

Characterisation of the surface Lewis acid–base properties of poly(butylene terephthalate) by inverse gas chromatography

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Abstract

The surface of poly(butylene terephthalate) (PBT) was analysed by means of inverse gas chromatography (IGC). The specific component of the adsorption of polar probes on the surface of poly(butylene terephthalate) was found to be endothermic, and the change in the entropy of the system, positive, which is not a common case in IGC. An interpretation is given, based on the contribution of cleavage of hydrogen bonds in the PBT and formation of hydrogen bonds between the probe-molecules and the polymer. The surface Lewis acidity and basicity constants, K_a and K_b , respectively, were determined and found to correlate well with an analysis of the repeating unit and end-groups in this polymer.

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1. Introduction

This study is part of a broad investigation dealing with the acid–base interactions in pigmented, impact-modified, semi-crystalline/amorphous polymer blends. The surface of poly(butylene terephthalate) (PBT) was analysed by means of inverse gas chromatography (IGC). The parameters determined were the dispersive component of the surface free energy, the enthalpy and entropy of adsorption of polar probes and of apolar probes, and the surface Lewis acidity and Lewis basicity constants, K_a and K_b , respectively.

The analysis of the surface Lewis acidic/basic properties of PBT is particularly interesting because

this material is a partially crystalline polymer, with very good chemical resistance and thermal stability. It is widely used in commercial pigmented, impact-modified, semi-crystalline/amorphous polymer blends. IGC, at infinite dilution, was used as a tool to assess the surface properties, in terms of Lewis acidity/basicity, and as a contribution to a better understanding of the influence of these characteristics on the physical and the mechanical properties of poly(butylene terephthalate).

No reference has been found in the literature concerning the study of the surface properties (surface free energy, surface Lewis acidity and surface Lewis basicity) of poly(butylene terephthalate), by means of IGC. The only reference found in the literature, regarding surface tension studies on PBT, made use of contact angle measurements to determine the dispersive component of the surface tension. From that value, the specific component of the surface tension (without quantifying the contribu-

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tion of the Lewis acidic sites and of the Lewis basic sites) was evaluated [1].

Another aspect of relevance in this study is the fact that the specific component of the enthalpy of adsorption of the polar probes on the surface was found to be positive (endothermic adsorption). This is not the common case in the IGC literature. The specific component of the enthalpy of adsorption of polar molecules on polymeric surfaces and inorganic particulate surfaces is usually reported to be negative (exothermic adsorption). Nevertheless, endothermic values for the specific component of the adsorption energy have been reported in the literature, for the adsorption of polar probe molecules on a surface-treated titanium dioxide pigment [2], and on a copolymer of vinyl acetate and vinyl alcohol [3]. The endothermic nature of the adsorption and the increase of the system's entropy, upon adsorption of polar probes on PBT, is interpreted in terms of the balance of the contribution, for the adsorption process, of the breaking of existing hydrogen bonds within the PBT and of the formation of new hydrogen bonds between the probe molecules and the PBT molecules.

2. Experimental

2.1. Materials

The poly(butylene terephthalate) (Valox[®]) was supplied by GE Plastics Europe, Bergen op Zoom, The Netherlands. The weight-average molar mass, polydispersity, and number-average molar mass of this polymer are 46,000 g/mol, 2.70 and 17,000 g/mol, respectively (source: GE Plastics Europe). The glass transition temperature and the melting temperature of PBT are 318 K and 503 K, respectively (determined by DSC, at the Department of Colour Chemistry, University of Leeds, UK).

For the IGC analysis, analytical grade probes were used without further purification. The apolar probes used were *n*-heptane, *n*-octane, *n*-nonane, *n*-decane. The polar probes used were tetrahydrofuran (THF), acetone (Acet), diethyl ether (DEE), trichloromethane (TCM), dichloromethane (DCM), and ethyl acetate (EtAcet). All of these chemicals were obtained from Sigma–Aldrich, Poole, UK. Methane

(Phase Separations, Deeside, UK) was used as a non-interacting reference probe and the carrier gas utilised was helium (99.999+% purity, BOC Gases, Guildford, UK).

