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Study of a core-shell type impact modifier by inverse gas chromatography

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Abstract

Inverse gas chromatography (IGC) has been used to study the Lewis acid–base properties of a technologically and commercially important core-shell type elastomer (MBS rubber). The parameters determined were the dispersive component of the surface tension, the surface free energy, the enthalpy and the entropy of adsorption of polar and apolar probes, the surface Lewis acidity constant (K_a), and the surface Lewis basicity constant (K_b). The results show that the MBS rubber is amphoteric but strongly Lewis basic. It is weakly Lewis acidic. The results are in accord with the analysis of the molecular structure of PMMA, the shell component of this impact modifier (IM). The interactivity of this elastomer with the remaining materials in multicomponent polymeric systems is expected to be strongly influenced by the particular surface energetic properties of the MBS rubber. The results presented would contribute to the interpretation, forecast and optimization of the adhesion properties and phase preferences shown by this impact modifier when incorporated in such complex polymeric systems as polymer blends and composites.

Keywords: MBS rubber; Impact modifier; Inverse gas chromatography; Acid–base interactions; Core-shell particulates

1. Introduction

Generally speaking, a polymer can be classified as brittle or ductile. Brittle polymers are characterized by having weak crack initiation and usually fail by crazing phenomena. Conversely, ductile polymers have significant crack initiation energy, significant crack propagation energy and break through yielding phenomena. In order to improve the impact strength of a brittle polymer, elastomeric particles of adequate particle size and adhesion characteristics (in relation to the polymeric matrix) are usually included in the composite formulation. It is well established that rubber particles with low moduli act as stress concentrators in both thermoplastic materials and in thermoset resins, favouring the dissipation of the impact energy by enhancing shear yielding and/or crazing, depending on the nature of the matrix, and, thus, improving the impact toughness of the blend. Also, the voids created by the cavitated rubber particles act further as stress concentrators [1]. The inclusion of rubber in polymers does, nevertheless, reduce the elastic modulus and the yield stress [2]. The phase separation between the polymer and the rubber is an important requirement, and mechanical resistance increases if the rubber has low elastic modulus in relation to the matrix, good adhesion to the matrix, adequate crosslinking, optimised average particle size and distribution and low glass transition temperature [2]. The separating distance between the elastomeric zones also plays an important role in the toughening mechanisms.

In the case of PMMA and PS toughening, the impact modifiers (IMs) include: poly(vinyl acetate) (PVAc), copolymers of methacrylonitrile and ethyl acrylate, the ethylene-vinyl acetate-vinyl chloride copolymer (EVAc-VC), the methyl methacrylate-methyl acrylate copolymer (MMMA) and the styrene-acrylonitrile copolymer (SAN). In blends of polymers based on styrene, the styrene-butadiene-styrene

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tri-block polymer (SBS) or the styrene-ethylene/butylene-styrene tri-block polymer (SEBS) are typical impact modifiers. Several elastomeric modifiers have been specifically synthesized for PVC. These are generally core-shell type rubbers with a rubbery core (typically poly(butadiene), styrene-butadiene rubber, poly(*n*-butyl acrylate) that has a rigid grafted outer shell (typically based on systems such as styrene-co-acrylonitrile (SAN), styrene-co-methyl methacrylate (S-MMA) copolymers or PMMA. The PP matrixes contain EPDM (an elastomeric terpolymer from ethylene, propylene and a nonconjugated diene) as the usual impact modifier. In order to improve its impact strength, namely the low temperature notched Izod impact, polycarbonates have been blended with a variety of low T_g, elastomeric impact modifiers, in particular core-shell rubbers such as PMMA-g-polybutadiene, PMMA-g-SBR, and PMMA-g-*n*-butyl acrylate (acrylic core-shell). Commercial impact modified PBT grades generally contain core-shell rubber modifiers, such as: PMMA-g-SBR, PMMA-g-poly(*n*-BuA) (acrylic core-shell rubbers), SAN-g-PBD and SAN-g-poly(*n*-BuA).

The commercially important binary blends of PET/PC and PBT/PC (e.g. Xenoy, Makroblend, Sabre 1600, Stapron E, Ultrablend KR, Dialoy P, Ektar MB, Idemitsu SC, Novadol, Pocan, Sabre) exhibit good ductility and tensile properties but the notched Izod impact strengths are low in blend compositions containing less than 80% of the PC. Thus, the commercial PET/PC and PBT/PC blends typically contain 15–20% (w/w) of an elastomeric impact modifier [3,4]. Typical impact modifiers include poly(methyl methacrylate)-grafted-butadiene-styrene rubber (MBS), poly (MMA-g-*n*-BuA), ABS (with high poly(butadiene) content $\geq$50%), and ASA rubber ($\geq$50% acrylate rubber). Several papers have been published that deal with the inclusion of an elastomer in PC/PBT blends in order to improve the impact resistance of these commercially important blends [5,6].

