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Characterisation of the surface Lewis acid–base properties of the components of pigmented, impact-modified, bisphenol A polycarbonate–poly(butylene terephthalate) blends by inverse gas chromatography–phase separation and phase preferences

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Abstract

Inverse gas chromatography was used to study the surface Lewis acid–base properties of the major components of pigmented, impact-modified, polycarbonate–poly(butylene terephthalate) blends. An investigation of the Lewis acid–base interactions in these polymeric systems has been carried out, based on the values determined for the surface Lewis acidity constant (K_a), surface Lewis basicity constant (K_b) and on the chemical and physical structure of the materials involved. This analysis provided the rationale for an interpretation of the phase separation and the phase preference that exist in these polymer blends, and of the consequences to their physical and mechanical properties.

Keywords: Inverse gas chromatography; Acid–base interactions; Bisphenol A polycarbonate; Poly(butylene terephthalate); Polymer; Pigments; Cobalt aluminate

1. Introduction

This paper concerns the use of C.I. Pigment Blue 28 (cobalt aluminate), to impart colour to impact-modified, bisphenol A polycarbonate–poly(butylene terephthalate) (PC–PBT) blends, and the effect of such pigmentation on the physical and mechanical properties of the resultant composites. As far as UV-stability and weatherability is concerned, this pigment performs positively in these blends. The objective of the overall study is to gain a better understanding of the interactions that occur in these polymer blends, and their effect on performance, particularly with respect to mechanical properties.

The relationship between intermolecular interactions and system properties is particularly important in polymer compositions, bearing in mind the variety of polymers and additives that are used to achieve desired performance requirements. Intermolecular forces between molecular segments of polymers and at particulate interfaces are frequently cited in the literature [1–10] as being responsible for the properties of the system as a whole. Control of Lewis acid–base interactions has gained increasing significance in industrial practice [11,12] for optimising the performance of polymer composites. This is because such intermolecular forces are known to dominate over dispersion and dipole–dipole intermolecular forces [6,8,11–19]. This is clear in the definition of

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specific interaction given by Huyskens et al. [14]: ''Specific interactions are short-range, site-bounded cohesion forces that considerably weaken a given chemical bond of one of the partners''.

The growing awareness of the importance of solid surfaces, interfaces and interphases in determining the useful properties of polymeric systems, has led to 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 [3,11,12].

The polymeric system studied consists of a blend of a bisphenol A polycarbonate (PC) and a poly(butylene terephthalate) (PBT). A core–shell type elastomer (IM) is added to the polymer blend to improve its impact toughness. The amorphous PC provides impact resistance, toughness, and dimensional stability at elevated temperatures. The semicrystalline PBT provides chemical resistance and thermal stability. The pigment being studied is C.I. Pigment Blue 28.

The properties of impact-modified PBT–PC blends are directly related to the phase separation, that is, miscibility, of the PC phase and the PBT phase, and the phase preference of the impact modifier for the PBT phase and/or the PC phase. However, studies relating to the phase preference of the pigment, and consequences thereafter on the physical, the mechanical, the colouristic and the weathering properties of these blends have not been found in the literature.

With regard to the miscibility of PC and PBT, it is well documented that in PC–PBT (50:50, w/w) blends, partial miscibility exists [20–25] both in the melt and after melt blending, with phase separation occurring during PBT crystallisation [25]. It has been found that in such blends, the PC phase is less than 10% miscible in the PBT phase [26]. Nevertheless, questions still arise as completely immiscible PC–PBT blends have been reported in recent literature [27]. The partial miscibility of the amorphous phases (amorphous PBT and amorphous PC) in this polymer blend has been attributed to various factors such as the morphology of the crystalline phase [27], transesterification reaction resulting in PC–PBT copolyester [27], and the closeness of the solubility parameters of PC and PBT [26].

Another aspect of the polymer blends studied is the preferential presence of the IM in the PC phase [23]. This is thought to be caused partially by the expulsion of the impact modifier particles from the crystallising PBT, by 'bad' interaction of the shell of the modifier with the molten matrix during blending and by the values for the spreading coefficients of the blend components [20].

The techniques involved in the study of such polymer blends include thermal analysis [differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), thermogravimetric analysis (TGA)], microscopy [scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical microscopy (OM)], spectroscopy (FTIR), or other techniques such as NMR, density measurements, melting temperature depression [27] and the measurement of contact angles [20].

An analysis of the Lewis acid–base interactions between the major components of the polymeric systems being studied was carried out. This analysis was based on the values determined for the Lewis acidity constant, $K_{a,}$ and for the Lewis basicity constant, K_b, and on the chemical and physical structure of the materials. The accessibility of the interactions sites plays an important role in the formation of acid–base intermolecular forces, when hydrogen bonds are involved, due to the highly directional and specific character of these bonds.

The information gathered was then used to interpret the reported phase separation of the PC and the PBT phases, and also the phase preference of the impact modifier for the PC phase. The phase preference of the pigment for the interphase of the amorphous PBT and PC, supported by mechanical testing and thermal analysis, was also interpreted in terms of Lewis acid–base interactions, as characterised by IGC.

2. Experimental

DSC was used to assess the effect of the pigment on the phase transitions and on the bulk structural features of the impact-modified PC–PBT blends. The parameters analysed were the enthalpy of crystallisation, the crystallisation temperature, and the glass transition temperature.

DMTA, and tensile testing, were used in a study of viscoelasticity related parameters such as the tensile modulus, the stress at yield, the strain at yield, the strain at break, the stress at break, the storage modulus, the loss modulus and the loss tangent. Impact testing was used to assess the impact toughness of the pigmented, impact-modified, PC–PBT blends.

