

Study on the Surface Properties of Grafted Polyethylene Particles by Inverse Gas Chromatography

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ABSTRACT: Inverse gas chromatography (IGC) studies on the surface of polyethylene (PE) particles grafted with acrylic acid and acryl amide have been reported. Surface properties of the virgin and grafting-modified PE were compared by IGC. The dispersive contributions of the surface free energy γ_s^d and the K_A and K_B parameters expressing the ability of the stationary phase to act as Lewis acid or Lewis base were calculated. The results showed that the γ_s^d value increased significantly after grafting. The PE samples

grafted with acrylic acid and acrylamide showed a predominantly basic character while the virgin PE was acidic. All of these suggested that the surface of PE has been modified through the grafting reaction, and thus is expected to improve its adhesions with other polymers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 4049–4053, 2008

Key words: polyethylene; enzymatic grafting; inverse gas chromatography

INTRODUCTION

Polyethylene (PE) has some excellent properties, which is advantageous for their technical application,¹ but the nonpolar surfaces characteristic limited its field of use. To make blends and composites or to improve the adhesion of PE, it is necessary to introduce polar groups into the surface of PE.

The mechanical properties of materials with two or more components are strongly influenced by the properties of the interface or interphase upon the other. In case where there is no chemical bonding between the components and the surface of the material is smooth, the interaction between the components is of physical nature and the strength of the dispersive and acid-base interaction forces is essential for the adhesion between the components and therefore for the properties of the material. For a specific design of interfaces (and interphases), it is essential to know the surface thermodynamics of the components. Inverse gas chromatography (IGC) at infinite dilution is a straightforward and very sensitive technique for the characterization of polymer systems.^{2,3} The IGC is based on interactions of known probe molecules with an unknown sample that serves as stationary phase of a chromatographic column. From these interactions, sample properties can be concluded. In recent

years, numerous parameters such as degree of crystallinity,⁴ glass transition and melting temperature,⁵ solution parameters,⁶ enthalpy of mixing, enthalpy of adsorption,⁷ and interaction parameters of polymer-polymer systems⁸ had been determined by IGC. IGC was also successfully used to evaluate the dispersive and acid-base surface characteristics of polymers.^{9–11} K_A and K_B parameters reflecting the ability of the examined surface to act as an electron acceptor and donor (respectively) were calculated using the specific interaction contribution to the adsorption enthalpy of the selected probe molecules.¹² Of all the methods available for investigating the surfaces of polymers, IGC has been useful for this type of work.¹³

This study compared the surface properties of PE before and after grafting modification by IGC. The properties of the polymers were compared by means of dispersive contributions of the surface free energy, which is a measurement of dispersive interactions, as well as the K_A and K_B values, which describe the ability of a polymer surface to act as electron acceptor or donor. The results showed that the dispersive contributions of the surface free energy γ_s^d increased after grafting, and the grafted PE showed a predominantly basic surface though the virgin PE surface exhibits an acidic character.

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EXPERIMENTS

Materials

Acrylamide (AAm) was purchased from Tianjin Si Tong chemical company (Tianjin, China); hydrogen

peroxide, hexane, heptane, trichloromethane, and benzene were purchased from Xi'an Chemical Reagent (Shaanxi, China); pentane, acrylic acid (AA), octane, nonane, *o*-methoxy-phenol, pyridine, and 1,4-dioxane were purchased from Shanghai Chemical Reagent; acetone was purchased from Tianjin Chemical Reagent (Tianjin, China). Tetrahydrofuran was purchased from Tianjin Bodi Chemical (Tianjin, China). All the solvents used are of analysis grade.

Powders of PE purchased from Yang Zi Chemical (Nanjing, China) were modified by AAm and AA with horseradish peroxidase as previously reported.¹⁴ The diameter of the actual particles of PE is 300 μm , which is determined by Fluorescence Microscope IBE-2003 purchased from Chongqing Photoelectric (Chongqing, China) with object glass LPL4/0.10-160/1.5. The particle size of the powders was not changed during the modification procedure.

IGC measurement

Adsorption properties of the prepared polymer samples were examined using a Hewlett-Packard 6890 gas chromatography, with a flame ionization detector (FID) maintained at 150°C. The detector was operated in its maximum sensitivity mode and Hewlett-Packard Chemstation software was employed to collect the data. To ensure flash vaporization of the adsorbate vapor, the injector was set at 150°C. Dry nitrogen at a flow rate in the range from 15 to 18 cm^3/min was used as the carrier gas, whereas methane as an unretained compound was used to determine the dead volume.