Among the abovementioned additives, MBS impact modifiers have demonstrated a significant impact-modifying effect at low temperatures [3,5,6] and are the most common impact modifier used in commercial PC/PBT blends. Developed in the 1950’s, the core-shell, emulsion type methyl methacrylate-butadiene-styrene terpolymer (MBS) was originally aimed at improving the impact resistance of PVC and of PC. Currently, there is a great diversity of the MBS copolymer architectures, viz. graft, core-shell, or multilayer types. The MBS rubber used in the impact modification of PC/PBT blends consists of a core of poly(styrene), an inner layer of poly(butadiene) and a shell of poly(methyl methacrylate). The PMMA-shell of this impact modifier gives “good adhesion” with polycarbonates, in which the impact modifier is to be dispersed. The poly(butadiene) is the component that causes the higher impact strength. The poly(styrene) layer has an aesthetic function. It is used in the impact modifier to ensure the proper reflection of light. Functional MBS impact modifiers for PC/PBT blends are also reported in the literature. Tseng and Lee [5] grafted three different types of functional-group containing monomers in the outer layer of the MBS, namely glycidyl methacrylate, acrylamide, and methacrylic acid. The introduction of a functional group to improve the adhesion between the MBS rubber and the PC/PBT alloy has an effect on the impact strength of these blends. The impact strength improved if the amount of functional monomer was between 4 and 6% (w/w), thus allowing a smaller amount of impact modifier to be used in achieving the required specific properties.

The growing awareness of the importance of solid surfaces, interfaces and interphases in determining the useful properties of polymeric systems, has led to the use and the development of inverse gas chromatography (IGC) as a valuable technique for evaluating the potential for interaction of different components of polymer blends, composites, and multicomponent polymeric systems in general. The ability of the IGC technique to provide information concerning the acid–base interaction potentials of polymer surfaces is widely recognised in the literature. Data obtained from IGC experiments may, in favourable cases, correlate directly with observed performance criteria, such as colour development, gloss, rheological properties, adhesion and mechanical properties [7–9].

This study is part of a wider study relating to the analysis and rationalization of the intermolecular interactions that occur in pigmented, impact-modified PC/PBT blends [10]. IGC, carried out at infinite dilution, was used to study the surface Lewis acid–base properties of the major components of pigmented PC/PBT/MBS blends (45/45/10%, w/w). Additionally, the dispersive component of the surface tension of the materials studied was determined, allowing for an assessment of the interaction capability through dispersive forces. These analyses provided the rationale for an interpretation of the phase separation and the phase preferences that exist in these polymer blends and of the consequences of these phenomena to their physical properties and to their mechanical properties.

To the best of our knowledge, inverse gas chromatography has been seldom used to study the thermodynamic properties of core-shell type elastomers. The only study found relates to the characterization of a SBR rubber, below and above its glass transition temperature [8]. The barrier properties, the bulk composition and bulk pores dimension are discussed by Mukhopadhyay and Schreiber. An interaction parameter based on the values of the surface Lewis acidity and basicity constants, K_a and K_b, respectively, is developed. Also, the polar group orientation at polymeric surfaces is addressed. The surface thermodynamic properties are compared to those relating to the bulk of the SBR elastomer.

This paper concerns the study of the surface Lewis acid–base properties, and of the dispersive component of the surface tension, of a poly(methyl methacrylate)-poly(butadiene)-poly(styrene) rubber. These analyses allowed for an evaluation of the specific forces and dispersion forces interaction nature and potential of the MBS rubber.

IGC finite concentration experiments can be carried out aiming mainly the study of the surface chemical heterogeneity, i.e. of the energy distribution of "surface active sites", and determination of surface areas. IGC carried out under infinite dilution conditions is more sensitive to the higher energy sites. The interaction capability of a material is dominated by the higher energy sites. Thus, it was decided to determine the values of K_a and K_b under probe infinite dilution conditions.

2. Experimental

2.1. Materials

The MBS rubber studied was acquired from the Rohm and Haas Company. The glass transition temperature and the melting temperature were determined by DSC as being −70 °C and 132–149 °C, respectively. The average particle size of the MBS rubber is 0.1 μm, from technical data sheets.

