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Surface and thermodynamic characterization of conducting polymers by inverse gas chromatography

II. Polyaniline and its blend

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Abstract

Inverse gas chromatography was used to characterize both doped, the undoped polyaniline (PANI), and its blend with nylon-6 using 27 solutes. The change in the morphology of these polymers was detected between 80 and 180 °C and was complemented by the degree of crystallinity. ΔH_s^1 values of all solutes – pure polymers were found endothermic and exothermic for the blend. The χ'_{23} depended on the chemical nature of solutes; a correction measure was not successful in obtaining the true values of χ'_{23}. χ'_{23} showed a phase separation of the blend (60:40 w/w) between 80 and 180 °C. Blending nylon-6 with PANI has lowered the dispersive surface energy of PANI while increasing the surface energy of nylon-6.

Keywords: Surface energy; Interaction parameters; Polymer–polymer interaction parameters; Conducting polyaniline; Crystallinity; Heat of sorption; Retention diagrams; Blends of polyaniline and nylon-6

1. Introduction

In our first series of publications in this journal on the characterization of conducting and non-conducting polyaniline using the inverse gas chromatography (IGC) method, we concluded that IGC can be used as an alternative method for the analysis and characterization of polymers, particularly, high energy polymers such as polyaniline (PANI) [1,2]. We have shown that the dispersive component of surface energy of the insulated PANI emeraldine base (PANI-EB) and conductive polyaniline (PANI-HEBSA) can be obtained with ease and accuracy using IGC. Our results showed that the dispersive surface energy of PANI-EB ranged from 29.13 mJ/m^2 at 140 °C to 94.05 mJ/m^2 at 170 °C, while the surface energy of PANI-HEBSA showed higher values (150.24 mJ/m^2 at 80 °C to 74.27 mJ/m^2 at 130 °C). IGC is often called the molecular probe technique, it has emerged as a promising method for polymers and polymer blends characterization [3]. It was shown that the IGC method can be useful in obtaining thermodynamic data on polymeric systems even when the morphology is complex [4]. PANI has a limited solubility in solvents; however, IGC has made this task easier because at infinite dilution, all small organic molecules will have measurable solubilities in solid organic polymers. Hence the range of interactions that can be probed by the IGC techniques is unlimited. IGC is also a valuable tool for the identification of several types of interactions in molecular and macromolecular systems, and a useful technique for the study of surface energetic of several systems and their response to actual conditions [5,6].

Inherently conducting polymers (ICPs) such as PANI constitute a novel class of materials. They are used in paint technology and corrosion control, thermoplastics welding, conducting textiles, energy storage, electronics, photovoltaic devices, conducting polymer blends, composites, biosensors, biomedical agglutination assays, and primer in paint technology.

It is interesting to notice that when conducting PANI is blended with another non-conducting polymer, remarkable improvement in the physical or mechanical properties may be achieved. The discovery of solution processibility of PANI by doping it with functionalized organic acids has allowed the preparation of a blend solution of PANI and a number of conventional polymers that enabled the coating of a chromatographic column [7,8]. The remarkable feature of the blending process of

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conducting and non-conducting polymers, is the achievement of high blend conductivity values approaching those of the pure conducting PANI using a minor fraction of PANI's concentration of the total composition [8].

Although the properties of blends containing conducting and other polymers were explored [6,8,9], only a few applications of IGC on such a blend were reported. Chehimi et al. [6] reported the adsorption effect of polymers onto conducting polypyrrole, the solvent nature from which the blends were coated, influenced the adsorption rate and the morphology of the blend. No other reports cited to date, for the characterization of this kind of blends and their surface, mechanical and crystallinity properties using IGC. However, IGC was successfully applied for the determination of surface energy of several polymeric systems and fillers [10–26], and only a few applications of IGC to conducting polymers were reported [27–32].

It is the purpose of this paper to extend our previous surface thermodynamic studies on the conducting and non-conducting polyaniline using a variety of solutes with specific functional groups. Also to apply the IGC studies on a blend containing PANI-HEBSA and nylon-6. Since nylon-6 is mostly crystalline at our experiments' temperature range, we will refer to PANI as the diluent polymer and nylon-6 as the host polymer. We will explore the effect of the blending process on the crystallinity of nylon-6, and the surface energy of PANI-HEBSA. It is also our goal to test the capability of the IGC method in obtaining physiochemical properties on the bulk and on the surface of a complex system, such as a blend containing conducting and non-conducting polymers.

