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STRUCTURE OF COMPOSITE FILMS CONTAINING POLYANILINE STUDIED BY DSC

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Abstract

A structural study of conductive composite films consisting of ethylene-co-vinyl acetate (EVA) copolymer, polyaniline (PANI) and dodecylbenzenesulfonic acid (DBSA), a part of which being complexed with PANI, was performed by using differential scanning calorimetry (DSC) and presented for the first time. An additional crystalline phase is formed during the film formation by thickening EVA chain-folded lamellae with participation of 'free' DBSA molecules at lower net PANI content (up to 5 mass%) and of both 'free' and complexed DBSA molecules (up to 7.5 mass%). At higher PANI content PANI-DBSA complex starts to form its own crystals and at 17.5 mass% of PANI mixed crystals of EVA with 'free' DBSA alkyl chains are preferably formed. It is also found that the Fox's equation correlating the glass transition temperature of a miscible blend system with its composition can be actually used in estimating the miscibility of EVA/PANI blends no matter the presence of DBSA.

Keywords: composite films, crystallinity, differential scanning calorimetry, dodecylbenzenesulfonic acid, ethylene-co-vinyl acetate copolymer, glass transition, polyaniline

Introduction

Among the conducting polymers polyaniline (PANI) has been a topic of considerable scientific and industrial interest because of its controllable electrical properties [1, 2], good environmental stability [3–6] and the simplicity of its polymerization (chemical or electrochemical).

In order to increase the mobility of the rigid-rod PANI chains and to improve the polymer processability alkyl- or alkoxy-N-, or ring-substituted polyanilines have been prepared by polymerizing the corresponding monomers and via chemical modification [7–9]. Besides the covalent alkyl substitution, much more important is the significant progress towards solubility and processability of PANI attained by Cao *et al.* [10–12], Oesterholm *et al.* [13]. In this approach, a functionalized protonic acid which usually serves as a surfactant, such as camphorsulfonic acid (CSA) [14–18], dodecylbenzenesulfonic acid (DBSA) [19–22] or other acids with long alkyl chains

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[23–26], have been used in doping of PANI instead of conventional inorganic acids. The bulky non-polar hydrophobic tail of the dopant renders the polyanilines in the conducting form soluble in non-polar or weakly polar organic solvents and processable over an intermediate temperature ranges. The complexation of PANI and DBSA has been achieved by mechanical or solution mixing the emeraldine base of PANI with DBSA [27] or through a thermal doping process [28]. It was shown [8–10, 29] that the long aliphatic chains of DBSA facilitates the processing of PANI by using conventional techniques. The glass transition of such PANI-DBSA complex is low enough for optimal processing with other thermoplastic polymers. It is also assumable that the long hydrocarbon tail can modify the polymer–polymer interface in the composites [27].

In our recent studies [30] we suggested a novel route to prepare conductive PANI composites with common thermoplastic host such as ethylene-co-vinyl acetate (EVA) copolymer. It consists in mixing of a solution of the host polymer with preliminary formed colloidal PANI dispersion obtained by oxidative polymerization of aniline in the presence of DBSA in aqueous medium.

To the best of our knowledge, only the phase behaviour of EVA copolymer blends with N-alkylated polyanilines, i.e. PANI derivatives with various alkyl side-chain substituents covalently bound to PANI chains, has been investigated up to now [7, 31, 32]. It has been found that the miscibility of the polymers is determined by the hydrophobic interaction between the hydrocarbon unit in the both constituents and by the hydrogen bonding.

Now for the first time we present a structural study by using differential scanning calorimetry (DSC) of conductive composite films of EVA copolymer and PANI-DBSA complex, cast from water-xylene medium, PANI-DBSA being prepared *in situ* by oxidative polymerization of aniline in presence of DBSA. During processing and storage, such composites can be exposed to elevated temperature and changes in their structure can take place (chain defects, crosslinking, etc.). Thus, we consider that the thermal analysis is important for elucidating the interactions among the three constituents in the systems studied (PANI, DBSA and EVA copolymer) which are responsible for the structural changes, phase transitions and electrical conductivity of the composites.