For the IGC analysis, analytical grade probes were used without further purification. The apolar probes used were *n*-hexane, *n*-heptane, *n*-octane and *n*-nonane. The polar probes used were tetrahydrofuran (THF), acetone (Acet), diethyl ether (DEE), trichloromethane (TCM), dichloromethane (DCM) and ethyl acetate (EtAcet). In Table 2 are summarised relevant properties of the probe molecules mentioned [9,11–15]. The chemicals used as probe molecules 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). Chromosorb W AW DCMS (from Sigma–Aldrich) was used as the column stationary phase support for the MBS rubber particles.

2.2. Inverse gas chromatography

2.2.1. Column preparation

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 columns were 0.5 m in length, with an outside diameter and inside diameter of 6.4 and 4.4 mm, respectively. Cleaning was achieved via sequential rinsing with a hot aqueous detergent solution (Decon 905%, from Sigma–Aldrich), followed by acetone and drying at 150 °C, in a vacuum oven, for 1 day.

The column stationary phase was prepared using customary procedures, widely described in the IGC literature, for the study of polymers and particulates [16–20]. The MBS rubber stationary phases were prepared by mixing the impact modifier with an "inert" support, Chromosorb W AW DCMS, particle size 60–80 mesh. This procedure is necessary to avoid any undesirable pressure drop in the column, a consequence of the small particle size of the IM particles. The columns studied, along with the quantities of support material, of stationary phase, and of material being analysed, are summarised in Table 1.

2.2.2. IGC data processing

The main difference between conventional gas chromatography (GC) and IGC lies in the fact that the species of primary interest are not the volatile components injected but the material acting as the stationary phase, typically a powder, fibre or film. This material may be packed directly into the column, coated onto a suitable support or coated onto the walls of the column. This allows the investigation of the interactive nature via the degree of interaction with well-characterised volatile liquids/vapours ("probes"). Quantification of this interaction may be achieved by the determination of the retention time, t_r, for a given probe. In most uses, the quantity of probe vapour injected into the carrier gas is extremely small. Thus, the retention data relate to the thermodynamic interaction that occurs between polymer and the vapour when the polymer is highly concentrated, as in most practical situations. Furthermore, IGC experiments may be carried out over appreciable temperature ranges, so that the temperature dependence of thermodynamic interactions is no longer indeterminate.

IGC data processing was carried out according to methods described in the literature (see for instance references [10,13,21,22]. The retention times of apolar probe molecules and of polar probe molecules were determined at specific temperatures, and the values of the retention volume, the energy of adsorption, the enthalpy and entropy of adsorption (dispersive and specific components) of the probes, and of the surface Lewis acidity and basicity constants, K_a and K_b, respectively, were computed.

Due to the interactions between the stationary phase and the gas phase, the probe molecules are retained for a certain time, t_r, which is used to calculate the net retention volume, V_n, according to Eq. (1):

$$V_n = (t_r - t_0)CFJ \tag{1}$$

Here, t_o is the retention time of a non-interacting probe species, either air, or more commonly, methane. F is the carrier gas flow rate, J a term correcting for the compressibility of the carrier gas (Eq. (2)), and C 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 (Eq. (3)).

$$J = 1.5\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \tag{2}$$

Here, P_i and P_o are the inlet and outlet pressures of the carrier gas, respectively.

$$C = 1 - \frac{P_{H_2O}}{P_o} \tag{3}$$

Here, P_{H_2O} is the vapour pressure of the water in the flow meter, at the temperature of measurement.

The retention time was determined using the geometric technique outlined by Condor and Young [23,24]. If only

Table 1
IGC columns analysed

Designation	Support weight (g)	Coating material	Coating weight (g)	Total weight (g)	Percent coating (%)
RefW1	2.020	n/a	n/a	2.020	n/a
RefW2	1.475	n/a	n/a	1.475	n/a
1	1.915	MBS rubber	0.055	1.970	2.81
2	2.460	MBS rubber	0.137	2.597	5.27
3	2.216	MBS rubber	0.188	2.404	7.80
4	2.001	MBS rubber	0.231	2.232	10.33

n-alkane molecular probes are used the dispersive component of the surface tension can be determined from the slope of Eq. (4):

$$2N(\gamma_s^d)^{1/2}a(\gamma_l^d)^{1/2}+C=RT\ \ln(V_n) \tag{4}$$

Here, N is Avogadro's number, a the cross-sectional area of the probe to be tested (Table 2), γ_s^d and γ_l^d are, respectively, the dispersive components of surface tension of the solid (stationary phase) and of the probe-molecule, C a constant, R the ideal gas constant, and T the absolute column temperature It should be mentioned that the dispersive component of the surface tension as the same numerical value than that of the dispersive component of surface energy. Throughout the IGC studies, the standard deviation of the energy of adsorption values of the probe molecules was calculated as being typically below 5%.