The individual components of these polymeric systems were characterised for their physical and chemical properties. DSC was used in the characterisation of the phase transitions of the polymeric components (glass transition temperature, melting temperature, enthalpy of crystallisation, crystallisation temperature). The pigments studied were characterised by determining the average particle size and the particle size distribution, the particle shape (SEM) and the BET surface area.

The surface Lewis acidic–basic character of the polymers, impact modifier and pigment was quantified by means of IGC, and, therefore, the Lewis acid–base intermolecular interaction potential of the major components of the blends was evaluated.

2.1. Materials

The materials studied were C.I. Pigment Blue 28 (Sicopal® Blue K6310, from BASF, Cheshire, UK), a bisphenol A polycarbonate (Lexan®, from GE Plastics Europe, Bergen op Zoom, The Netherlands), a poly(butylene terephthalate) (Valox®, from GE Plastics Europe), and an impact modifier (supplied by GE Plastics Europe). The physical properties of the pigment, of the polymers, and of the impact modifier (IM) are summarised in Tables 1 and 2, respectively. The IM is a core–shell type material, with an outside layer of PMMA. The average particle size of the IM is 0.1 μm (source: GE Plastics Europe).

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), and dichloromethane (DCM). All of these chemicals were obtained from Sigma–Aldrich (Poole, UK). Methane (Phase Separations, Deeside, UK) was used as a noninteracting reference probe and the carrier gas utilised was helium (99.999+% purity, BOC Gases, Guildford, UK). Chromosorb® W AW DCMS (from Sigma–Aldrich, Poole, UK) was used as the column stationary phase support for the pigment BASF Sicopal Blue K6310 and the impact modifier. Chromosorb P AW DCMS (also from Sigma–Aldrich) was used as the column stationary phase support for the PC.

Table 1
Some characteristics of the C.I. Pigment Blue 28 pigment studied. The average particle size was determined using a Coulter N4M submicron analyser; the BET surface area was determined using a Strentoline unit

	BASF Sicopal K6310
Specific gravity (g/cm^3)$^+$	4.5
Average particle size (μm)	1.18[a]/0.40[b]
Specific surface area (m^2/g)	20[a]/22.8[b]

[a] From Technical Data Sheets.
[b] From characterisation at the Department of Colour Chemistry, University of Leeds, UK.

2.2. Blends

The basic formulation composition of the prepared blends was PC–PBT–IM (45:45:10, w/w). Pigmented samples were prepared with pigment (BASF Sicopal® K6310) loadings of 0.1, 0.3 and 0.5% (w/w). Additives (antioxidants, stabilisers) were added as 0.55% (w/w) of the total blend mass. These blends were extruded using a Werner and Pfleiderer Supercompounder generation ZSK-30 twin-screw unit (melt temperature: 255–270 °C), and injection-moulded into impact testing bars, tensile testing bars and circular plaques, using a Netstal injection moulder unit (mould temperature: 60 °C). A laboratory-scale tape extruder was used to produce tape ribbons (thickness: 1 mm, width: 10 mm) from the extruded pellets. The tape extruder was operated at 265 °C. The tape-extruded samples were used in DSC studies.

2.3. Inverse gas chromatography

2.3.1. Column preparation

The columns were cut from stainless steel tubing

Table 2
Weight-average molar mass, polydispersity, and number-average molar mass of PC and PBT (determined by gel permeation chromatography, source: GE Plastics), and T_g and T_m for PC, PBT and the IM; T_g and T_m determined by DSC, at the Department of Colour Chemistry, University of Leeds, UK

	M_w (g/mol)	D	M_n (g/mol)	T_g (K)	T_m (K)
PC	37 000	2.30	17 000	418	N/A
PBT	46 000	2.70	17 000	318	503
IM	Not available	Not available	Not available	203	405–422

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×6.4 O.D.×4.4 mm I.D. Cleaning was achieved via sequential rinsing with a hot aqueous detergent solution (Decon 90 5%, 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. In the particular case of the PBT, due to the lack of an appropriate solvent, instead of coating a support material, the polymer was used as received, after grinding and sieving to achieve an appropriate particle size. To obtain an appropriate particle size, the polymer particles were processed in a grinder while being cooled with liquid nitrogen, and sieved through 125- and 250-μm filter gauzes. The PC loading on the support (Chromosorb P AW DCMS) was determined by TGA. The IM stationary phases were prepared by a procedure analogous to that used for the columns containing the C.I. Pigment Blue 28 pigments (and using Chromosorb W AW DCMS as the support material).

2.3.2. IGC experimental set-up

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

In the study of the BASF Sicopal K6310 pigment, a Perkin-Elmer GC8410 unit (Perkin-Elmer, Buckinghamshire UK), equipped with a flame ionisation detection (FID) system, HS-101 headspace autosampler and coupled to a GP100 thermal printer/plotter, was used. For the study of PC, PBT and IM, the instrument used was a Fisons GC9100 unit (Fisons Scientific Equipment, Loughborough, UK), equipped with an FID detector.

