Journal of Alloys and Compounds 621 (2015) 389–395

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Surface properties studies of bivalve shell waste by the IGC technique: Probing its significant potential application in the polymer industry

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ARTICLE INFO

Article history:
Received 16 August 2014
Received in revised form 24 September 2014
Accepted 2 October 2014
Available online 13 October 2014

Keywords:
Shellfish waste
Bio-filler
Inverse gas chromatography
Surface energy
Surface energy analyzer (SEA)
Polymer industry

ABSTRACT

Bivalve shell waste has the potential to be used as a bio-filler. In this work, the dispersive component (γ_s^d) of surface free energies of the surfaces of clam shell waste (CS) and commercial calcium carbonate (CC) were evaluated using inverse gas chromatography with both the Dorris–Gray method and the Schultz method. Their acid-base character was investigated as well. The mechanical properties of PP composites filled with CS and CC were then studied. The results showed that the γ_s^d calculated with Dorris–Gray method was a bit smaller than that calculated with Schultz method, with a $\frac{\gamma_{s,Dorris-Gray}^d}{\gamma_{s,Schultz}^d}$ ratio of 0.98. The surface energy of the CS was significantly heterogeneous and its calculated γ_s^d decreased drastically with increasing surface coverage from 0.5% to 2%, then slightly increased with surface coverage larger than 2%. The K_a/K_b ratio was 7.65 for CS and 1.48 for CC, indicating a more acidic character for the surfaces of CS. The mechanical properties analysis showed that the inclusion of CS powder played mainly a toughening role in the filled PP.

1. Introduction

Calcium carbonate ($CaCO_3$) is one of the most widely used inorganic fillers for polymers. Adding excessive amounts of it, however, can decrease the impact properties of polymer [1]. Furthermore, the resulting smaller particles cause more particle-to-particle interactions and consequently powder agglomeration, making the polymer difficult to process and further degrading its mechanical properties [2,3]. Bivalve shell waste, however, with its predominantly $CaCO_3$ content and biomacromolecules, can be used as a substitute filler, yielding a polymer with unique mechanical properties [4]. Fombuena et al. [5] for example, prepared composites from epoxy resin with seashell waste. Lin et al. [6] reported that the incorporation of shell powder greatly increased the impact strength of the PP matrix. de Melo et al. [7] found that the incorporation of mollusc shell waste could increase the degree of crystallinity and stiffness of high-density polyethylene. And our own previous studies have indicated that adding organo-modified shell powder could significantly increase the impact strength, the elongation at the breaking point and the flexural modulus of the PP matrix [8].

It has been widely recognized that the reinforcing effect of a filler depends on its nature, the polymer matrix type, and the filler loading [9–11]. The filler nature influences the reinforcement capability via the properties of particle size, specific surface area, functional groups on the surface, surface activity, etc [12]. The surface activity, for example, influences the reinforcement capability through its physicochemical properties, because the chemical nature of a particle's surface determines the interactions both among different fillers and between the fillers and the polymer. These interactions in turn influence the filler's dispersion in the matrix and thus affect the performance of composites [13]. Therefore, a better understanding of a filler's surface properties is critical to determining the most effective polymer reinforcement and processing.

As an alternative to classic contact angle measurement, inverse gas chromatography (IGC) has proved to be a reliable and sensitive technique for the characterization of surface properties [14–16]. The surface properties of $CaCO_3$ have been previously studied by IGC. Jeong et al. [17] examined the surface properties of $CaCO_3$, both with and without stearic acid treatment. Fekete et al. [18] reported that $CaCO_3$ coated with stearic acid showed relatively strong acidity. Shi et al. [19] determined the surface energy of precipitated $CaCO_3$ and the results agreed well with those derived from other methods. However, to the best of our knowledge, there are no reports on the surface characterization of shellfish waste.

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http://dx.doi.org/10.1016/j.jallcom.2014.10.017
0925-8388/

Thus, in this study we attempt to investigate the surface energy and acid-base character of clam-shell waste, in hopes of providing scientific and technical bases for recycling shell waste, especially for use in the polymer industry.

2. IGC theory

2.1. Adsorption behavior of molecular probes

In IGC, the term "inverse" indicates that the solid state materials to be characterized was packed into the chromatographic column and this material was probed by known gas mixtures which were injected into the column [20]. The injection of known molecule probes enabled us to characterize the surface properties of the packed materials. The stationary phase characterization was achieved by partitioning the sample between the mobile phase and the stationary phase, indicated by the time taken to elute the samples. The molecular probes were injected at infinite dilution in order to rule out lateral probe-probe interactions and favor probe-stationary phase interactions only [21].

The surface partition coefficient K_s of a probe between the mobile phase and the stationary phase is expressed by Eq. (1):

$$K_s = \frac{V_N}{A} \tag{1}$$

where V_N is the net retention volume and A is the total surface area of the stationary phase. V_N is related to the net retention time t_N of the injected molecular probes by Eq. (2), which expresses the level of interaction between the solid surface and an isolated probe [22].

$$V_N = \frac{j}{m} \cdot F \cdot (t_r - t_0) \cdot \frac{T}{273.15} \tag{2}$$

where j is the James-Martin gas compressibility correction factor [23]; m is the samples mass; F is the carrier gas exit flow rate; t_r and t_0 are the retention time of the adsorbing probe and the mobile phase hold-up time (dead time), respectively; T is the column temperature.