The slope of the straight line, referred to as the reference line, obtained by plotting $RT\ln(V_n)$ versus $2N(\gamma_l^d)^{1/2}a$, for a homologous *n*-alkane series (Fig. 1), leads to the determination of γ_s^d for a given temperature.

Acid–base characteristics of surfaces are determined by analysing the interaction of the polar probes with the solid surface and quantifying the deviation from the reference line, leading to the estimation of the specific free energy, ΔG^s, as:

$$-\Delta G^s = RT\ \ln(V_n) - RT\ \ln(V_{n_{ref}}) \tag{5}$$

Here, $V_{n_{ref}}$ is the retention volume established by the *n*-alkanes reference line (Eq. (1)), V_n being now the retention volume of the polar probes. This calculation is also illustrated in Fig. 1.

Table 2
Relevant characteristics of commonly used IGC probes

Probe	$a(\gamma_l^d)^{0.5}$ (cm^2 (mJ cm^{-2})$^{0.5}$)	AN* (kJ/mol)	DN (kJ/mol)
n-Hexane	2.21E − 16	n/a	n/a
n-Heptane	2.57E − 16	n/a	n/a
n-Octane	2.91E − 16	n/a	n/a
n-Nonane	3.29E − 16	n/a	n/a
Trichloromethane	2.24E − 16	22.7	0.0
Dichloromethane	1.65E − 16	16.4	0.0
Diethyl ether	1.82E − 16	5.9	80.6
Acetone	1.73E − 16	10.5	71.4
Tetrahydrofuran	2.13E − 16	2.1	84.4
Ethyl acetate	1.95E − 16	6.3	71.8

By carrying out experiments at different temperatures, it is possible to determine the enthalpy of adsorption and the entropy of adsorption, respectively ΔH and ΔS, from plots of $\Delta G/T$ versus $1/T$, (Figs. 2 and 3), according to the following equation:

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

The acidic and basic constants, respectively K_a and K_b, are calculated from the plot of $-\Delta H^s/\mathrm{AN}^*$ versus $\mathrm{DN}/\mathrm{AN}^*$,

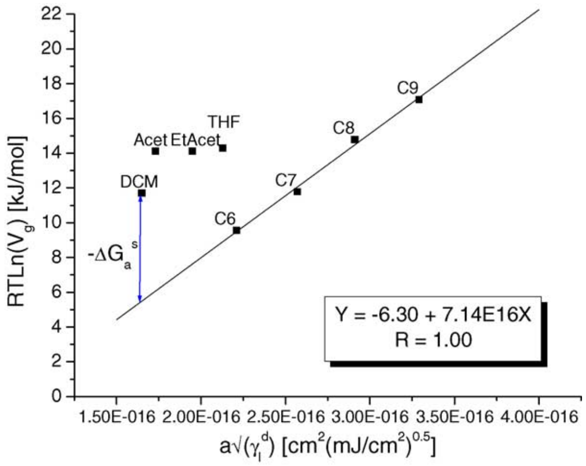

Fig. 1. Energy of adsorption vs. $a\sqrt{\gamma_l^d}$ for *n*-alkanes and polar probes on the surface of the MBS rubber, at $T = 333$ K.

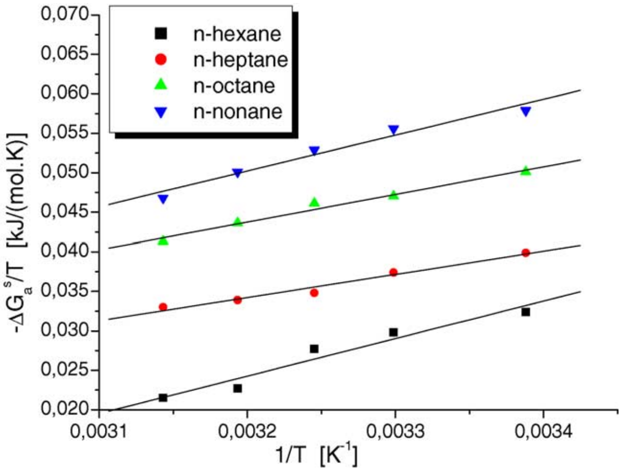

Fig. 2. Determination of the enthalpy, and of the entropy of adsorption of *n*-alkanes on the surface of the MBS rubber.

