

Examination of surfaces of solid polymers by inverse gas chromatography:

1. Dispersive properties

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The application of inverse gas chromatography (i.g.c.) for the examination of surface properties of solid materials is discussed. A group of analogous poly(dimethacrylate)s differing only by the presence and type of the heteroatom in the ester group and two reference polymers were characterized by means of this method. In this paper the dispersive properties expressed by γ_s^d and $C'P_{DS}$ determined at various temperatures (50–70°C) are presented and discussed. It was found that chemically similar polymers may be differentiated in terms of their dispersive parameters. The values of γ_s^d and $C'P_{DS}$ depend on the temperature of the i.g.c. measurement, which is determined by the relative temperature gradient. During heat treatment at 80°C and 160°C, the surfaces of the polymers undergo significant modification depending on the annealing atmosphere (helium or air). This modification is revealed by changes in the dispersive parameters and variations in the relative temperature gradients. The relationship between γ_s^d and $C'P_{DS}$ is linear, but the plots are unique for each polymer.

(Keywords: inverse gas chromatography; poly(dimethacrylate)s; surface properties)

INTRODUCTION

The surface properties of solid organic polymers significantly influence their adhesive properties, wettability, friction, coating ability, permeability, corrosion and biocompatibility. The presence of acidic and basic centres on the polymer surface increases the specific intermolecular interactions with solvents, plasticizers, other polymers and fillers. The susceptibility of the surface to change its acid–base characteristics combined with a change in dispersive properties determines the practical applications of the polymer. The surfaces of polymers of different types have been examined by inverse gas chromatography (i.g.c.)^{1–6}.

Inverse gas chromatography is an extension of conventional gas chromatography in which a non-volatile material to be investigated is immobilized within a column. This stationary phase is then characterized by monitoring the passage of volatile probe molecules of known properties as they are carried through the column by an inert gas. I.g.c. is now used to study synthetic and biological polymers, copolymers, polymer blends, glass and carbon fibres, coal, solid food, modified silicas, surfactants, petroleum pitches and heavy residues of oil distillation¹. This technique has also been used to study the water sorption abilities of different materials.

Adsorbate–adsorbent interactions are the leading cause of adsorption effects. When no chemical bonds are involved, a thermodynamic function such as the

work of adhesion W_A between the components of a multiphase system comes from physical forces only. W_A may be attributed to dispersive and electron acceptor–donor (Lewis acid–base) interactions

$$W_A = W_A^D + W_A^{ab} + W_A^{\text{dipole}} \quad (1)$$

where W_A^D , W_A^{ab} and W_A^{dipole} are parts of the work of adhesion corresponding to dispersive, acid–base and dipole–dipole interactions, respectively, and $W_A^{\text{dipole}} \rightarrow 0$. Dispersive and specific interactions are considered to contribute independently to the adsorption of probe molecules at the adsorbent surface. It has been shown that the adhesion at the fibre–matrix interface depends clearly on the measured strength of the acid–base interactions of both the fibre and the polymeric matrix. Fowkes and coworkers^{7,8} have indicated also that the surfaces of fillers can be chemically modified to enhance the acid–base interactions and increase adsorption.

Inverse gas chromatographic measurements may be carried out both at infinite dilution and at finite solute concentrations¹. In the first case, vapours of the test solutes are injected onto the column and their concentrations in the adsorbed layer drop to zero. The test substances interact with strongly active sites on the examined surface. The retention data are then converted into, for example, the dispersive component of the surface free energy and the specific component of the free energy of adsorption. In the second case, i.e. at finite solute concentrations, the appropriate adsorption isotherms are used to describe the surface properties of the polymer or filler. The differential isosteric heat of adsorption is also calculated under the assumption that

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the isotherms were obtained at small temperature intervals.

Acidic or basic solvents tend to compete for the polymer or the filler active sites. Such competition of these solvents with polymers or fillers is a means of measuring the acidity or basicity of the materials. However, Papirer and coworkers^{9-14,19} and many others^{15-18,20-23} have shown that characterization of the solid surfaces with only the use of the dispersive component of the surface free energy is fruitful and possible. This dispersive forces parameter appears to be sensitive to the changes in the examined surfaces caused by grinding, annealing and other types of surface modification.

Dispersive component of the surface free energy and the specific component of the free energy of adsorption

Intermolecular interactions in an adsorbent-adsorbate system may be dispersive and specific, corresponding to the dispersive (γ_s^d) and specific (γ_s^s) components of the surface free energy (γ_s) of the adsorbent

$$\gamma_s = \gamma_s^d + \gamma_s^s \quad (2)$$

The standard free energy of transferring a mole of vapour from the gas phase to a standard state on the surface, i.e. the adsorption energy, is given by

$$\Delta G^\circ = -RT \ln \left(\frac{BV_N}{Sg} \right) \quad (3)$$

where $B = 299$ (according to the deBoers definition of the surface pressure in the adsorbed state), S is the specific area of the adsorbent ($\text{m}^2 \text{g}^{-1}$), g is the mass of the adsorbent in the column (g) and V_N is the net retention volume (m^3). For a given system, B , S and g are constant and equation (3) becomes

$$\Delta G^\circ = -RT \ln V_N + \text{constant} \quad (4)$$

Note that the value of the constant in equation (4) depends on the arbitrarily chosen reference state of the adsorbed molecule.