2. Data reduction

2.1. Thermodynamics of polymer blends using IGC

In our first series publication on PANI-Solute system [1], we reported the complete analysis of the thermodynamics of IGC using solutes from three chemically different families, a series of alkanes, acetates and alcohols. Specific retention volume V_g^o, was determined from the measured chromatographic quantities in IGC experiments. V_g^o is the key term in thermodynamic analysis of both polymer-solvent and polymer–polymer interactions. Our thermodynamic analysis published earlier [1] can be continued to cover the thermodynamic analysis of a complex polymer blend containing a conducting and a non-conducting polymer.

When two conducting polymers are blended, the key term in the miscibility of a polymer–polymer pair is the free energy of mixing, ΔG_{mix}. Utilizing the specific retention volume, V_g^o, the polymer–polymer interaction coefficient, χ_{23} can be derived from ΔG_{mix} (Eq. (1)). When a polymer pair such as PANI-HEBSA-nylon-6, is used as a stationary (liquid) phase in a chromatographic column, subscripts 2 and 3 will be used to represent polymer 2 (nylon-6) and 3 (PANI-HEBSA), respectively. Subscript 1 refers to the test solute. The interaction between the two polymers is expressed in terms of the free energy of mixing ΔG_{mix} has the same form as χ_{23} reported in the first series [2], the first two (entropic) terms in Eq. (1) are negligible for polymer blends. Thus, for a polymer blend to be miscible (ΔG_{mix} being negative), χ_{23} must be negative. When considering the IGC of polymer blends, the free energy of mixing [3] must be written for a three-component system. It is usually expressed as:

$$\Delta G_{\text{mix}} = RT[n_1 \ln \varphi_1 + n_2 \ln \varphi_2 + n_3 \ln \varphi_3 + n_1\varphi_2\chi_{12} + n_1\varphi_3\chi_{13} + n_2\varphi_3\chi_{23}] \tag{1}$$

where n_i and φ_i are the number of moles and the volume fraction of the ith component, RT has its usual meaning, χ_{12} and χ_{13} are parameters which are inversely proportional to absolute temperature. They are defined as enthalpic contact parameters for polymer 2 and 3 respectively. Recognizing that for a polymer blend containing polymer 2 and polymer 3, the polymer specific volumes of 2 and 3 are expressed in terms of $(w_2v_2 + w_3v_3)$, where w_2 and w_3 are the weight fractions and v_2 and v_3 are the specific volumes of the two polymers (2 and 3) in the blend, the χ'_{23} [3] can be derived from

$$\chi'_{23} = \frac{\ln \frac{V^o_{g,\text{blend}}}{w_2v_2+w_3v_3} - \varphi_2 \ln \frac{V^o_{g,2}}{v_2} - \varphi_3 \ln \frac{V^o_{g,3}}{v_3}}{\varphi_2\varphi_3} \tag{2}$$

where φ_2 and φ_3 are the volume fractions of the two polymers in the blend. To obtain χ'_{23} for a polymer blend, utilizing IGC, χ_{12} and χ_{13} have to be known. Three columns are usually prepared; two from the homopolymers and the third prepared from a blend of the two samples used for the homopolymer columns. These columns should be studied under identical conditions of column temperature, carrier gas flow rate and inlet pressure of the carrier gas, and with the same solutes.

Using Eq. (2), the contact energy parameter, $B_{23,}$ as another indicator of the miscibility of the polymer pair can be calculated [3]

$$B_{23} = \left(\frac{RT}{V_1\varphi_2\varphi_3}\right) \frac{\ln \frac{V^o_{g,\text{blend}}}{w_2v_2+w_3v_3} - \varphi_2 \ln \frac{V^o_{g,2}}{v_2} - \varphi_3 \ln \frac{V^o_{g,3}}{v_3}}{\varphi_2\varphi_3} \tag{3}$$

B_{23} determines the miscibility of the blend with a negative value being necessary for mixing.

Utilizing V_g^o from the chromatographic quantities, the molar heat of adsorption [3] can be calculated as:

$$\Delta H_1^s = -R\frac{\mathrm{d} \ln V_g^o}{\mathrm{d}(1/T)} \tag{4}$$

For polymer blends containing complex mixtures such as PANI-HEBSA and crystalline nylon-6, the morphology of the blend will be more complex as compared with the amorphous-amorphous polymer pair. In this case, it is possible to obtain the χ'_{23} and B_{23} experimentally in a different way than the one described earlier, by measuring the melting point depression of a polymer mixture (blend). Eq. (5) is usually used for the calculation of the melting point depression [3]:

$$\frac{1}{T_m} - \frac{1}{T^o} = -R\left(\frac{V_{2u}}{\Delta H_{2u}}\right)\left[\rho_2 \ln\left(\frac{v_2}{M_2}\right) + \left(\frac{\rho_2}{M_2} - \frac{\rho_3}{M_3}\right)v_3 + \left(\frac{B_{23}}{RT_m}\right){v_3}^2\right] \tag{5}$$