In the experiments carried out using the Perkin-Elmer GC8410 unit, typically, 0.1 μl of liquid probe was injected into each vial using a 1.0-μl Hamilton syringe. In what concerns the experiments carried out in the Fisons GC9100 unit, typically, the syringe was filled with 0.1 μl 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. In both gas chromatographs, the flow-rate was controlled using a needle valve pressure regulator and determined using a bubble flow meter 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 temperatures, and carrier gas flow-rates, used in the study of each material were different. This was due to the need to use a temperature range and flow-rate that would not give rise to extremely short or extremely long retention times, for all the apolar and polar probes used. Extremely short or long retention times are prone to a large experimental error, bearing in mind the Condor and Young method [28] (used in the determination of the probes retention time). Also the value of T_g and T_m (Table 2) had to be taken into account, as the aim was to determine the Lewis acidic–basic properties of the surface and not of the bulk. The temperature range and flow-rate used in the determination of K_a and K_b of each material are summarised in Table 3.

Table 3
Temperature range and flow-rate used in the determination of K_a and K_b

	Temperature range (K)	Temperature increment (K)	Flow-rate (cm^3/min)
Pigment BASF Sicopal K6310	313.15–353.15	10.00	20
PC	353.15–393.15	10.00	45
PBT	298.15–318.15	5.00	10
IM	333.15–373.15	10.00	30

2.3.3. IGC data processing

The main difference between conventional 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. This allows for the investigation of its interactive nature via its degree of interaction with well-characterised volatile liquids/vapours (‘probes’). The quantification of this interaction may be achieved by the determination of the retention time, t_R, for a given probe.

IGC data processing was carried out according to methods described in the literature (see for instance reference [29]). The retention time was determined using the geometric technique outlined by Condor and Young [30]. 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%.

2.3.3.1. Lewis acid–base interaction numbers

The ability of the IGC technique to provide Lewis acid–base parameters for polymers and other materials used in polymeric systems, led to the development of Lewis acid–base pair interaction numbers. In this manner, an attempt to quantify the acid–base interactions at interfaces and/or interphases between a polymer matrix and additives present in the composition, making use of K_a and K_b, can be carried out. The lack of theory to guide such a calculation results in the use of empiricism. In this context, several Lewis acid–base interaction parameters, based on K_a and K_b, can be found in the literature [31]:

$$I_{sp1} = (K_a)_1(K_b)_2 + (K_a)_2(K_b)_1 \tag{1}$$

$$I_{sp2} = [(K_a)_1(K_b)_2]^{1/2} + [(K_a)_2(K_b)_1]^{1/2} \tag{2}$$

$$I_{sp3} = (K_a)_1(K_b)_2 + (K_a)_2(K_b)_1 - (K_a)_1(K_a)_2 - (K_b)_1(K_b)_2 \tag{3}$$

Here, $(K_a)_1$ and $(K_b)_1$ correspond to the Lewis acidity–basicity constants of species 1, and $(K_a)_2$ and $(K_b)_2$, to those of species 2. All of these parameters are reported [31] to correlate usefully with adhesion phenomena and other properties influenced by the strength of Lewis acid–base intermolecular forces. However, several remarks must be made on the use of the interaction parameters represented by Eqs. (1)–(3).

Firstly, the parameters I_{sp1} and I_{sp2}, do not take into account the Lewis base–base and Lewis acid–acid repulsion forces. The Lewis base–base and Lewis acid–acid repulsions, and the Lewis acid–base attraction, do not contribute equally to the overall specific interactions. The latter has a greater contribution, as mentioned by Fowkes in Ref. [32]. Nevertheless, Lewis acid–acid and Lewis base–base repulsions make a significant contribution in systems were Lewis acid–base attraction does not exist or is very weak, as has been postulated by Schreiber et al. [6] and Utracki et al. [16]. This has led to the proposal of a new parameter, I_{sp3} [6]. However, in the formulation of parameter I_{sp3}, it is assumed that acid–acid and base–base repulsion have the same contribution as acid–base attraction for the overall interaction potential. However, when determining the interaction parameter concerning the interaction of a hypothetical material with itself or between identical molecules (Table 4, values of K_a and K_b are presented as examples), the value of I_{sp3} is always negative or zero and, thus, interaction is not

Table 4
Values of I_{sp3}, for the acid–base interaction potential of a hypothetical material with itself; values of K_a and K_b are given only as an example

K_a	K_b	I_{sp3}
Low (0.1)	Low (0.1)	0.00
Low (0.1)	High (1)	−0.81
High (1)	Low (0.1)	−0.81
High (1)	High (1)	0.00

favoured. Consequently, no polar molecule would interact through acid–base intermolecular interactions (from the attractive point of view) with another molecule that was chemically identical.

Secondly, the contribution of acid–base attraction, and acid–acid and base–base repulsion, to the total interaction potential is a function not only of the intrinsic Lewis acidity and Lewis basicity of the molecules, but is also a function of the accessibility of such interaction sites [14,32–35]. This is of considerable importance when long chains (as is the case with polymers) are present, or when particulates are involved. In such instances, conformational and configurational factors influence the accessibility of the interaction sites. Factors such as the localisation and the distribution of the Lewis acidic and Lewis basic sites, and their accessibility by the Lewis acidic and Lewis basic sites of the interacting species, influenced by the existence of bulky side groups, for instance, will affect the effectiveness of any acid–base interactions. The type and strength of bonding is not only dependent on the atomic arrangement, molecular conformation and chemical constitution of the species involved, but also on their morphological properties [32,33]. Steric hindrance influences the interaction of the probe molecules used in IGC with the surface, and, thus, it is quantified in K_a and K_b. However, when the material interacts with another surface (particulates, polymers), instead of with a probe molecule, the accessibility of the Lewis acidic and Lewis basic sites in the materials involved is by far more influenced by conformational and morphological factors.

