Surface characterisation of montmorillonite/PVC nanocomposites by inverse gas chromatography

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ABSTRACT

Inverse gas chromatography is a rather useful technique for evaluating the potential of the interaction of polymers, polymer nanocomposites and their different components. In this study, the dispersive component of the surface free energy and surface acid–base constants of montmorillonite/PVC and organo-montmorillonite/PVC nanocomposites, prepared using the solution blending method, will be determined using the inverse gas chromatography. The glass transition temperatures of nanocomposites have been determined using a differential scanning calorimeter (DSC). Furthermore, the morphology and surface functional groups of the materials have been analysed with the aid of x-ray diffraction (XRD) and Fourier Transform Infrared (FT-IR) spectroscopy. The dispersive component values (γ_S^d) of the surface free energy of PVC nanocomposites containing 1%, 5%, and 10% oMMT and 5% MMT wt% at 50 °C have been calculated as 39.6, 40.2, 41.6, and 34.0 mJ/m^2 respectively, and the K_D/K_A values have been determined as 1.83, 2.18, 2.47, and 1.46 respectively. It was observed that there is an increase in the K_D/K_A value, and the nanocomposites display a more basic character with the increasing amount of organo-bentonite in the PVC.

1. Introduction

Bentonite is a term generally used for clays containing the base mineral montmorillonite, and is an aluminium hydrosilicate with a soft colloidal characteristic containing at least 85% montmorillonite (MMT) [1]. As it is well known that Turkey possesses large beds of bentonite and sepiolite, several of these are actually being exploited. With a majority of these minerals being easily accessible at little expense, it is guaranteed that they will be utilized in the future [2].

After x-ray diffraction (XRD) had come into use in 1913, research into the subject of organic molecules being intercalated with the layers of clay minerals began in the 1920s [3]. In the process of ion exchange, cations added later or originally found among the layers of clay can be exchanged with organo-cations in an aqueous solution [4]. This procedure is carried out with the aim of altering the surface chemistry and increasing the spaces between the layers. The most commonly used cations for ion exchange are alkylammonium ions. However, other "onium" salts, such as sulfonium and phosphonium are also used [5].

According to the International Organization for Standardization, composite materials are multi-phased substances composed from the integration of two or more materials which have different physical and chemical properties. In composite materials, generally one phase is continuous and is known as the matrix, while the other phase is the strengthening material and is known as the dispersed phase [6].

Traditionally, synthetic or natural inorganic compounds are blended to polymeric materials in order to improve the characteristics of the final product or simply to keep the costs down. However, with the addition of these fillers, the presence of some bad effects on the final material, such as an increase in the weight, fragility, and opacity, is frequently encountered [5]. The physical attraction between organic and inorganic compounds in traditionally filled polymers is weak, and the dimension of the particles within the polymer is in micrometres, and this can bring about the production of weaker materials [7]. On the other hand, in nanocomposites at least one dimension of the dispersed particles needs to be measured in nanometres [8]. Thus, the surface area between the matrix and the filler increases to a significant degree, and this provides the material with many superior qualities.

Inverse gas chromatography (IGC) is a dynamic sorption technique. Unlike conventional gas chromatography, inverse gas chromatography focuses primarily on the solid material which is filled inside the column in the form of a powder, fibre or film, and non-volatile compounds are also injected into the column. In this method, the roles of the phases are exchanged, and this is where the name of inverse gas chromatography comes from [9,10].

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In inverse gas chromatography, the column of chromatography is filled with the material under investigation, and the volatile probes with different properties are sequentially injected into the column in very small amounts and transported throughout the column using an inert gas flow [11].

Inverse gas chromatography may be carried out using two different methods, namely infinite dilution (ID-IGC) and finite concentration (FC-IGC). In infinite dilution, the probe vapour is injected into the column in very small quantities. The quantity being injected is so small that the interaction of a probe molecule with the other one is negligible, and at the zero surface coverage only the interaction of the solid and the probe molecules is taken into account. Under these conditions, Henry's law comes into play, and the retention volume is independent of the probe concentration [12]. When infinite dilution is studied, the surface characteristic of the material such as dispersive component of the surface energy, thermodynamic parameters and acid/base constants can be analysed [13–15]. Furthermore, the interaction parameters and the thermal transitions of the polymers can be calculated from the acquired data [13].

The surface characteristics of various types of clay, such as kaolin [16], smectite [17,18], illite [16], attapulgite [19,20], and sepiolite [21], are analysed using inverse gas chromatography.

In recent years, inverse gas chromatography has often been used in the analysis of the characteristics of polymers, such as poly (ether imide) [22], polyethylene [23], poly (butylene terephthalate) [24], and poly (ethylene oxide) [25], and various polymer nanocomposites, such as silica/polypyrrole [26], rectorite/thermoplastic polyurethane [27], montmorillonite/polyamide 6 [28], and montmorillonite/polypyrrole [29,30].