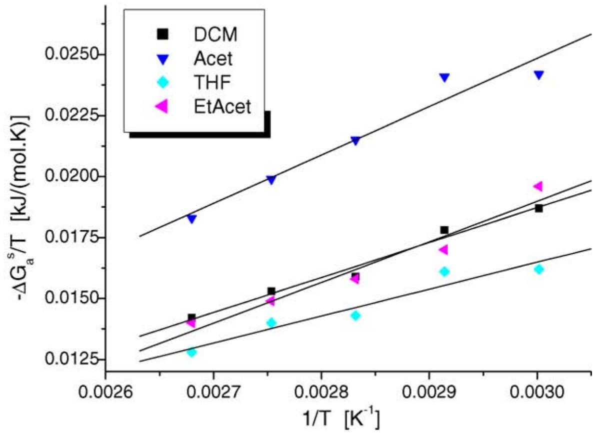

Fig. 3. Determination of the specific component of the enthalpy, and of the entropy of adsorption of polar probes on the surface of the MBS rubber.

according to Eq. (7) (Fig. 4).

$$\frac{(-\Delta H^{\mathrm{s}})}{\mathrm{AN}^*} = K_{\mathrm{a}}\frac{\mathrm{DN}}{\mathrm{AN}^*} + K_{\mathrm{b}} \qquad (7)$$

Here AN* and DN are, respectively, the Gutmann's modified acceptor and donor numbers of the probes tested [11,12] (Table 2).

2.2.3. *IGC experimental set-up*

Experimental work in IGC requires no specialised instrumentation and conventional GC equipment is generally used, with some adaptations. Prior to measurement, each column was conditioned overnight, at the highest temperature of measurement, using helium at a flow rate of approximately 10 cm^3/min. This pre-treatment of the column was aimed at ensuring the removal of any residual volatiles that could otherwise have affected the retention of the probes on the material being studied.

The instrument used was a Fisons GC9100 unit (Fisons Scientific Equipment, Loughborough, UK), equipped with a FID system. The experimental data were acquired by coupling this GC with a personal computer that was equipped with a data acquisition card. This system has the advantage of providing a better data storage and manipulation. Typically, the syringe was filled 0.1 μl of gaseous probe, flushed with air around 10 times, in order to ensure the creation of a Henry's infinite dilution region, and injected manually. The injector was heated to 150 °C and the FID system to 180 °C. The attenuation was set to 1. The flow rate was controlled using a needle valve pressure regulator and determined using a bubble flow meter that was equipped with a helium trap [17] and thermometer. The inlet pressure, P_{i}, 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/).

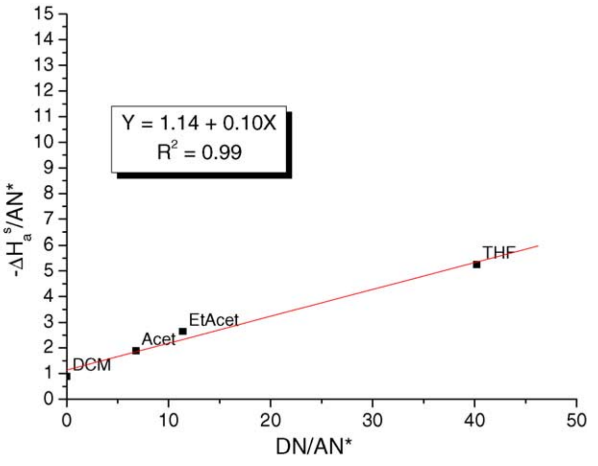

Fig. 4. Determination of K_{a} and K_{b} of the surface of the MBS rubber.

The temperatures and the carrier gas flow rates should be chosen so that they do not give rise to extremely short retention times or extremely long retention times, for all the apolar probes used and for all the polar probes used. Extremely short retention times (less than 10 s) or extremely long retention times (more than 45 min) are prone to a large experimental error, bearing in mind the Condor and Young method [23], used in the determination of the probes retention time.

Preliminary studies concerning the influence of the carrier gas flow rate, and of the support material (Chromosorb W AW DCMS), on the specific retention volumes of the probe molecules, were carried out. These involved the use of flow rates in the range 10–45 cm^3/min and varying the loading of the interacting material on the support. In addition, the influence of temperature of measurement on this study was evaluated. The probe molecule used was *n*-octane. Non-polar probes were chosen for the preliminary studies as they interact only through dispersive forces, and thus, the influence of specific interaction sites at the surface of the stationary phase is eliminated.