2.2. Inverse gas chromatography

The instrument used was a Fisons GC9100 unit, equipped with flame ionization detection (FID) system (Fisons, Loughborough, UK). The injector was heated to 423 K and the FID detector to 453 K. The attenuation was set to 1. The probe was injected manually, using a 1.0- μ l Hamilton syringe. Typically, the syringe was filled with 0.1 μ l of gaseous probe and flushed with air around 10 times. This allows a small amount of probe to be transferred to the column, in order to ensure the creation of a Henry's infinite dilution region. The carrier gas flow-rate was controlled using a needle valve pressure regulator and determined using a bubble flow meter that was equipped with a helium trap and thermometer. The inlet pressure, P_{in} , was measured using a pressure gauge and the atmospheric pressure, P_o , was obtained through The British Atmospheric Data Centre (www.badc.rl.ac.uk).

The columns were cut from stainless steel tubing and shaped in a smooth "U" shape to fit the detector/injector geometry of the instrument. The dimensions of the columns were 0.5 m (length), with an outside and inside diameter of 6.4 and 4.4 mm, respectively. Cleaning was achieved via sequential rinsing with a hot aqueous detergent solution (Decon[®] 90 5%, from Sigma–Aldrich), followed by acetone and drying at 423 K, in a vacuum oven, for 1 day.

Prior to 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 support to achieve even packing, following each addition of the stationary phase. This procedure was continued until the column was filled to within \sim 6 mm of the ends. The stationary phase was then retained in the column by the introduction of small plugs of silanised wool. The column was then re-weighed and the mass of support contained in the column was obtained by difference.

Due to the lack of an appropriate solvent for PBT, it was not possible to coat a support material such as Chromosorb. Therefore, the polymer was used after processing it in a grinder that was cooled with liquid nitrogen, to achieve an appropriate particle size. The polymer particles were then sieved through 125 μm and 250 μm filter gauzes. The column was filled with the particles. For IGC characterisation of the surface of PBT, and bearing in mind the T_g of PBT (318 K), the temperature range used was 295–318 K, in 5 K increments, and the flow-rate 10 ml/min. For IGC characterisation studies concerning the bulk PBT, the temperature range used was 353–393 K, in 20 K increments, and the flow-rate range used was 5 to 30 ml/min.

Prior to measurement, each column was conditioned overnight at a temperature that was identical to the highest temperature of the IGC studies, under a helium flow-rate of ~ 10 ml/min. This was to ensure the removal of any residual volatiles, which could otherwise have affected the retention of the probes on the material being studied.

2.2.1. IGC data processing

IGC data processing was carried out according to customary methods, well described in the literature (see for instance Ref. [4]). The retention time of the probe molecules was determined using the geometric technique outlined by Condor and Young [5]. This is necessary due to the “tailing” exhibited by some of the peaks obtained using polar probes. At least three retention times were obtained for each probe and the mean value used for further calculations, the standard deviation being less than 5%.

The value of the net retention volume, V_n , was calculated according to Eq. (1):

$$V_n = (t_r - t_0)FCJ \quad (1)$$

Here, t_0 is the retention time of a non-interacting probe species, (either air, or more commonly, methane), F is the carrier gas flow-rate, J is a term that corrects for the compressibility of the carrier gas and C is a correction factor, allowing for the vapour pressure of the water at the temperature of the bubble flow meter used to determine the flow-rate.

The free energy of adsorption, $-\Delta G_a$, and the dispersive component of the surface tension, γ_s^d , were determined using Fowkes approach [6] (Eq.

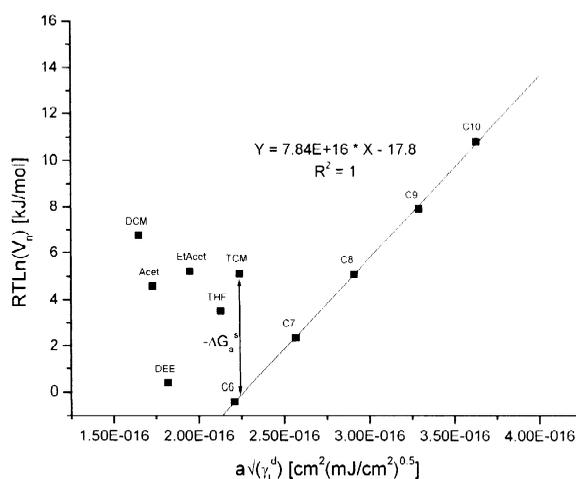


Fig. 1. Surface free energy of adsorption vs. $a\sqrt{\gamma_1^d}$, for the surface adsorption of n -alkanes, and polar probes, on PBT, at 295 K.