For a test substance, the free energy of adsorption (ΔG°) is the sum of the energies of adsorption attributable to dispersive and specific interactions. Adsorption of non-polar probes such as n-alkanes occurs through dispersive interactions, whereas for polar probes both London and acid-base interactions contribute to ΔG°

$$\Delta G^\circ = \Delta G^d + \Delta G^s \quad (5)$$

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

For n-alkanes, $\Delta G^\circ = \Delta G^d$ and this changes with the number of carbon atoms in the molecule. The part of the adsorption energy corresponding to the methylene group may be calculated from

$$\Delta G_{\text{CH}_2} = -RT \ln(V_{N,n}/V_{N,n+1}) \quad (6)$$

where $V_{N,n}$ and $V_{N,n+1}$ denote the net retention volumes of two n-alkanes having n and $n+1$ carbon atoms in their molecules. ΔG_{CH_2} is independent of the chosen reference state of the adsorbed molecule.

According to Dorris and Gray²⁴

$$\Delta G_{\text{CH}_2} = (6.023 \times 10^{23}) \times 2a_{\text{CH}_2}(\gamma_s^d \gamma_{\text{CH}_2})^{1/2} \quad (7)$$

where a_{CH_2} denotes the surface covered by one methylene group (0.06 nm^2) and γ_{CH_2} is the surface free energy of polyethylene. Most often, γ_{CH_2} is taken as 35.6 mJ m^{-2} or its variation with temperature is taken into account

$$\gamma_{\text{CH}_2} = 35.6 + 0.058(293 - T) \quad (8)$$

The dispersive component of the surface free energy γ_s^d may be calculated from equation (7) using the experimentally determined ΔG_{CH_2} value⁹⁻²³.

Saint-Flour and Papirer²⁵ have proposed $\log P^\circ$, where P° is the saturated vapour pressure, as the physicochemical parameter that should be used for definition of the reference state. Dong *et al.*²⁶ defined another reference state in terms of the molecular polarizability of n-alkanes. In such a case the expression derived from equations (4) and (5) is

$$RT \ln V_N + C - C' P_{\text{DS}} P_{\text{DP}} - \Delta G_s \quad (9)$$

where C and C' are constants relating to the same reference state, P_D is the molar deformation polarization and the subscripts S and P refer to solid (investigated substance) and the test probe, respectively.

In the case of adsorption of n-alkanes, $\Delta G^s = 0$ and equation (9) becomes

$$RT \ln V_N + C = C' P_{\text{DS}} P_{\text{DP}} \quad (10)$$

Dong *et al.*²⁶ showed that the plot of $RT \ln V_N$ as a function of the molar deformation polarization of n-alkanes P_D is a straight line with slope equal to $C' P_{\text{DS}}$, which is proportional to the ability of the surface to participate in dispersive interactions. So, $C' P_{\text{DS}}$ is also proportional to the dispersive component of the surface energy γ_s^d , and therefore may be treated as the parameter characterizing the ability of the surface to participate in dispersive interactions.

Donnet *et al.*²⁷ proposed to use equation (4) in the form

$$RT \ln V_N + C = \theta_L = K(h\nu_S)^{1/2} \alpha_{0S} (h\nu_L)^{1/2} \alpha_{0L} \quad (11)$$

where $h\nu_S$ and $h\nu_L$ are the ionization potentials of the interacting materials, α_0 is the deformation polarizability and K is a constant which takes into account the vacuum permittivity, the distance between interacting molecules and the Avogadro constant. S and L refer to solid and liquid, respectively. The term $K(h\nu_S)^{1/2} \alpha_{0S}$ in equation (11) is characteristic of a given solid surface and is related to the London dispersive component γ_s^d of this surface.

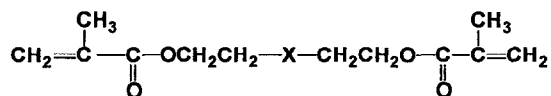
The use of other reference states is also possible. Chehimi and Pigois-Landureau³ compared six reference states where $RT \ln V_N$ was plotted against ΔH_{vap}^d , ΔH_{vap} , T_b , $\log P^\circ$, $a(\gamma_L^d)^{1/2}$ and $10^{49} (h\nu)^{1/2} \alpha_0$. However, these plots were only used in evaluation of the specific component ΔG^s of the free energy of adsorption.