Experimental

Materials

Reagent-grade aniline, xylene and ammonium peroxydisulfate (APDS) were purchased from Fluka. Ethylene-co-vinyl acetate copolymer (EVA) containing 11 mol% of vinyl acetate units (Elvax 210, DuPont) and dodecylbenzenesulfonic acid (DBSA) (Tokyo Kasei) were commercial products, used as received.

Preparation of PANI-EVA composites

PANI was prepared by oxidative polymerization of aniline in the presence of DBSA in aqueous media, using APDS as the oxidant, following the procedure described previously [30].

PANI-DBSA/EVA composites were prepared by mixing appropriate amount of thus obtained aqueous dispersion of PANI-DBSA complex with 1% xylene solution of EVA. They were formulated based on different contents of the net PANI in the composites, varying from 0.25 up to 17.5% by the mass of EVA/PANI blend (Table 1). After stirring for 2 h at room temperature, free standing films of the composites were cast in Petri-dishes and the solvents were evaporated in vacuum. The thickness of the films was ca 120 μm. The samples were not kept under any special conditions, i.e. they were exposed to the ambient atmosphere (20–25°C, ca 80% humidity).

Differential scanning calorimetry

Thermal studies were performed on a Perkin Elmer DSC 7 differential scanning calorimeter in nitrogen atmosphere in the temperature range of –40–180°C and heating rate of 10°C min^{-1}. The instrument was calibrated by using indium and lead as standards. Samples of about 10 mg were sealed in standard aluminum pans with holes.

Results and discussion

DSC is the most common method of investigating polymer miscibility or the degree of interaction between the constituent polymers of a blend. Interaction on molecular level between the amorphous phases of two polymers of sufficiently separated glass transition temperatures (T_g) leads to a single T_g for a blend pair, intermediate between those of the homopolymers, although different methods of measuring T_g are sensitive to different scales of homogeneity [33]. This is generally accepted as an indication of polymer miscibility. A significant mutual shift of the two T_g values towards some intermediate positions is recognized as a sign of miscibility or interfacial interaction. In our previous DSC investigation, T_g for PANI in the PANI-DBSA complex was observed to be about 65°C [34]. In the present DSC study, with an increasing content of PANI in the PANI-DBSA/EVA composites, T_g gradually increases according to the classical Fox's equation [35] that correlates the glass transition temperature of a miscible blend system with its composition:

$$T_g=W_1T_{g1}+W_2T_{g2}$$

where T_g, T_{g1} and T_{g2} are the glass transition temperatures of the blend, homopolymer 1 and homopolymer 2, respectively. W_1 and W_2 are the corresponding mass fractions. Data presented in Table 1 show that T_g values calculated from the Fox's equation correspond fairly well to the glass transition temperatures experimentally determined from DSC traces.

Table 1 Dependence of the relaxation transition temperatures on the blends composition, calculated according to Fox's equation, T_g (calc.), and experimentally found by DSC, T_g (exp.)

Blend No.	EVA/mass%	PANI/mass%	T_g (calc.)/°C	T_g (exp.)/°C
1	100	0		–25.0
2	99.75	0.25	–24.7	–23.8
3	98	2	–23.2	–21.6
4	95	5	–20.5	–19.0
5	92.5	7.5	–18.2	–17.3
6	90	10	–16.0	–15.5
7	82.5	17.5	–11.1	–10.7
8	0	100		65.0

This demonstrates that the amorphous phases of the two polymers are mixing into homogeneous blend with no obvious sign of phase separation. It has been found [10, 31, 36, 37] that, since the flexible chains of DBSA in the composites behave as a bound solvent they influence the change of entropy of the isotropic EVA phase transition and can induce compatibility and miscibility with PANI main chains. The rigid-rod PANI molecules, however, hinder the movement of the flexible EVA units and side DBSA tails. This effect is likely to be dominant, that is why the higher the PANI content in the blends, the higher the thermal transition temperature.

Besides, the very good coincidence between the calculated and experimentally found T_g values confirms that the Fox's equation can be actually used in estimating the miscibility of EVA/PANI blends no matter the presence of DBSA.