(2)) with values for the probe's surface area given by Schultz and Lavielle [7]. The procedure is illustrated in Fig. 1 for the surface adsorption of n -alkanes, and polar probes, on PBT, at 295 K:

$$-\Delta G_a = RT \ln(V_n) = 2N_A a(\gamma_s^d)^{0.5}(\gamma_1^d)^{0.5} + K'' \quad (2)$$

Here, T is the temperature, R the ideal gas constant, N_A is Avogadro's constant, “ a ” is the molecular surface area of the adsorbed species, γ_s^d and γ_1^d are the dispersive component of the surface free energy of the solid and the probe, respectively, and K'' is a constant related to the reference gas pressure and the reference surface pressure. From a plot of $-\Delta G_a$ against $a(\gamma_1^d)^{0.5}$, for the adsorption of n -alkanes, the value of γ_s^d is calculated.

The free energy of adsorption of TCM and THF on the bulk PBT was evaluated by determining the free energy of adsorption of these probes at different carrier gas flow-rates, and extrapolating the data to zero flow-rate, as described in the literature when the bulk of semi-crystalline polymer is to be studied [8]. The procedure is illustrated in Fig. 2 for the temperature of 373 K.

The value of the specific component of the energy of adsorption, $-\Delta G_a^s$, was determined by the method outlined in Fig. 1, and corresponds to the difference between the total free energy of adsorption, $-\Delta G_a$,

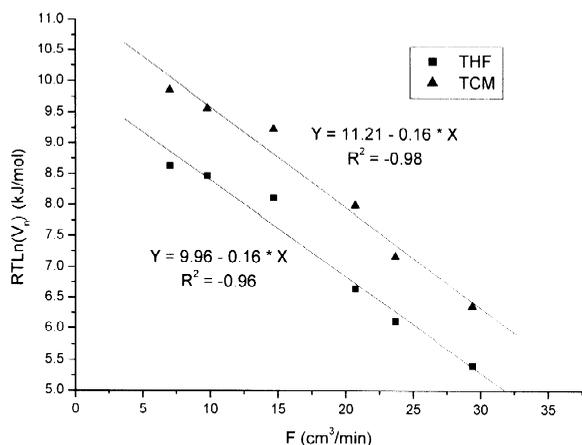


Fig. 2. Determination of the free energy of adsorption of TCM and THF, on the bulk PBT, at 373 K.

and the dispersive component of the free energy of adsorption, $-\Delta G_a^d$, as determined using the n -alkanes reference line (Eq. (3)):

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

The enthalpy of adsorption and the entropy of adsorption of the probes used were calculated from the slope and intercept of $-\Delta G_a/T$ vs. $1/T$, respectively, according to Eq. (4). The procedure is illustrated in Fig. 3, for the determination of the

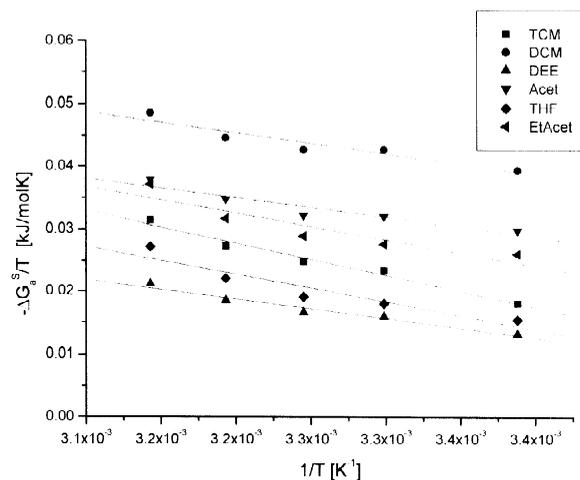


Fig. 3. Determination of the specific component of the enthalpy of adsorption, and the entropy of adsorption, of the polar probes, on PBT.