As the acid–base interaction most frequently found is the H-bond (along with the n–σ EDA (Electron Donor Acceptor) bonding [14]), and due to its highly directional and specific character [14,35], the acid–base interaction will be strongly affected by the orientation and accessibility of the functional groups. Accordingly, and in conjunction with the acid–base properties of each material/molecule, the contribution of acid–acid and base–base repulsion to the interaction potential will vary with the chemical as well as with the spatial structure of the species involved. The repulsive interaction is expected to be significant in such cases where, in both materials, either the Lewis basic or Lewis acidic sites are dominant to a large extent [17], and are easily accessible.

Thirdly, in what concerns interactions between different materials used as part of a multicomponent polymeric system, the probability of acid–base interaction is a function, not only of the interaction potential, but also of the number of interaction opportunities, as defined by the relative presence of each species in the polymeric system.

Therefore, an interaction parameter considered to be suitable for multicomponent polymeric systems, whose components are able to interact through specific interaction forces, should take into account the following factors:

(a) K_a and K_b, the Lewis acidic and Lewis basic constants for each species
(b) The accessibility of the Lewis acidic and Lewis basic sites in each species, relative to the Lewis acidic and Lewis basic sites of the interacting species, due to the presence of bulky-side groups, molecular conformation, and morphological structure of the species involved
(c) The larger contribution of acid–base attraction forces for the overall interaction
(d) The relative presence of each species in the blend.

In view of the above comments, an analysis of K_a and K_b, taking into account the chemical structure of the species involved, their relative amounts in the blend, and their physical properties (size, morphology) is thought to be the best way of predicting the acid–base interaction capability for the species present in multicomponent polymeric systems.

2.4. DSC

The instrument used was a DSC 2010 DSCalorimeter. The sample amounts ranged from 4 to 10 mg. The parameters determined were the crystallisation onset temperature, $T_{c,on}$, the crystallisation offset temperature, $T_{c,off}$, the crystallisation temperature, T_c, and the enthalpy of crystallisation, $-\Delta H_c$. The following temperature program was used. The sample was heated from room temperature to 250 °C at the maximum heating rate possible, keeping the sample at this temperature for 1 min, to release all the stresses and ensuring a consistent thermal history in the material. The sample was then cooled from 250 to 162 °C, at a constant rate (8 °C/min).

2.5. DMTA

The instrument used was a Polymer Labs. PL-DMTA MkII (bending mode). The samples were cut from tensile bars, and had the dimensions: length, 30 mm; width, 4.25 mm; and thickness 1 mm. The temperature range used was 25–200 °C. The heating rate was 2 °C/min. The strain used was 64 μm and the frequency was set to 1 Hz.

2.6. Tensile testing

Tensile testing was performed according to the standard ISO 527, using a Zwick 1474 tensile testing unit, at room temperature, and at a test speed of 50 mm/min. Five bars were tested per batch.

2.7. Izod notched impact testing

Izod notched impact testing was performed using a pendulum impact machine. The standard test used was the ISO 180/1A test, specimen type I and notch type A. The bars were notched with a rotational single tooth miller. After notching, samples were conditioned for at least 1 h before testing, in order to release possible stresses introduced by notching. The temperatures used were: −20, −10, 0 and 23 °C. The temperature was decreased from 23 °C until the sample exhibited brittle fracture. Each sample was conditioned at the desired temperature, for a sufficient time to reach temperature equilibrium. The time between taking the specimen out of the conditioning chamber and testing was kept as short as possible. Five bars were notched and tested per batch.

3. Results and discussion

3.1. IGC

3.1.1. Dispersive component of the surface free energy

The free energy of adsorption, $-\Delta G_a$, and the dispersive component of the surface tension, γ_s^d, were determined using Fowkes approach [36], with values for the probes surface area given by Schultz and Lavielle [12]. The procedure is illustrated in Fig. 1. for the surface adsorption of *n*-alkanes and polar probes on pigment C.I. Pigment Blue 28 (BASF Sicopal K6310), at 313 K.

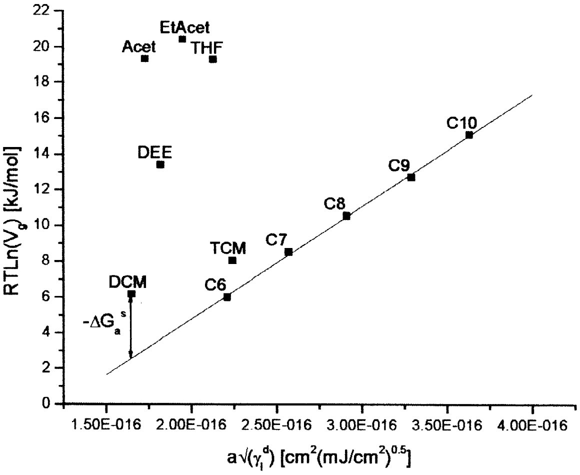

Fig. 1. Surface free energy of adsorption for the surface adsorption of *n*-alkanes and polar probes on the C.I. Pigment Blue 28 pigment, at 313 K.

The values determined for the dispersive component of the surface tension, γ_s^d, of the materials studied are presented in Table 5. These agree well with data published in the literature for PBT (40.0 mJ/m^2 at 293.2 K, from contact angle measurements [20]), PC (32.8±0.5 mJ/m^2 in the temperature range 303.2 –353.2 K [37]) and poly(methyl methacrylate) (PMMA—the shell material of the IM) (40.9 mJ/m^2 in the temperature range 343.2–383.2 K [38]). No values were found in the literature concerning the dispersive component of the surface tension of the cobalt aluminate pigments. The major observation from Table 5 is that γ_s^d is practically constant for the polymeric materials involved, in the temperature range studied. On the other hand, it can be seen that, for the inorganic pigments, the value of γ_s^d decreases linearly with increasing temperature.