The absence of kinetic effects as well as diffusion phenomena on the column stationary phase was confirmed, in order to validate the use of Fowkes' approach [25]. The influence of the support material was found to be negligible. For the temperature ranges used, the net retention volume was independent of the carrier gas flow rate (thus, ensuring surface adsorption only) when this is included in the range 10–45 cm^3/min.

The minimum loading value of the MBS rubber that ensures full coverage of the support material was found to be 5%. This is critical to ensuring that the influence of the material support is negligible, and therefore, that one is quantifying solely the interactions of the probe molecules with the material being studied, and not with the support material [17].

The temperature range, temperature range increment and the flow rate that were used in the determination of K_{a} and K_{b} were 333–383 K, 10 K and 30 cm^3/min, respectively.

Table 3
Values of the dispersive component of the surface tension of the MBS rubber

T (K)	γ_s^d (mJ/m^2)	R^2
333	35.1 ± 3.7	0.99
343	37.5 ± 2.9	1.00
353	38.5 ± 6.6	0.99
363	39.1 ± 5.5	0.99
373	38.5 ± 5.5	0.97
Average	37.7 ± 1.6	n/a

Table 4
Enthalpy of adsorption, ΔH_a, and entropy of adsorption, ΔS_a, of the n-alkanes on the surface of the MBS rubber

Probe molecule	$a(\gamma_l^d)^{0.5}$ (cm^2 (mJ cm^{-2})$^{0.5}$)	$-\Delta H_a$ (kJ/mol)	ΔS_a (J/molK)	R^2
C_6H_{14}	2.21E − 16	47.6	−128.0	0.97
C_7H_{16}	2.57E − 16	29.2	−59.3	0.98
C_8H_{18}	2.91E − 16	34.9	−68.0	0.99
C_9H_{20}	3.29E − 16	45.3	−94.6	0.98

3. Results and discussion

3.1. Determination of the dispersive component of the surface tension

Fig. 1 illustrates the determination of the dispersive component of the surface tension of the MBS rubber, at 333 K, according to the approach of Fowkes. Table 3 summarises the values determined for the dispersive component of the surface tension in the temperature range analysed. The dispersive component of the surface tension remains reasonably constant, within experimental error and is equal to 37.7 ± 1.6 mJ/m^2, for the temperature range studied.

The value of γ_s^d at the temperature of 333 K falls slightly below expectation. This is thought to be due to a ß relaxation process, known to occur in PMMA at this temperature [26]. This ß transition is a consequence of the movement of the side chains.

It was noticed that, at 383 K, the apolar probes were able to penetrate into the bulk of the polymer, the value of γ_s^d, 19.46 mJ/m^2, being significantly different from the value obtained for lower temperatures. This value cannot be regarded as a surface-related value but does indicate that the surface of the material as suffered structured changes that allowed for the penetration of the probe molecules into the bulk polymer. In order to check if experimental errors were involved, this determination was repeated and a value of 23.32 mJ/m^2 was obtained. Thus, the relatively low value of γ_s^d determined for this temperature is not thought to be due to experimental inaccuracies. The trend observed, i.e. decreasing value of γ_s^d at 383 K, is consistent with the value of T_g for PMMA (383 K [26]). Similar phenomena are found in the literature for the IGC characterisation of a SBR rubber, below it T_g and above its T_g [8].

The value of γ_s^d for the surface of the MBS rubber is in good agreement with values found in the literature for PMMA, the shell component of the IM: 38.8 mJ/m^2 (at 295 K), 40.9 mJ/m^2 (343–383 K) [27], 40.9/43 mJ/m^2 (343–383 K) [18], 41.1 mJ/m^2 (at 293 K) [28], and 41.5 mJ/m^2 (at room temperature) [29].

The enthalpy and the entropy of adsorption of the n-alkanes on the surface of the MBS rubber were determined from plots of $\Delta G/T$ versus $1/T$, (Fig. 2). The results are summarised in Table 4. The value of the enthalpy of adsorption and of the entropy, of adsorption of the apolar probes increases with increasing value of $a\sqrt{\gamma_l^d}$, with the exception of n-hexane. For this molecule, the values of $-\Delta H_a$ and of ΔS_a are greater than expected. This is thought to be due to experimental errors in the determination of the retention times of n-hexane at the higher temperatures, derived from their low values (4.3 and 4.8 s at 373 and 363 K, respectively). For the remaining apolar probes, the results agree with expectation as the dispersive forces interaction capability of the probe molecules increases with increasing value of $a\sqrt{\gamma_l^d}$. Thus, with increasing dispersive component of the surface tension and with increasing molecular surface area.