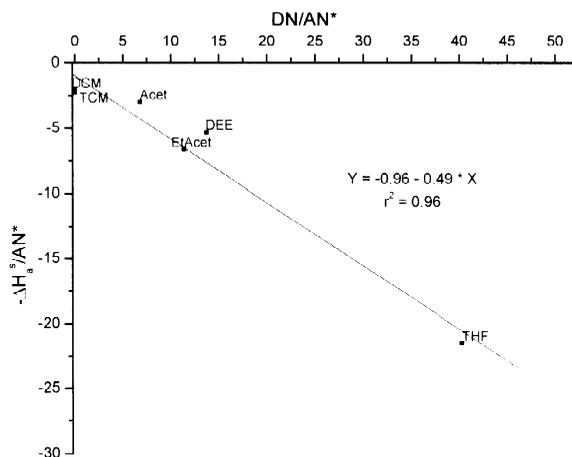


Fig. 4. Determination of K_a and K_b for the surface of PBT.

specific component of the enthalpy of adsorption, and of the entropy of adsorption, of the polar probes, on PBT:

$$\Delta G_a = \Delta H_a - T\Delta S_a \quad (4)$$

The values of K_a and K_b were calculated using Eq. (5) [4]:

$$-\Delta H_a = K_a \cdot DN + K_b \cdot AN^* \quad (5)$$

Here DN and AN* are Gutmann's donor and modified acceptor numbers, respectively, corresponding to the polar probes [6,9]. Representing $-\Delta H_a^s/AN^*$ versus DN/AN^* , one gets K_a as the slope and K_b as the intercept (Fig. 4).

3. Results

3.1. Dispersive component of the surface free energy of PBT

The value determined for the dispersive component of the surface free energy of PBT was $42.3 \pm 1.52 \text{ mJ/m}^2$ (average value for the temperature range studied). The only reference found in the literature regarding surface tension studies on PBT is a contact angle measurement with a value of 52.4 mJ/m^2 at 293 K [1]. From the data presented in Ref. [1], the component derived from specific forces is 12.4 mJ/m^2 , and the component resulting from

dispersive forces is 40.0 mJ/m^2 . Thus, the value found in the present study agrees very well with the data published. Furthermore, for poly(ethylene terephthalate) (PET), using IGC at infinite dilution and contact angle measurements, the values found for γ_s^d are quite close to the value for PBT determined in this study, which agrees with expectation bearing in mind the chemical similarity between these two polymers. For PET, using IGC at infinite dilution, the values of 44.6 mJ/m^2 at 293 K [10], and 40 mJ/m^2 [11] (average value for the temperature range 288–313 K) were found. For the same polymer, from contact angle measurements, the values of 41 mJ/m^2 [12] and 43.2 mJ/m^2 [11] are also mentioned in the literature.

3.2. Adsorption of polar probes on PBT

The values determined for the specific component, and for the dispersive component, of the energy of adsorption of the polar probes on PBT, are summarised in Table 1. The values for the energy of adsorption of the polar molecules on the bulk PBT are summarised in Table 2.

As far as the adsorption of TCM and THF on the bulk of PBT is concerned, it was not possible to determine the dispersive component (and, thus, the specific component) of the energy of adsorption, due to difficulties relating to the penetration of large *n*-alkane molecules, such as *n*-nonane and *n*-decane, into the bulk of this polymer. In order to overcome this problem, measurements were made at 423.15 K, so as to facilitate the penetration of the *n*-alkane probe-molecules. However, the noise level in the chromatogram, even after conditioning the column overnight at this temperature and at a high flow-rate,

Table 2

Enthalpy of adsorption, and entropy of adsorption, of TCM and of THF, on the bulk PBT

Probe	$-\Delta H_a$ (kJ/mol)	ΔS_a (kJ/mol K)	r^2
TCM	-11.7	0.063	0.90
THF	-14.5	0.067	0.98

was too high to allow for the determination of the retention times of any of the probe molecules. Nevertheless, the endothermic character of the adsorption of TCM and THF on the bulk of PBT confirms the results obtained for its surface.