3.1.2. K_a and K_b

The value of the specific component of the energy of adsorption, $-\Delta G_a^s$, corresponds to the difference between the total free energy of adsorption, $-\Delta G_a$, and the dispersive component of the free energy of

Table 5
Values of γ_s^d (mJ/m^2) determined for C.I. Pigment Blue 28, IM, PC and PBT

T (K)	K6310	T (K)	IM	T (K)	PC	T (K)	PBT
313	27.2±1.2	333	35.1±3.7	353	33.7±2.3	295	42.4±1.0
323	23.2±2.5	343	37.5±2.9	363	37.3±2.6	303	42.5±2.8
333	20.1±2.2	353	38.5±6.6	373	33.1±2.5	308	41.4±2.6
343	19.7±3.4	363	39.1±5.5	383	33.2±1.9	313	40.7±1.3
353	17.4±3.2	373	38.5±5.5	393	29.3±3.2	318	44.7±9.9
$d\gamma_s^d/dT$	−0.23±0.04	Average	37.7±1.6	Average	33.3±2.8	Average	42.3±1.5

adsorption, $-\Delta G_a^d$, as determined using the n-alkanes reference line.

The enthalpy of adsorption, ΔH_a, and the entropy of adsorption, ΔS_a, of the probes used were calculated from the slope and intercept of $-\Delta G_a/T$ vs. $1/T$, respectively. Here, T is the temperature of measurement in degrees Kelvin. The procedure is illustrated in Fig. 2, for the determination of the specific component of the enthalpy of adsorption, and of the entropy of adsorption, of acetone, on the surface of C.I. Pigment Blue 28 (BASF Sicopal K6310).

The values of K_a and K_b were calculated using Eq. (4) [29]:

$$-\Delta H_a = K_a \cdot \mathrm{DN} + K_b \cdot \mathrm{AN}^* \tag{4}$$

Here DN and AN* are Gutmann's donor and modified acceptor numbers, respectively, corresponding to the polar probes [36,39]. Representing $-\Delta H_a^s/\mathrm{AN}^*$ versus DN/AN*, gives K_a as the slope and K_b as the intercept. The procedure is illustrated in Fig. 3 for the BASF Sicopal K6310 pigment.

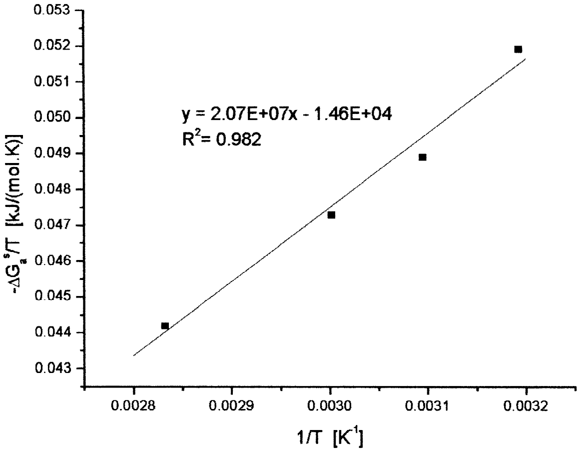

Fig. 2. Determination of the specific component of the enthalpy of adsorption and of the entropy of adsorption of acetone, on the surface of the C.I. Pigment Blue 28 pigment.

The values determined for K_a and K_b for all the materials studied are summarised in Table 6. From the values presented, it can be observed that all the materials are amphoteric, though predominantly Lewis basic. The more acidic materials are the C.I.

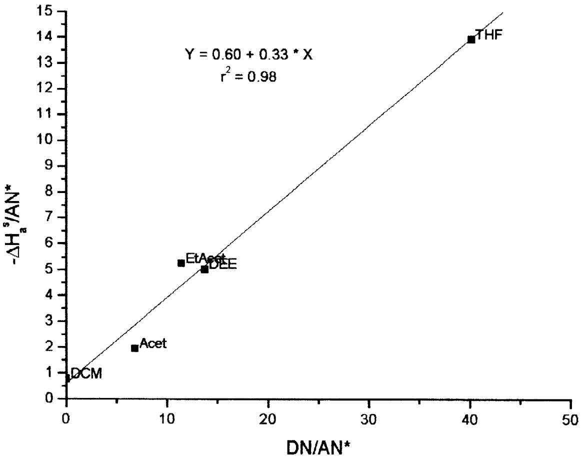

Fig. 3. Determination of K_a and K_b for the surface of the C.I. Pigment Blue 28 pigment (BASF Sicopal K6310).

Table 6
Temperature range used and values of K_a and K_b determined for the materials studied

	K_a	K_b	r^2
PC	0.09	0.48	0.96
BASF Sicopal K6310	0.33	0.60	0.98
IM	0.10	1.14	0.98
PBT	0.49	0.96	0.96

Pigment Blue 28 and the PBT. The more basic materials are the PBT and the impact modifier. The predominant surface Lewis basicity agrees with expectation, bearing in mind the structure of the macromolecules and particulates involved and similar studies reported in the literature.

