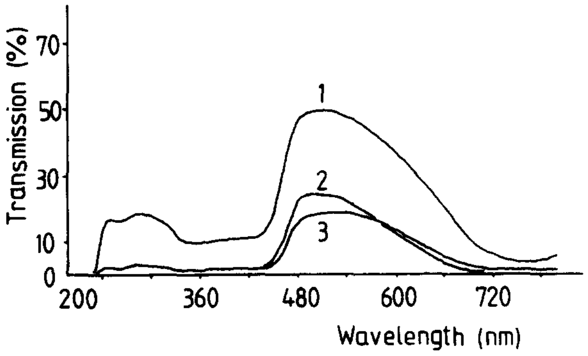

Figure 3 Transmission of PANI-PVAL films of PANI content: (1) 2.5 wt%; (2) 5 wt%; (3) 16 wt%

instead of HCl (*Figure 2*, curve 2), the shape of the dependence of conductivity on PANI content has an intermediate position between those corresponding to the two above described methods for preparation of composites. This is quite reasonable, since in this case formation of colloid PANI particles proceeds simultaneously with the participation of both PVAL and DBSA.

An important characteristic which depends on the design of composites is their transparency. As is evident from *Figure 3*, the PANI–PVAL composites prepared by using preformed colloidal PANI dispersion obtained in the presence of DBSA, showed high transparency. For the sake of comparison, a film of PANI–PVAL cast from a dispersion obtained by polymerizing ANI in the presence of PVAL, which has the same thickness (*ca* 50 μm) and the same PANI content (*ca* 16 wt%), is opaque and exhibits conductivity an order of magnitude lower (*ca* 10^{-1} S cm^{-1}).

Similar trends were also observed in the properties of PANI–EVA composites: the low percolation threshold (0.5–1.0 wt% of PANI); the shift of the percolation threshold towards the higher PANI content (2.5–5.0 wt%) on dilution of the dispersions with xylene, which results in increasing PANI particle size; the high conductivity of composites (up to 10^{-2} S cm^{-1}) at relatively low PANI content (*ca* 10 wt%); the possibility of preparation of transparent films.

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