3.2. Determination of the energy, the enthalpy and the entropy of adsorption of polar probes

The specific component of the free energy of adsorption, $-\Delta G_a^s$, corresponding to the polar probes, was determined by the method illustrated in Fig. 1 and consists of determining the difference between the value of the energy of adsorption of a particular polar probe and the corresponding value in the n-alkanes reference line. In Table 5 are presented the results concerning the retention time, t_r, specific retention volume, V_g, energy of adsorption, $RT\ln(V_g)$, and corresponding dispersive and specific components, $RT\ln(V_{g,ref}^d)$ and $RT\ln(V_g^s)$, respectively, for the adsorption of polar probes on the surface of the MBS rubber, at $T = 333$ K, $F = 35.29$ cm^3/min, $J = 0.86$, $C = 0.97$, $P_i = 131.87$ kPa, $P_o = 100.16$ kPa, and $T_{\text{flow meter}} = 296$ K.

The retention time values corresponding to DEE and to TCM were too low for a precise determination using with the current IGC system. This is thought to be due to structural restrictions from both the adsorbate and the adsorbent, hindering these molecules from spatial conformations that could be

Table 5
Retention time, specific retention volume, energy of adsorption, and corresponding dispersive and specific components, for the adsorption of polar probes on the surface of the MBS rubber, at $T = 333$ K

Probe molecule	t_r (s)	V_n (cm^3)	$RT\ln(V_n)$ (kJ/mol)	$RT\ \ln(V_{n,ref}^d)$ (kJ/mol)	$RT\ \ln(V_n^s)$ (kJ/mol)
CH_4	22.5	n/a	n/a	n/a	n/a
DCM	48.8	68.5	11.7	5.5	6.2
Acet	85.0	163.2	14.1	6.1	8.1
THF	89.5	175.0	14.3	8.9	5.4
EtAcet	85.7	164.9	14.1	7.6	6.5

Table 6
Dispersive and specific components of the enthalpy of adsorption, and of the entropy of adsorption, ΔH_a^d, ΔH_a^s and ΔS_a^d, ΔS_a^s, respectively, for the adsorption of polar probes on the surface of the MBS rubber

Probe molecule	$a(\gamma_l^d)^{0.5}$ (cm^2 (mJ cm^{-2})$^{0.5}$)	$-\Delta H_a^d$ (kJ/mol)	ΔS_a^d (J/mol K)	R^2	AN* (kJ/mol)	DN (kJ/mol)	$-\Delta H_a^s$ (kJ/mol)	ΔS_a^s (J/molK)	R^2
DCM	1.65E − 16	25.6	−60.4	0.99	16.4	0.0	14.4	−24.4	0.99
Acet	1.73E − 16	25.9	−59.7	0.99	10.5	71.4	19.8	−34.5	0.97
THF	2.13E − 16	27.7	−56.3	1.00	2.1	84.4	11.0	−16.5	0.97
EtAcet	1.95E − 16	26.9	−57.8	1.00	6.3	71.8	16.6	−30.8	0.98

effective in terms of specific intermolecular interactions. The oxygen atom (Lewis basic centre) of DEE is more susceptible to shielding by the neighbouring hydrogen atoms [30] than is that of, e.g. acetone, which is readily accessible for interaction. The bulkiness of the TCM molecule, due to the three chlorine atoms, hinders the access to the acidic centre in this molecule (the hydrogen atom). Furthermore, the side chain of the PMMA molecule further decreases the probability of establishment of the highly directional, specific, acid–base intermolecular interactions with the probe molecules. The determination of the retention times corresponding to TCM and to DEE was repeated in order to establish the nature of any possible experimental errors. However, the values found were identical, in magnitude, to those of the first determination. The fact that $a\sqrt{\gamma_l^d}$ for TCM is the highest of the polar molecules used, leads to the observation that the strong contribution of dispersive forces, and the occurrence of conformational changes on this molecule, upon adsorption, may be influencing the achievement of H-bonding with the surface due to the highly directional character of this bond. This effect would be more pronounced as the temperature increases.

The values of $-\Delta G_a^s$ at 333 K (Table 5) show that the values for Lewis acidic probes are close to those of the Lewis basic/amphoteric probes. Bearing in mind the relative low acidity of the acidic probe (DCM), when compared to the basicity of the basic probes (e.g. THF), Table 2, it can be concluded that the surface of the MBS rubber is amphoteric, with a strong Lewis basic feature.