The results obtained for the C.I. Pigment Blue 28 pigment are in agreement with results published in the literature for study of the basicity of alumina, as its surface has been shown to be amphoteric, predominantly basic [35,40]. In the case of the C.I. Pigment Blue 28 pigments, the acidity is localised in the cations Co^{2+}, Co^{3+} and Al^{3+} [35] and in the surface –OH groups [41]. The basicity of this inorganic pigment is localized in the anion O^{2-}, and also in the surface hydroxyl groups [35,42]. The surface was expected not to be strongly acidic, at least from the point of view of the abundance of sites, due to the fact that on the normal cobalt aluminate octahedral Al^{3+} ions predominate with respect to the tetrahedral ones [43].

As far as the IM is concerned, the Lewis amphoteric (predominantly Lewis basic) surface agrees with expectation from results of similar studies reported in the literature for PMMA [32], and from an analysis of the repeating unit in this polymer. The basic sites can be identified with the ester functionality in the side chain. On the other hand, the weak Lewis acidic sites are localised on the terminal $-CH_3$ moiety in the side chain.

With regard to the PC, the results also agree with expectation bearing in mind the structure of the repeating unit in this macromolecule and values reported in the literature [44]. The Lewis basic sites are identified with the carbonate group, and the Lewis acidic sites with the –OH endgroup.

No IGC studies concerning the determination of K_a and K_b of PBT have been found in the literature. The values obtained for PBT agree well with expectation bearing in mind the structure of its molecule. The Lewis basic sites are identified with the ester moiety, the oxygen atoms in the carboxylic endgroup, and also with the oxygen atom in the hydroxyl endgroup [14]; the Lewis acidic sites are identified with the hydrogen atoms in the $-O-CH_2$ moiety, and with the hydrogen atom in the hydroxyl endgroup and in the carboxylic endgroup.

3.1.3. Lewis acid–base interaction potential of the materials studied

The interaction parameters currently in use [Eqs. (1)–(3)] do not take into account the relative presence of each material in the polymeric system, the accessibility of the Lewis acidic and Lewis basic sites in relation to the Lewis acidic and Lewis basic sites available for interaction on the interactive species, and an appropriate balance of the contribution of the acid–acid and base–base repulsions to the overall acid–base interaction potential. Therefore, in the analysis of the Lewis acid–base interaction potential of the materials studied no use was made of the acid–base interaction parameters, at present found in the literature.

A qualitative analysis of the Lewis acid–base interaction potential between the major components of these blends is carried out, taking into account: (1) the structure of the repeating units and endgroups, of PC, PMMA (the shell component of the IM) and PBT, (2) the molecular structure of the C.I. Pigment Blue 28 pigment, (3) the relative surface Lewis acidity and surface Lewis basicity of these materials, as quantified by K_a and K_b, and (4) the relative presence of each material in the pigmented PC–PBT–IM blend.

Although different temperature ranges were used in the determination of the values of K_a and K_b, of the different materials, these values were determined assuming that the enthalpy of adsorption is independent of the temperature, proven to be true by the very good correlation coefficient relating the determination of $-\Delta H_a$. Only when 'high' temperatures are involved, (for instance temperatures greater than 310 °C, for PC [44]) the acid–base functionalities are decreased substantially and, if the temperature is high enough, are suppressed. Thus, for the temperature ranges used, the values of K_a and K_b are not expected to vary significantly.

From the values presented in Table 6 it is shown that the PBT has the strongest interaction potential [highest $(K_a + K_b)$ value], followed by the IM, the C.I. Pigment Blue 28 pigment, and, finally, the PC.

The PBT interacts preferentially with itself as it has both strong Lewis base and Lewis acid functionalities. In addition no steric hindrance, due to bulky side-groups, is expected and, thus, the basic and the acidic sites, are easily accessible to interaction through intermolecular forces and intramolecular forces. This, alongside with the chemically regular structure of the molecule, provides the structural requirements for the existence of crystallinity.

As far as the PC is concerned, the strong base–base repulsion and weak acid–base attraction, alongside with the steric hindrance due to the $-CH_3$ side-groups and the aromatic ring, contribute to the nonexistence of ordered domains in the PC. Thus, the polycarbonate is amorphous in nature.

A certain degree of Lewis acid–base attraction between PC and the PBT is expected as the former, although being a weak Lewis acid, has some Lewis base character and the PBT has strong Lewis acidic sites. Moreover, the PBT has strong Lewis basic sites and, thus, is able to interact to a certain extent with the Lewis acidic sites on PC. The PBT and the PC account for 90% (w/w) of the blend in an approximate 1:1 proportion and, therefore, the interaction opportunities are very considerable. It can then be said that, although naturally phase-separated, PC and PBT may be miscible to a certain, low, extent.

The C.I. Pigment Blue 28 is thought to interact preferentially with the PBT and then with the PC. This is due to the fact that the pigment is strong Lewis acidic and PBT is strong Lewis base. Also, PBT is a strong Lewis acidic and the pigment is not weakly Lewis basic. Nevertheless, as PBT prefers to interact with itself, it is expected that some acid–base interaction between the pigment and the PC would occur.

The IM interacts preferentially with the PC rather than PBT. This is due to the preference of the PBT to interact with itself. Also, the Lewis base–base repulsion between the PBT and the IM (the Lewis acidity of the IM is low and, therefore, it will interact mainly through the basic sites) is greater than between the IM and the PC. As the PC has the weakest Lewis basicity and weakest Lewis acidity, the base–base repulsion with the IM will not be as significant as between the IM and the PBT. Thus, acid–base attraction is thought to dominate in the pair IM–PC. Also, PBT and PC are used in an approximately 1:1 proportion, meaning that the interaction opportunities between the IM and the PC are substantial.