Before packing, the columns were weighed. The stationary phase was introduced via a funnel, small additions being made alternately to each end of the column. The column was then tapped gently for several minutes to allow the polymers to achieve even packing, following each addition of the stationary phase. This procedure was continued until the column was filled within -6 mm of the ends. The stationary phase was then retained in the column by the introduction of small plugs of silanized wool. The column was then reweighed and the mass of the support contained in the column was obtained by the difference. After that, the column was conditioned overnight at 150°C before measurement. A homologous series of *n*-alkanes was used to investigate dispersive interactions of the polymer surfaces. Chloroform, benzene, THF, dioxane, and pyridine were all used as polar probes.

RESULTS AND DISCUSSION

Enthalpy and entropy of adsorption

The primary measurement in IGC is the net retention volume V_n . The standard free energy change of adsorption, ΔG_a° , is related to V_n by:

$$\Delta G_a^\circ = -RT \ln V_n + C \quad (1)$$

where C is a constant depends on the standard states chosen for the free energy. The approach of de Boer¹⁵ is commonly adopted and hence, ΔG_a° can be calculated over a series of temperature from measurement of V_n allowing the calculation of the enthalpy of adsorption.

$$\Delta G_a^\circ = \Delta H_a^\circ - T\Delta S_a^\circ \quad (2)$$

Thus, if ΔG_a° is plotted versus T , ΔH_a° can be calculated from the intercept and ΔS_a° the slope, with the assumption that both parameters do not depend on temperature over the range investigated.

The plots of ΔG_a° versus temperature for a series of alkane probes on the 20% AA-g-PE (acrylic acid grafted on PE) are shown in Figure 1, the enthalpies of adsorption for the probes were determined and given in Table I. It can be seen that the ΔG_a° values decreases with the increasing temperature for all alkane probes used. And the ΔH_a° values of the virgin polymer were large, whereas after grafting, the ΔH_a° values decreased significantly. The degree of surface modification of PE by IGC had been evaluated, and the strong correlation between the degree of coating and adsorption enthalpy also had been found.¹² Thus we may conclude that the decrease of ΔH_a° is caused by the grafting reaction, which changed the surface polarity of PE.

Determination of the dispersive component of the surface free energies

For a given adsorbate, the standard free energy change of adsorption (ΔG_a°) is the sum of energies of adsorption attributed to dispersive and specific inter-

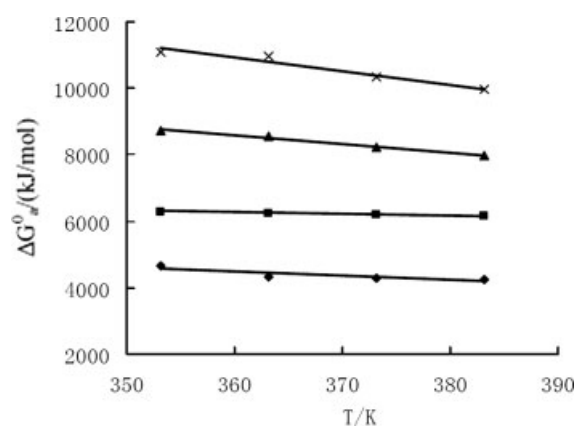


Figure 1 The plots of ΔG_a° versus temperature for a series of alkane probes on the 20% AA-g-PE, hexane probes \square , heptane probes \blacksquare , octane probes \blacktriangle , nonane probes \times .

TABLE I
Enthalpies of Adsorption and Entropies of Adsorption of the Probes
on Polymer Samples

| Polymer sample | Heptane | | Octane | | Nonane | |
|----------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| | $-\Delta H_a^\circ$ | $-\Delta S_a^\circ$ | $-\Delta H_a^\circ$ | $-\Delta S_a^\circ$ | $-\Delta H_a^\circ$ | $-\Delta S_a^\circ$ |
| Virgin PE | 11,190 | 21.82 | 197,77 | 30.72 | 30,749 | 50.47 |
| 10% AA-g-PE | 9703.2 | 10.33 | 18,945 | 29.66 | 30,030 | 50.47 |
| 20% AA-g-PE | 8092.6 | 19.13 | 17,893 | 25.89 | 25,532 | 40.57 |
| 10% AAm-g-PE | 10445 | 14.63 | 19,273 | 27.26 | 24,608 | 32.77 |
| 20% AAm-g-PE | 9636.6 | 8.628 | 18,126 | 25.52 | 22,475 | 31.78 |

actions. Adsorption of nonpolar adsorbates, such as n -alkanes, is caused by dispersive interactions, whereas for polar adsorbates both London and acid-base interactions contribute to ΔG_a° :

$$\Delta G_a^\circ = \Delta G_a^d + \Delta G_a^s \quad (3)$$

where ΔG_a^d and ΔG_a^s are the dispersive and the specific components of standard free energy change of adsorption, respectively.