As seen from DSC-trace 1 in Fig. 1, the neat EVA copolymer has a bimodal melting transition in the first heating scan denoted as T_1 (34.5°C) and T_2 (48.9°C). It

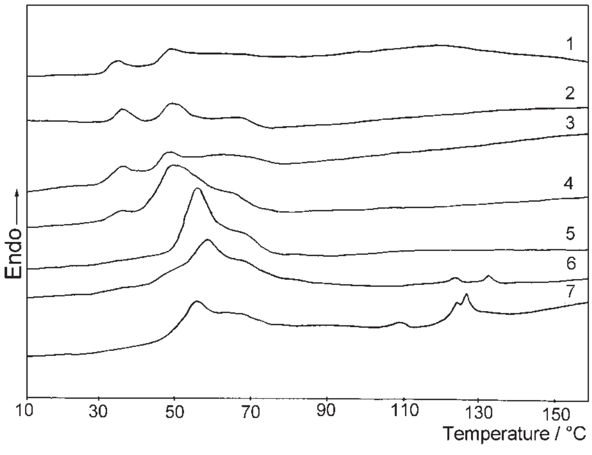

Fig. 1 DSC curves of PANI-DBSA/EVA composite films with different PANI content, registered upon heating up to 180°C at a heating rate of 10°C $\min^{-1}$ (1 – 0 mass%, 2 – 0.25 mass%, 3 – 2 mass%, 4 – 5mass%, 5 – 7.5 mass%, 6 – 10 mass% and 7 – 17.5 mass%)

has been well established by differential thermal analysis (DTA) [38] that two or three melting peaks appear depending on the crystallization temperature and the composition of the EVA copolymer, reflecting the original texture of the samples. The lower temperature peak (at T_1) is assigned to the melting of fringed micellar crystals, the higher one (at T_2) to the melting of more perfect chain-folded crystals. The bimodal crystallization can be regarded as a consequence of both the compositional and configurational heterogeneity in the copolymer [39].

As presented in Fig. 1, traces 2–7, the two melting peaks of EVA copolymer appear also in the composites, the peak at T_2 being always predominant. T_1 and T_2 of the composites refer also to melting of fringed micelle and more perfect chain-folded EVA crystals, respectively.

For the composites of low PANI-DBSA content, i.e. up to 5 mass% of net PANI (traces 2, 3 and 4), T_1 and T_2 keep their values almost unchanged. The intensity of the peak at T_1, however, decreases and the peak becomes more diffuse. This means that during the film formation the rigid-rod PANI chains affect the fringed micelle crystallization. On the other hand, the DBSA presented in the initial solutions, especially free DBSA molecules, facilitates the systems mobility. Thus, EVA folded-chain crystals can be formed more easily and the higher PANI-DBSA content, the greater the peak at T_2, i.e. the chain-folded crystallization prevails to the fringed micelle one.

As seen in Fig. 2, the heat of fusion (ΔH_m) of the composites rises with increasing the PANI content up to 7.5 mass%. Due to difficult differentiation of the melting peaks at T_1 and T_2, ΔH_m for EVA melting was analyzed by determining the whole broad area of the bimodal peak. If the amount of folded crystalline phase is growing at the expense of fringed micelle one, the total ΔH_m should keep its value constant. On the other hand, if EVA folded crystals become more perfect, T_2 has to enhance. But we can see that ΔH_m of the composites rises and it is always higher than ΔH_m of neat EVA copolymer, and T_2 does not change, either.

It is known [40] that the crystalline polymer structures always become more defective by mixing with more amorphous component or by forming mixed crystals. On the other hand, when mixed crystals are obtained, the amount of crystalline phase increases. In the case at hand, since the composites reveal single T_g and single T_m, obviously PANI-DBSA complex and EVA copolymer are compatible. That is why they can co-crystallize and their heat of fusion, ΔH_m, rises. Thus, it can be stated that ΔH_m increase is not due to the formation of more perfect chain-folded EVA crystals, but it is a result of co-crystallization between the long alkyl chains of DBSA molecules and EVA copolymer during the film formation.

As mentioned above: a) both free DBSA and DBSA electrostatically bonded to PANI rigid-rod chains exist in the systems from which the films are obtained; b) T_2 does not change its value when small amount of PANI-DBSA complex (up to 5 mass% net PANI) is mixed with EVA copolymer; and c) the two components can form mixed structures upon solution crystallization. It is also known when chain ends or side chains of a crystallizing polymer are involved into the crystal lattice of another polymer, melting is retarded, i.e. T_m increases [40]. Consequently, we can assume that, at PANI content up to 5 mass%, the mobile DBSA free molecules ordering around the chain-folded EVA crystals take part in the co-crystallization with EVA copolymer thickening its lamella. Increased crystallinity due to greater amount of crystalline phase is obtained, even when the size of the individual crystals may decrease.