Both the weak acid–base attraction and the strong base–base repulsion in PMMA, in conjunction with the presence of the bulky side-chain, and the lack of complete stereoregularity, contribute to the lack of acid–base attractive interaction of PMMA with itself, or other Lewis basic materials. This indicates that PMMA is an amorphous polymer.

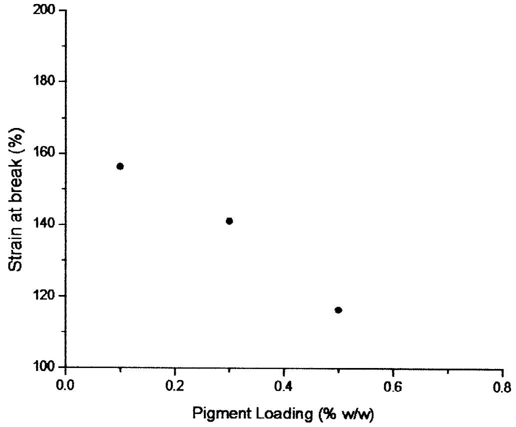

Fig. 4. Strain at break vs. pigment (BASF Sicopal K6310) loading of the pigmented, impact-modified, PC–PBT blends.

3.2. Tensile testing

Figs. 4 and 5 relate to the variation of the strain at failure and the tensile modulus as a function of the pigment loading, respectively, for the samples prepared. The other parameters, determined by tensile testing (stress at yield, strain at yield, stress at break), did not show any significant variation, with increas-

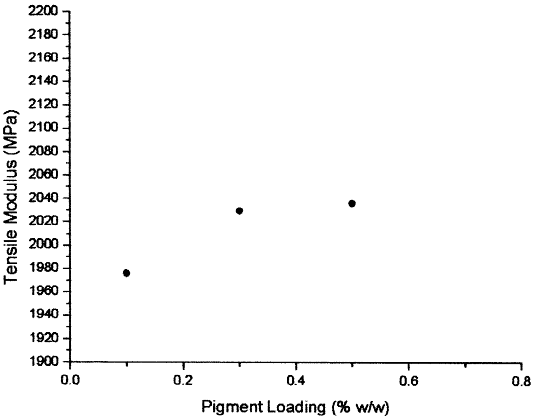

Fig. 5. Tensile modulus vs. pigment (BASF Sicopal K6310) loading, of the pigmented, impact-modified, PC–PBT blends.

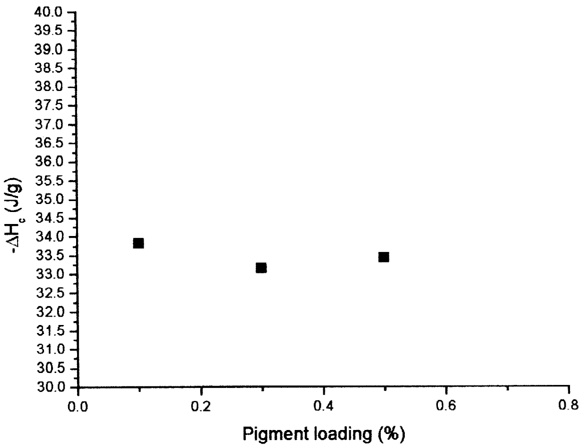

Fig. 6. Enthalpy of crystallisation vs. pigment (BASF Sicopal K6310) loading of the pigmented, impact-modified, PC–PBT blends.

ing pigment loading, within experimental error, and, thus, are not included here.

It is clear from Fig. 4 that the viscous response of the blend is reduced as the pigment loading is increased, the strain at failure decreasing with increasing pigment loading. The tensile modulus increases, although not in a pronounced manner, with increasing pigment loading, indicating that the pigment is having an effect on the crystalline phase of the PBT. Thus, the crystallisation temperature, and the enthalpy of crystallisation, of the PBT phase were determined from DSC experiments.

3.3. DSC

Figs. 6 and 7 summarise the variation of the crystallisation temperature, and of the enthalpy of crystallisation, for the samples studied. From Figs. 6 and 7, it can be concluded that increasing the pigment loading has little effect on the crystallisation temperature, and on the enthalpy of crystallisation, within experimental error, for the pigment loading range used. This finding leads to the conclusion that, for the pigment loading range used, the pigment has a negligible effect on the crystalline phase.

3.4. DMTA

The parameters determined by DMTA were the storage modulus, the loss modulus and the loss tangent. From the results (Fig. 8), it can be concluded that the pigment improves the miscibility of the amorphous PBT phase and amorphous PC phase. This conclusion is based on the fact that the glass transition temperature of the PC phase decreases as the pigment loading increases (Table 7). Also, the glass transition temperature of the PBT phase, although identified only as a shoulder in the plot, (at around 75 °C), increases with increasing pigment

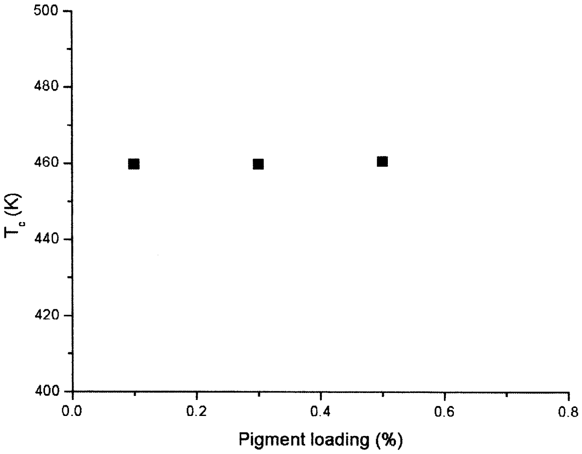

Fig. 7. Crystallisation temperature vs. pigment (BASF Sicopal K6310) loading of the pigmented, impact-modified, PC–PBT blends.