The specific component of the adsorption energy of polar probes on the surface of PBT is endothermic. Although this is quite unusual, endothermic adsorption processes have been reported in the literature for the adsorption of polar probe molecules on a surface-treated titanium dioxide pigment [2], and on a copolymer of vinyl acetate (94.8 mol.%) and vinyl alcohol [3].

The adsorption of polar probes on a surface occurs via dispersive and specific intermolecular forces. In the case of dispersive forces, ΔH_a is always negative and smaller than $T\Delta S_a$ [13]. The specific interactions originate mainly from the interaction between the Lewis acidic sites and the Lewis basic sites in the interacting species. In the particular case of PBT, bearing in mind its molecular structure, the dominant specific interactions are H-bonds. Therefore, chemisorption, and rearrangement of the surface upon adsorption of polar molecules are thought to occur [13], leading to an increase in the entropy of the system (Table 1). An increase of the system's entropy implies an increase in the number of degrees of freedom and a considerable increase in the

Table 1

Specific component, and dispersive component, of the enthalpy of adsorption, and of the entropy of adsorption, of the polar probes, on the surface of PBT

Probe	Specific component			Dispersive component		
	$-\Delta H_a^s$ (kJ/mol)	ΔS_a^s (kJ/mol K)	r^2	$-\Delta H_a^d$ (kJ/mol)	$-\Delta S_a^d$ (kJ/mol K)	r^2
TCM	-51.5	0.193	0.98	47.8	-0.174	0.97
DCM	-34.2	0.155	0.90	43.8	-0.176	0.94
DEE	-31.2	0.119	0.96	44.9	-0.176	0.95
Acet	-31.2	0.135	0.90	44.3	-0.176	0.94
THF	-44.9	0.167	0.90	47.0	-0.175	0.96
EtAcet	-41.9	0.166	0.84	45.8	-0.175	0.95

disorder of the system. This may be the case, if the entropy of the adsorbent increases sufficiently owing to adsorption. The experimentally verified phenomena of swelling, adsorbent expansion, dissolution of the adsorbate in the adsorbent structure, and re-arrangement of the surface layers due to chemisorption, support this idea [13].

The enthalpy of formation of the individual hydrogen bond is always negative. However, the overall enthalpy (and entropy) associated with the formation of hydrogen bonds will depend on the balance between three contributions [14]:

- a positive contribution to the enthalpy (and entropy), that is the result of breaking hydrogen bonds in the self-associating polymer;
- a negative contribution to the enthalpy (and entropy), that is the result of forming hydrogen bonds between the self-associating polymer and the adsorbent molecule;
- contributions from other interactions (van der Waals, dipole forces, etc.)

The specific component of the energy of adsorption (Table 1) quantifies the contribution from the breaking and forming of H-bonds, alongside with the contribution from dipole–dipole forces. On the other hand, the dispersive component of the energy of adsorption (Table 1) quantifies the Van der Waals interactions. With respect to the adsorption of polar groups on PBT, the positive contribution to the enthalpy (and entropy) of adsorption due to the breaking of hydrogen bonds in the self-associating polymer is thought to dominate. This results in an endothermic adsorption, and increased entropy of the system. A necessary condition for adsorption of a

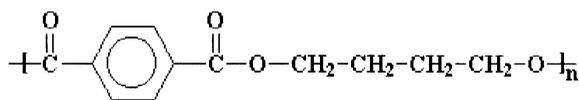


Fig. 5. Repeating unit in PBT.

molecule on a surface is the existence of a negative value of the free energy change, ΔG_a , of the entire system, between the initial state and the final state with adsorption. In the system under study, the value of $T\Delta S_a$ is greater than the value of ΔH_a and, thus, the thermodynamic condition for adsorption to occur is obeyed.

Agreeing with expectation, the dispersive component of the energy of adsorption (Table 1) is exothermic and the corresponding change in entropy is negative. Furthermore, the values of $-\Delta H_a^d$ increase in the following order: DCM < Acet < DEE < EtAcet < THF < TCM, which is in agreement with the increasing value of $a(\gamma_1^d)^{0.5}$ for the polar molecules (Table 3).