The ΔG_a° result is equal to the ΔG_a^d result for n -alkanes and it changes with the number of carbon atoms in the molecules. The increment of adsorption energy corresponding to the methylene group may be calculated from $\Delta G_{\text{CH}_2} = -RT \ln (V_{N,n}/V_{N,n+1})$, where $V_{N,n}$ and $V_{N,n+1}$ are the net retention volume of two consecutive n -alkanes having n and $(n + 1)$ carbon atoms, respectively. This parameter is independent of the chosen state of the adsorbed molecule. Therefore, γ_s^d can then be calculated from

$$\gamma_s^d = \frac{(-\Delta G_{\text{CH}_2})^2}{4N^2\alpha_{\text{CH}_2}^2\gamma_{\text{CH}_2}} \quad (4)$$

where N is Avogadro's number; γ_{CH_2} is the surface tension of a hypothetical surface containing only methylene groups ($\gamma_{\text{CH}_2} = 36.8 - 0.058 T$ ($^\circ\text{C}$) mJ/m^2) and α_{CH_2} is the cross-sectional area of methylene groups ($\approx 0.06 \text{ nm}^2$).³ Thus at constant temperature,

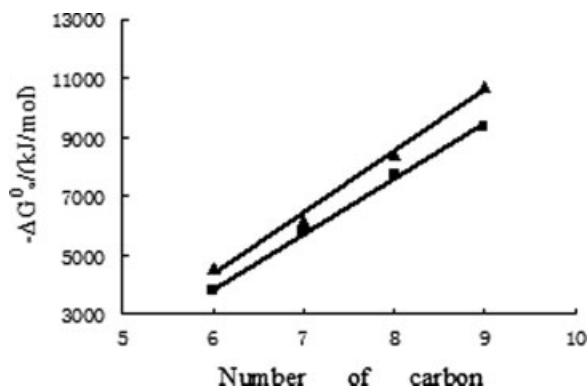


Figure 2 The plot of $-\Delta G_a^\circ$ versus carbon number of alkane probes at 363 and 383 K on 10% AAm-g-PE, 383 K ■, 363 K ▲.

for a series of alkane probes, a plot $RTLnV_n$ versus the number of carbon atoms should give a straight line from which ΔG_{CH_2} can be obtained.

The plot of $-\Delta G_a^\circ$ versus carbon number of alkane probes at 363 and 383 K on 10% AAm-g-PE (acrylamide grafted on PE) is shown in Figure 2. The relationships between the γ_s^d value and the temperature on all the polymer samples were determined; the results are shown in Table II. For all the samples, the γ_s^d values of the grafted PE obviously increased compared to the virgin PE. That is because the surface of the AA-g-PE and the AAm-g-PE were changed to be rough after modification. The γ_s^d values also gradually decreased with increasing temperature, which is in consistent with the literature.¹⁶ In our experiment, the γ_s^d values of grafting-modified PE increased significantly when compared with the virgin PE. These changes may be caused by the introduction of stronger polar groups such as $-\text{CO}$ and NH_2 . In addition, there is little different between the AA-g-PE and the AAm-g-PE in the table. That is because the nonpolar groups in the two molecular formulas are the same.

Evaluation of the acid-base properties

Acid-base interactions are important components of polar forces and play a significant role in adhesion of AA and AAm to the PE surface. The presence of acid and base sites on the polymer surface also enhances the possibility of specific intermolecular interactions with solvents, other polymers or fillers, which is of significance to the composite or blend performance.¹⁷ In this work, the ΔG_a^s values were obtained by Brookman and Sawyer's method.¹⁸ Sawyer and Brookman plotted $RTLnV_n$ versus the boiling

TABLE II
The Relationships Between the γ_s^d Value and the Temperature on the Polymer Samples

| Polymer sample | 353 (K) | 363 (K) | 373 (K) | 383 (K) |
|----------------|---------|---------|---------|---------|
| Virgin PE | 27.92 | 25.37 | 21.22 | 19.35 |
| 10% AA-g-PE | 34.13 | 31.43 | 29.20 | 26.60 |
| 20% AA-g-PE | 33.86 | 30.70 | 24.60 | 21.71 |
| 10% AAm-g-PE | 32.12 | 26.42 | 22.73 | 21.88 |
| 20% AAm-g-PE | 35.82 | 33.55 | 27.34 | 24.02 |

temperatures of solvents. ΔG_a^s resulted from the distance between the $RTLnV_n$ values of polar solutes and the straight n -alkane line. From its temperature and the enthalpy of specific interactions, ΔH_a^s , can be calculated from

$$\Delta G_a^s = \Delta H_a^s - T\Delta S_a^s \quad (5)$$

where ΔS_a^s is the specific entropy of adsorption. ΔH_a^s results from the slope of the $\Delta G_a^s/T$ versus $1/T$ plot. The ΔH_a^s value is the basis for the estimation of the semiquantitative K_A and K_B parameters, which characterize the Lewis-base properties of surface:

$$-\Delta H_a^s = ANK_B + DNK_A \quad (6)$$

DN and AN are donor and acceptor number introduced by Gutmann,¹⁹ which give information as to whether a solvent is able to act as electron donor or electron acceptor. When $-\Delta H_a^s/AN$, is plotted versus DN/AN, a straight line should be obtained. The slope of the line gives K_A and the intercept K_B .