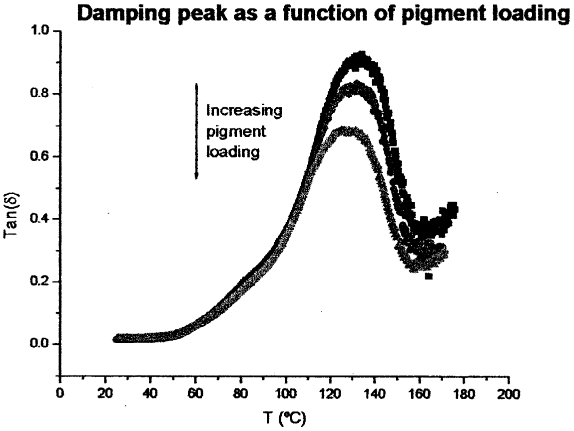

Fig. 8. Loss tangent vs. pigment (BASF Sicopal K6310) loading of the pigmented, impact-modified, PC–PBT blends. Pigment loading: top curve: 0.1%, middle curve: 0.3%, bottom curve: 0.5% w/w.

Table 7
T_g of the PC phase of the pigmented, impact-modified, PC–PBT blends

Pigment loading (%, w/w)	T_g (°C)
0.1	133
0.3	131
0.5	128

loading. Furthermore, the damping peak decreases with increasing pigment loading, indicating an increase on the elastic energy absorption of the amorphous phase of the blend. This confirms the results obtained during studies of the strain at failure.

From the above inferences, it is concluded that the C.I. Pigment Blue 28 particles are located at the interphase of the amorphous PBT phase and amorphous PC phase. If the pigment were not located at the interphase, the miscibility of the amorphous PBT phase and the PC phase would not be improved. Also, if the pigment particles were located solely in the PC phase, the T_g of this phase would increase with increasing pigment loading, instead of decreasing, due to increased restrictions to the motion of the PC polymeric chains.

3.5. Izod notched impact testing

Fig. 9 shows the variation of the impact energy absorption as a function of the pigment loading, for the samples studied. It can be concluded that there is a continuous decrease of the impact strength with increasing pigment loading. The trend observed is thought to be a consequence of the presence of the rigid pigment particles in the amorphous phase and consequences thereafter on the fracture mechanisms.

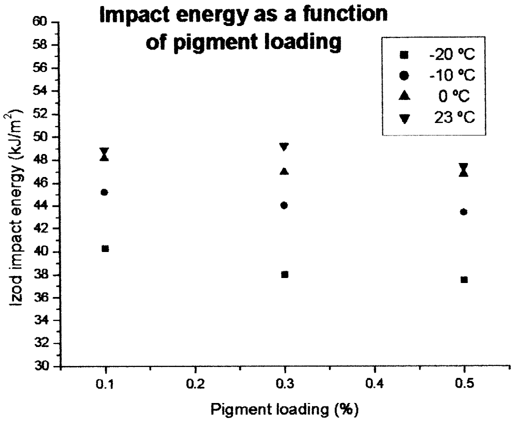

Fig. 9. Notched Izod impact energy vs. pigment (BASF Sicopal K6310) loading of the pigmented, impact-modified, PC–PBT blends.

4. Conclusions

From all the data and discussion presented, concerning the analysis of the Lewis acid–base interaction potential, the following conclusions can be drawn:

(a) Phase separation exists in these PC–PBT–IM blends as the interaction sites of PBT are preferentially involved in specific intermolecular (and intramolecular) interactions within PBT, rather than with PC;
(b) The C.I. Pigment Blue 28 ought to interact preferentially with PBT, and then with PC;
(c) The impact modifier interacts preferentially with the PC phase rather than with the PBT. This is due to the preference of PBT to interact with itself, and also due to the strong Lewis base–base repulsion between the impact modifier (through its PMMA shell) and PBT.

Pigmented PBT–PC–IM blends tested for impact resistance, and tensile properties, revealed an effect of the pigment on the mechanical properties of the blend, namely on the strain at failure, modulus and impact toughness. The results concerning the influence of the pigments on the strain at failure of the blends show a decrease of the viscous response as the pigment loading is increased. This indicates that the pigment is having an effect on the amorphous phase of the blends. DSC studies showed that no alterations to the PBT crystallisation temperature and degree of crystallinity occur and, thus, that the pigment does not influence the crystalline phase, to a noticeable extent (within the pigment loading studied). From DMTA, the pigment is shown to improve the miscibility of the amorphous PBT and amorphous PC. Thus, it is concluded that the pigment particles are located at the interphase of the amorphous PBT and amorphous PC, confirming expectation from the analysis of the Lewis acid–base interaction potential.

5. Nomenclature

K_a	Surface Lewis acidity
K_b	Surface Lewis basicity
P_{in}	Column inlet pressure
P_o	Column outlet pressure
t_R	retention time of the probe molecule
$-\Delta G_a$	Free energy of adsorption
γ_s^d	Dispersive component of the surface free energy of the solid
$-\Delta G_a^s$	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
$T_{c,on}$	crystallisation onset temperature
$T_{c,off}$	crystallisation offset temperature
T_c	crystallisation temperature
$-\Delta H_c$	enthalpy of crystallisation

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