3.3. K_a and K_b for the surface of PBT

The values of K_a and K_b are found to be -0.49 and -0.96 , respectively, (correlation coefficient 0.96). The determination of the surface K_a and K_b , measured below T_g , results in negative values due to the endothermic adsorption of the probe-molecules.

From the values obtained for K_a and K_b , the surface of PBT is shown to be Lewis amphoteric, though more strongly Lewis basic. The values obtained agree well with expectation bearing in mind the structure of this molecule (Fig. 5). The Lewis

Table 3

Values of $a(\gamma_1^d)^{0.5}$ [7,9], DN and AN* [6] for the *n*-alkanes and polar molecules used as probes

Probe molecule	$a(\gamma_1^d)^{0.5}$ ($\text{cm}^2 (\text{mJ cm}^{-2})^{0.5}$)	DN (kJ/mol)	AN* (kJ/mol)
<i>n</i> -Hexane	2.21E-16		
<i>n</i> -Heptane	2.57E-16	–	–
<i>n</i> -Octane	2.91E-16	–	–
<i>n</i> -Nonane	3.29E-16	–	–
<i>n</i> -Decane	3.63E-16	–	–
THF	2.13E-16	84.42	2.10
TCM	2.24E-16	0.00	22.68
DCM	1.73E-16	0.00	16.38
DEE	1.82E-16	80.64	5.88
Acet	1.65E-16	71.40	10.50
EtAcet	1.95E-16	71.82	6.30

basic sites are identified with the ester moiety, the oxygen atoms in the carboxylic end-group, and also with the oxygen atom in the hydroxyl end-group [15]; the Lewis acidic sites are identified with the hydrogen atoms in the $-\text{O}-\text{CH}_2-$ moiety, and with the hydrogen atom in the hydroxyl end-group and in the carboxylic end-group.

The values of K_a and K_b for PBT indicate that the polymer interacts strongly with itself, as it has both strong Lewis basic and Lewis acidic sites. This together with the chemically regular structure of the molecule, and the non-existence of bulky side-groups, provides the structural requirements for crystallinity, and, consequently, for the excellent solvent resistance and thermal stability that are shown by PBT.

4. Conclusions

The specific component of the adsorption of polar molecules on PBT is endothermic. The results have been interpreted assuming a predominant contribution to the enthalpy (and entropy) of adsorption, from the breaking of hydrogen bonds in the self-associating polymer, in relation to the formation of hydrogen bonds between the polar probe molecules and the PBT molecules.

The surface Lewis acidity and surface Lewis basicity, as quantified by K_a and K_b and determined by IGC, alongside the analysis of the physical structure of these polymers, have been useful in the interpretation of the crystallinity, excellent solvent resistance and thermal stability of PBT.

5. Nomenclature

IGC	inverse gas chromatography
PBT	poly(butylene terephthalate)
PET	poly(ethylene terephthalate)
K_a	surface Lewis acidity
K_b	surface Lewis basicity
THF	tetrahydrofuran
Acet	acetone
DEE	diethyl ether
TCM	trichloromethane

DCM	dichloromethane
EtAcet	ethyl acetate
P_{in}	column inlet pressure
P_o	column outlet pressure
V_n	net retention volume
t_r	retention time of the probe molecule
t_o	retention time of methane
F	carrier gas flow-rate
J	correction factor for the compressibility of the carrier gas
C	correction factor for the vapour pressure of the water at the temperature of the bubble flow meter used to determine the flow-rate
$-\Delta G_a$	free energy of adsorption
γ_s^d	dispersive component of the surface tension
T	temperature of measurement
R	ideal gas constant
N_A	Avogadro's constant
a	molecular surface area of the adsorbed species
γ_s^d	dispersive component of the surface free energy of the solid
γ_1^d	dispersive component of the surface free energy of the probe
K''	constant related to the reference gas pressure and the reference surface pressure
$-\Delta G_a^s$	specific component of the energy of adsorption
$-\Delta G_a^d$	dispersive component of the free energy of adsorption
ΔH_a	enthalpy of adsorption
ΔS_a	entropy of adsorption
DN	Gutmann's donor number
AN*	Gutmann's modified acceptor number
M_w	weight-average molar mass
D	polydispersity
M_n	number-average molar mass

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