Thus, we can summarize, that at PANI content in the composites up to 5 mass%, the extra heat of fusion can be regarded as a consequence of increasing (during the film formation) the amount of crystalline phase formed by thickening EVA chain-folded crystalline lamellae with participation of alkyl chains of free DBSA molecules present in the systems.

As seen from Fig. 1, traces 2–7, at temperatures higher than T_2, a shoulder of bimodal melting peak appears and it becomes more pronounced with increasing PANI-DBSA content (up to 17.5 mass% net PANI) in the composites. We consider it also as melting of more stable mixed crystals, but it will be a subject of further investigations.

On increasing PANI content of more than 5 mass%, the peak at T_1 disappears and T_2 as well as the whole temperature range where the phase transition occurs, are shifted up to higher values. The greatest height of the peak and its maximal temperature are observed for the composite containing 7.5 mass% net PANI. We consider this increase as a result of involving into the chain-folded structures also of alkyl side chains of DBSA electrostatically bonded to PANI. The limited mobility of these tails results in retarded melting of the mixed crystals. At this PANI content, ΔH_m has also its maximal value in a narrowest temperature range. Thus, it can be stated that the highest amount of crystalline phase with participation of both free and bonded DBSA alkyl chains can be best achieved at net PANI content of 7.5 mass%.

In our previous paper [34] it was shown that DBSA induces crystallinity in the rigid PANI matrix of the PANI-DBSA complex. It was found by wide angle X-ray diffraction that this semicrystalline system consists of three types of crystals, corresponding to a multiple melting peaks in the temperature region between 120 and 150°C: 1. free DBSA molecules ordered between fixed alkyl tails electrostatically

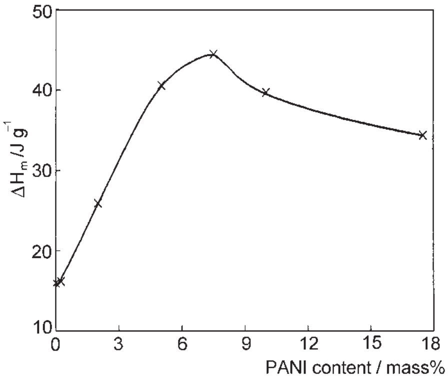

Fig. 2 Heat of fusion (ΔH_m) *vs.* PANI content in PANI-DBSA/EVA composite films, determined upon heating up to 180°C at a heating rate of 10°C min^{-1}

bonded to PANI chains; 2. fixed adjacent DBSA alkyl tails electrostatically bonded to PANI chains and 3. ordered free DBSA molecules. It is now observed that upon heating, after the melting of EVA crystals a crystalline phase separation can occur and the above mentioned melting peaks of PANI-DBSA complex are obvious at PANI content more than 7.5 mass%. DBSA alkyl chains of the complex form more easily their own crystals, thus, the peak intensity and also the heat of fusion (Fig. 2) decrease. The systems remain compatible (single T_g is still observed) but the higher content of PANI rigid-rod chains hinder the co-crystallization between EVA and DBSA tails. Even at PANI content of 17.5 mass%, however, the heat of fusion is still greater than this determined for the neat EVA copolymer. That is why mixed crystals with free DBSA molecules are still preferably formed.

Conclusions

In conclusion, it can be stated that at PANI content up to 5 mass%, an additional amount of crystalline phase (as compared to EVA copolymer) is formed in the composites by thickening EVA chain-folded crystalline lamellae with participation of alkyl chains of free DBSA molecules present in the system. The highest amount of crystalline phase with participation of both free and bonded DBSA alkyl chains can be attained at a net PANI content of 7.5 mass%. At higher PANI content, DBSA alkyl chains of the complex form their own crystals and PANI rigid-rod chains hinder the co-crystallization between EVA and DBSA, but even at 17.5 mass% of PANI, mixed crystals of EVA with free DBSA molecules are still preferably formed.

It is also found that Fox's equation correlating the glass transition temperature of a miscible blend system with its composition can be actually used in estimating the miscibility of EVA/PANI blends no matter of the presence of DBSA.

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