The plot of $RTLnV_n$ values versus boiling temperature of the respective solvents for 20% AA-*g*-PE were plotted as shown in Figure 3, where the values for the n -alkanes were on a straight line, and the ΔG_a^s values of the polar probes located above the n -alkane line which indicated that the surfaces have both donor and acceptor character resulting from their specific interactions with the Lewis base (THF) and the Lewis acid (CHCl_3). To obtain the characteristic surface parameters K_A and K_B , the ΔH_a^s values related to the donor and acceptor numbers of the solvents according to eq. (6) and the resulting K_A and K_B values which were calculated are summarized in Table III. K_A and K_B reflect the ability of the grafted surface to act as electron acceptors and electron donors respectively. Significant K_A values reflect strong acidity and strong electron accept abilities of

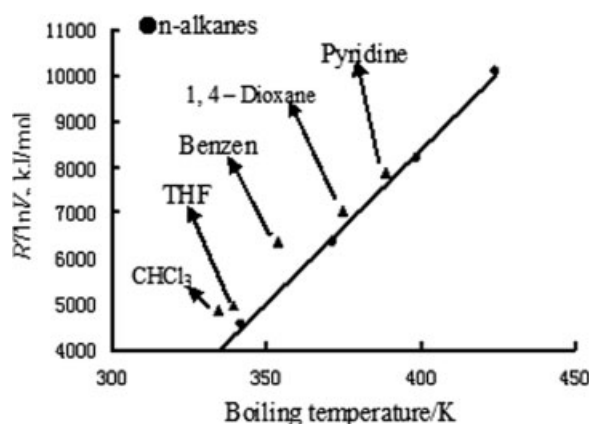


Figure 3 The plot of $RTLnV_n$ values versus boiling temperature of the respective solvents for 20% AA-*g*-PE, n -alkanes ●.

TABLE III
Determining the K_A and K_B Parameters of the Polymer Samples

| Polymer sample | K_A | K_B | K_B/K_A |
|-----------------------|-------------------|-------------------|-----------|
| Virgin PE | 0.328 ± 0.022 | 0.189 ± 0.018 | 0.576 |
| 10% AA- <i>g</i> -PE | 0.623 ± 0.015 | 1.981 ± 0.031 | 3.179 |
| 20% AA- <i>g</i> -PE | 0.473 ± 0.031 | 4.953 ± 0.024 | 10.46 |
| 10% AAm- <i>g</i> -PE | 0.189 ± 0.019 | 1.348 ± 0.027 | 7.120 |
| 20% AAm- <i>g</i> -PE | 0.772 ± 0.021 | 3.272 ± 0.023 | 4.240 |

compounds. The overall acid/base character of the polymers can be evaluated from the ratio of K_B/K_A ration. For example, for $K_B/K_A > 1$, the surface is considered to be basic, and for $K_B/K_A < 1$ acidic. It can be seen that grafting with AA and AAm caused basic behaviors of the PE samples. Consequently, as seen from the data in Table III, the surface of the virgin PE showed acidic character and the surface of the grafted polymers all exhibits predominantly basic character. These changes may result from the polar groups introduced by enzymatic grafting, which may produce more active center on the polymer surface, and hence changed the acid/base character of the surface. An increasing amount of AA and AAm causes an increasing donor character of PE surface, subsequently an increasing of K_B values. As listed in the table, the K_B values of AA increase greater than the K_B values of AM. These may caused by the two isolated electron pairs on the oxygen atom, which shows a stronger donor character, and the one isolated electron pairs on the nitrogen atom, which shows a relative small donor character.

CONCLUSIONS

In our previous work, PE was enzymatically grafted with vinyl monomer in the mixed solvents of water and dioxane.¹⁴ This study compared the surface properties of PE before and after grafting modification by IGC. It was shown that after grafting reaction, the dispersive contributions of the surface free energy γ_s^d increased significantly and for all the samples investigated, the γ_s^d values showed a good linear dependence on the column temperature. K_A and K_B parameters expressing the ability of the stationary phase to act as Lewis acid or Lewis base were calculated, and the results showed that the surface of virgin PE exhibits an acid character, and the surface of the grafted PE showed its predominantly basic character.

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