The results concerning the determination of the enthalpy, and entropy, of adsorption of the polar probes, along with the corresponding dispersive and specific components, are summarised in Table 6, and illustrated in Fig. 3.

Due to the above mentioned constraints concerning the use of TCM and DEE probes, it was not possible to determine the enthalpy and entropy of adsorption corresponding to these probe molecules. With respect to $-\Delta H_a^d$, it can be seen, in Table 6, that the values increase with increasing value of $a\sqrt{\gamma_l^d}$ for the probe molecule. The dispersive component of the entropy of the system does not vary significantly with the nature of the probe molecule adsorbed.

The value of $-\Delta H_a^s$, is greater for the amphoteric molecules (Acet and EtAcet) and for the acidic molecule (DCM), than for the basic molecule (THF). The probe molecules Acet and EtAcet having similar basicity constants (71.4 kJ/mol and 71.8 kJ/mol, respectively), and $-\Delta H_a^s$ is greater for the adsorption of Acet, which has a greater acidic character (10.5 and 6.3 kJ/mol, respectively). Thus, bearing in mind the values of AN* and of DN of the polar molecules, it can be concluded that the surface of the MBS rubber is Lewis amphoteric, with strong Lewis basic character. This analysis confirms the observations made on the basis of the values that were obtained for the energy of adsorption at 333 K, Table 5. As far as the values of ΔS_a^s are concerned, these follow the same trend as those for the determination of $-\Delta H_a^s$. The greater the enthalpy of adsorption, the greater would be the reduction in the entropy of the system probe-surface upon adsorption of the probe molecules.

3.3. Determination of K_a and K_b

The data relating to the determination of the surface Lewis acidity constant, K_a, and of the surface Lewis basicity constant, K_b, are represented in Fig. 4.

From linear regression of the data presented in Fig. 4, it follows that the values of K_a and K_b, are 0.10 ± 0.01 and 1.14 ± 0.20, respectively. Thus, the surface of the MBS rubber is amphoteric and predominantly Lewis basic, confirming the analysis of the enthalpy of adsorption and of the energy of adsorption of the polar probes. The conclusion that the MBS rubber has a Lewis amphoteric (predominantly Lewis basic) surface agrees with expectation from results of similar studies reported in the literature for PMMA [31], and from an examination of the repeating unit in this polymer. The basic sites are identified with the ester functionality in the side chains. The weak Lewis acidic sites are localised in the terminal –CH$_3$ moiety in the side chain and also in the hydrogen atoms of the –CH$_2$– moiety (the later used to be controversial but is now recognized [32,33]. Furthermore, each oxygen atom is able to interact with two hydrogen atoms and, thus, has a basic strength that is the double of the acidic strength of each hydrogen atom. Consequently, the surface of the MBS rubber would be expected to be strongly basic and relatively weak acidic. It should be noticed that the presence of such a bulky side group (–CH$_3$) plus the lack of complete stereoregularity make this polymer amorphous. On the one hand, the acidity is not sufficient to overcome the steric hindrance and, on the other hand, the basicity is quite high. Thus, the repulsion between basic sites further contributes to the non-existence of intramolecular H-bonds and intermolecular H-bonds characteristic of the ordered phases, due to the fact that basic sites and acidic sites cannot get close enough, along with the directional character of the H-bond.

An example of the lack of acid–base attraction interaction due to predominant base/base repulsion is the incapacity of an acetone molecule to form H-bonds with another acetone molecule [34]. The repulsive interaction is expected to be significant in such cases where, in both materials, either the Lewis basic sites or the Lewis acidic sites are dominant to a large extent [35], and are easily accessible.

4. Conclusions

The surface Lewis acidic/basic properties of a widely used impact modifier, MBS rubber, have been quantified by means of inverse gas chromatography, carried out under infinite dilution conditions. The results show that this technologically, and economically important elastomer is amphoteric but predominantly Lewis basic.

The weak surface Lewis acidity and the strong surface Lewis basicity are expected to significantly influence the ability of this impact modifier to interact with other components of complex polymeric systems. Thus, phenomena such as adhesion properties to the polymeric matrix and the phase preference (in the case of polymer blends), will determined to a large extent by the particular thermodynamic characteristics of this widely used elastomer.

It can also be concluded that the best approach to assess the surface energetic properties (surface tension, surface Lewis acidic/basic properties) of a material by IGC is the side-by-side analysis of the energy of adsorption, enthalpy of adsorption and surface Lewis acidity and basicity constants. This procedure allow for a coherent and systematic interpretation of the IGC results, leading to a more complete analysis than the solely analysis of K_a and K_b.

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