In this study, various nanocomposites were prepared via the solution blending method, by mixing polyvinyl chloride (PVC) and montmorillonite (MMT) or organo-montmorillonite (oMMT) in tetrahydrofuran (THF). Surface free energy and acid–base properties of oMMT have been analysed using inverse gas chromatography. In order to be able to characterise the materials better, auxiliary analysis techniques, such as DSC, XRD, FTIR, and TEM, have been used.

1.1. Theory

IGC is used to study the surface free energy and acid–base properties of solids; the study is generally performed in the area of infinite dilution where the interactions between the adsorbed probe molecules are negligible.

The basic value in ID-IGC is the net retention volume. The net retention volume is the volume of carrier gas required to elute a given probe [14]. The net retention volume (V_N) is calculated using the following equation:

$$V_N = F_o \frac{T}{T_o} \frac{3}{2} \left[\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \right] (t_A - t_0) \tag{1}$$

where t_A is the retention time of the probe, while t_o is the retention time of the probe when there is no interaction with the solid in the column (marker). P_i and P_o are, respectively, the inlet and outlet pressures of the carrier gas, while the T/T_o ratio is used in order to get the value of the flow rate at the column temperature (T) from the measurement of the flow rate at ambient temperature (T_o). The flow rate of the carrier gas measured at the column outlet and at ambient temperature is expressed as F_o [31].

The determination of the surface free energy of solids plays a key role in various applications and processes in the industry. For example, surface free energy is crucial in terms of its influence on phenomena such as the coherence of components with each other in composites and coatings, the catalytic and adsorption characteristics of catalysts and adsorbents, the agglomeration of solid particles and their wettability. The characterisation of the surface free energies of solids allows us to acquire important information so as to be able to improve their surface qualities and, particularly, make surface modifications [32].

Generally, surface free energy of a solid (γ_S) can be split into two components: the dispersive component (γ_S^d), and the specific component (γ_S^{sp}). The dispersive component depends on the van der Waals dispersion forces which are relatively weak, while the specific component contains all the polar forces [11,12].

$$\gamma_S = \gamma_S^d + \gamma_S^{sp} \tag{2}$$

There are various methods for calculating the dispersive component of the surface free energy using inverse gas chromatography, but two of these are the most widely used. These are the Dorris–Gray and Schultz methods [33]. In both these methods, when calculating γ_S^d, a homologue alkane series in extremely small concentrations (infinite dilution) and in isothermal conditions is injected into the column in sequence. A single numerical γ_S^d value is calculated from the acquired alkane series retention time data at studied column temperature [32]. The calculation of γ_S^d according to the Schultz method, using infinite dilution measurements, is done using the following equation [33]:

$$RT \ln(V_N) = 2N(\gamma_S^d)^{1/2} a (\gamma_L^d)^{1/2} + C \tag{3}$$

where V_N is the net retention volume of the n-alkane probe, R is the gas constant, T is the absolute column temperature (K), a is the molecular surface area coated with a kind of adsorbed alkane, N is Avogadro's number, and C is the constant. In this equation, γ_S^d is the dispersive component of the surface free energy of the solid phase, and γ_L^d is the dispersive component of the surface free energy of the probe. The plot of $RT \ln(V_N)$ versus $a(\gamma_L^d)^{1/2}$ can be useful. Such a plot is linear and the slope of the lines gives dispersive free energy of the solid phase. The values of $a(\gamma_L^d)^{1/2}$ are necessary for the calculations and can be easily found in the literature.

The free energy of adsorption (ΔG°) for any probe is composed of the dispersive (ΔG^d) and the specific (ΔG^{sp}) components [31,34]:

$$\Delta G^\circ = \Delta G^d + \Delta G^{sp} \tag{4}$$

The specific component of free energy of adsorption (ΔG^{sp}) is related to the solid phase's ability to act as an acceptor or donor of electrons. For alkane probes, because there are no polar interactions, ΔG^{sp} is equal to zero. Thus ΔG° is composed of only the dispersive component.

$$\Delta G^{sp} = -RT \ln \left(\frac{V_N}{V_{N_{ref}}} \right) \tag{5}$$

To evaluate the ΔG^{sp}, $RT \ln(V_N)$ for each probe (including the alkanes) is plotted against $a(\gamma_L^d)^{1/2}$. This plot gives a straight line for alkane series which is used as the reference line. The vertical distance between the n-alkane line and the point where the polar probe is gives the $-\Delta G^{sp}$ value of that polar probe. In Eq. (5), V_N is the net retention volume of the polar probe, while $V_{N_{ref}}$ is the hypothetical net retention volume in the n-alkane line [9,21]. According to the following equation, specific components of the adsorption enthalpy (ΔH^{sp}) and entropy (ΔS^{sp}) can be determined from ΔG^{sp}'s relationship with the temperature:

$$\Delta G^{sp} = \Delta H^{sp} - T \Delta S^{sp} \tag{6}$$

A plot of $\Delta G^{sp}/T$ versus $1/T$ should yield a straight line with slope ΔH^{sp} and intercept ΔS^{sp}. The acidic–basic parameters can be obtained from the calculated ΔH^{sp} values using the following