Since K_s is an equilibrium constant, we can determine the standard free energy required to transfer a mole of vapor from the gas phase to a standard state on the stationary phase surface using Eq. (3):

$$-\Delta G_a = RT \cdot \ln(V_N) + C \tag{3}$$

where ΔG_a is the change in Gibbs free energy due to adhesion; R is the gas constant; T is the column temperature and C is a constant that takes into account the weight and the surface area of the stationary phase and the reference standard states of the probe in the mobile and adsorbed phases [24].

The total surface energy of solid materials is often divided into two components: dispersive (γ_s^d) and specific (γ_s^{sd}). Dispersive (apolar) interactions, also known as Lifshitz-van der Waals interactions, consist of London, Keesom and Debye interactions. Specific (polar) interactions explain all other types of interactions.

2.2. Dispersive interactions

A standard method of surface characterization is that the dispersive component γ_s^d is first determined using a series of linear alkane liquids (n-alkanes) as molecular probes; then the acid-base parameters can be calculated from the dispersive parameters with acid-base liquid probes. For the calculation of γ_s^d, two different methods-Dorris–Gray [25] and Schultz [26] – are usually used.

2.2.1. Dorris–Gray method

A standard IGC method for determining γ_s^d of the stationary phase relies on a series of linear alkane molecular probes. The adsorption energy for the n-alkanes increases with the carbon numbers in the chain. The n-alkane line is obtained by plotting the adsorption free energy of probes against the carbon number n of the injected alkane probes. According to Dorris & Gray, the slope corresponds to the increment of free energy per methylene groups (ΔG_{CH_2}) and the ΔG_{CH_2} is given by Eq. (4):

$$\Delta G_{CH_2} = -RT \cdot \ln\left(\frac{V_{N,n+1}}{V_{N,n}}\right) \tag{4}$$

where R is the gas constant 8.31 J mol^{-1} K^{-1}; T is the temperature; $V_{N,n}$ and $V_{N,n+1}$ are the retention volumes of two n-alkanes probes with carbon numbers n and $n+1$. This last parameter is independent of the chosen state of the adsorbed molecule. Thus, at constant temperature, for a series of alkane probes, a plot of the adsorption free energy against the number of carbon atoms should give a straight line from which ΔG_{CH_2} can be found.

According to the Fowkes's relation for the work of adhesion (W_a) by dispersive free energy between two phases [27], for one methylene group, the work of adhesion is:

$$W_{aCH_2} = 2\sqrt{\gamma_s^d \cdot \gamma_{CH_2}} \tag{5}$$

where γ_{CH_2} is the surface dispersive free energy of a solid material constituted solely of methylene groups, such as linear polyethylene [$\gamma_{CH_2} = 35.6 + 0.058(293 - T)$]. According to Eq. (6):

$$-\Delta G_{CH_2} = N_A \cdot a_{CH_2} \cdot W_{aCH_2} \tag{6}$$

where N_A is Avogadro's number 6.022E23 mol^{-1}, and a_{CH_2} is the cross sectional area of an adsorbed methylene group (6 Å^2). Thus, the surface dispersive free energy of the solid stationary phase can be obtained by Eq. (7):

$$\gamma_s^d = \frac{1}{4\gamma_{CH_2}} \left(\frac{-\Delta G_{CH_2}}{N_A \cdot a_{CH_2}}\right)^2 \tag{7}$$

When combining Eq. (4) with Eq. (7), we can obtain:

$$\gamma_s^d = \frac{1}{4\gamma_{CH_2}} \left(\frac{RT \cdot \ln\left(\frac{V_{N,n+1}}{V_{N,n}}\right)}{N_A \cdot a_{CH_2}}\right)^2 \tag{8}$$

2.2.2. Schultz method

The basic principle of the Schultz method is: when a series of liquid n-alkanes are used as probes, the γ_s^d of a probe with the carbon number n is:

$$\gamma_s^d = RT \cdot \ln(V_{N,n}) + C \tag{9}$$

where V_N is the net retention volume of n-alkanes and the constant C depends on the reference state. According to the Fowkes's relation for the work of adhesion by dispersive free energy between two phases, the work of adhesion of the probe is:

$$Wa = 2\sqrt{\gamma_s^d \cdot \gamma_l^d} \tag{10}$$

where γ_s^d and γ_l^d are the dispersive components of the surface energies of the solid stationary phase and liquid alkane (probe), respectively.

Then, according to Eq. (11):

$$-\gamma_s^d = N_A \cdot a \cdot Wa \tag{11}$$

where a is the cross section area of the alkane molecule.

Combining Eqs. (9)–(11) obtains the following equation:

$$\mathrm{RT} \cdot \ln(V_{N,n}) = 2N_A \cdot a \cdot (\gamma_l^d)^{0.5} \cdot (\gamma_s^d)^{0.5} + C \tag{12}$$