In our preliminary reports^{5,6}, we presented the dispersive and acid-base properties of some highly crosslinked polymethacrylates described by γ_s^d and K_A and K_D parameters determined according to Saint-Flour and Papirer's method²⁵. Samples were obtained by photopolymerization. Our interest was motivated by the fact that multi(meth)acrylate monomers are the basic components of photocurable compositions for the

production of protective coatings widely used in many areas of industry. The surface properties of the resulting protective polymer layer are of special importance as they determine the adhesion of the layer to the substrate and its stability during exploitation. Usually, photopolymerization processes are carried out with a very high cure speed at temperatures near to ambient. However, the ultraviolet (u.v.) light sources used during the large scale u.v. curing of organic coatings generate a large amount of heat which may significantly elevate the polymerization temperature. Moreover, during exploitation the protective layers are also often exposed to elevated temperatures. The action of heat may affect the surface properties of the coating to a degree depending on both physical (temperature, presence of oxygen) and chemical (chemical structure) factors. As shown in our preliminary reports^{5,6}, the surfaces of poly(dimethacrylate)s are very sensitive to heat treatment.

In this work, we extended our investigations to a group of analogous model poly(dimethacrylate)s differing only by the presence and type of the heteroatom in the ester group. The aim of this paper is to discuss the surface properties of these polymers determined by means of i.g.c., and to describe the influence of heat treatment at various temperatures and under various atmospheric conditions on the estimated surface properties.

The investigated polymers were poly(2,2'-thiobisethanol dimethacrylate) (PTEDM), poly(2,2'-oxybisethanol dimethacrylate) (POEDM), poly(*N*-methyl diethanolamine dimethacrylate) (PNDM), poly(pentane-1,5-diol dimethacrylate) (PPDM) and poly(butane-1,4-diol dimethacrylate) (PBDM). The general formulae of the corresponding



monomers are

X = S, TEDM; X = O, OEDM; X = N(CH₃), NDM;

X = CH₂, PDM; X = -, BDM

As reference materials, poly(methyl methacrylate) (PMMA) as a linear polymer and the copolymer of BDM and methacrylic acid (P(BDM-co-MA)) as a polymer with an acidic surface were investigated.

This paper deals with the dispersive properties of the examined polymers. The acid-base properties quantified by a four-parameter scale with the use of K_A and K_D parameters will be presented and discussed in the second paper of this series.

EXPERIMENTAL

Materials

All the dimethacrylate monomers were synthesized by transesterification of methyl methacrylate (Zakłady Chemiczne Oświęcim, Poland) with the appropriate glycol (2,2'-thiobisethanol and 2,2'-oxybisethanol, Merck; pentane-1,5-diol, Merck-Suchard; butane-1,4-diol, BASF; *N*-methyl diethanolamine, Aldrich) in a solvent-free process in the presence of sodium methoxide (Merck)^{28,29}. The polymerizations and copolymerizations were initiated by u.v. irradiation and were carried out in the presence of 0.01 M α,α -dimethoxy- α -phenyl-

acetophenone (Irgacure 651, Ciba-Geigy) at 40°C in an argon atmosphere according to a procedure similar to that described elsewhere²⁸. PMMA was purchased from Zakłady Chemiczne Oświęcim. P(BDM-co-MA) contained 20 mol% of methacrylic acid.

The polymers obtained were crushed, extracted with *n*-hexane, sieved to 0.2–0.5 mm and placed into the chromatographic columns. The i.g.c. experiments used JEOL JGC 1100 (Japan) and Chrom 5 (Kovo, Czech Republic) gas chromatographs, a flame ionization detector (FID) detector, stainless steel columns (1 m long, 3 mm inner diameter), oven temperatures of 50°C, 60°C and 70°C, an injector and detector at 150°C, helium carrier gas at 30 cm³ min⁻¹ and a conditioning atmosphere of helium. The test probes were C₆–C₁₀ *n*-alkanes, ethanol, 1-propanol, 2-propanone, benzene, ether, chloroform, methylene chloride and 1,4-dioxane. Vapours of the test probes were injected using a 1 μ l Hamilton gas-tight syringe in amounts which assured infinite dilution, repeatability of the results and well-shaped chromatographic peaks. The chromatographic data were collected at 50°C, 60°C and 70°C.

Two series of experiments were carried out under helium and air to check the influence of the heat treatment on the surface properties of the polymers. The basic experiment (for the initial polymers) was done after a short conditioning of the polymer probe under helium. The next step was the heating of the polymer (in the column) in the chosen atmosphere at 80°C for 3 h followed by measurements of solute retention times. Subsequently, the same polymer was heated in the chosen atmosphere at 160°C for 3 h and retention times were again measured.

The temperatures of 80°C and 160°C were selected after differential thermal analysis and thermogravimetric analysis of the polymers³⁰. Just above 80°C in air, the polymers begin to lose weight slightly, whereas rapid destruction sets in at about 180°C for POEDM and PPDM and at 240°C for PTEDM.

The importance of the temperature of 80°C for the chemistry of the poly(dimethacrylate)s has also been checked in photopolymerization studies using isothermal differential scanning calorimetry²⁹.

Calculations

The dispersive properties of the examined polymers were quantified by

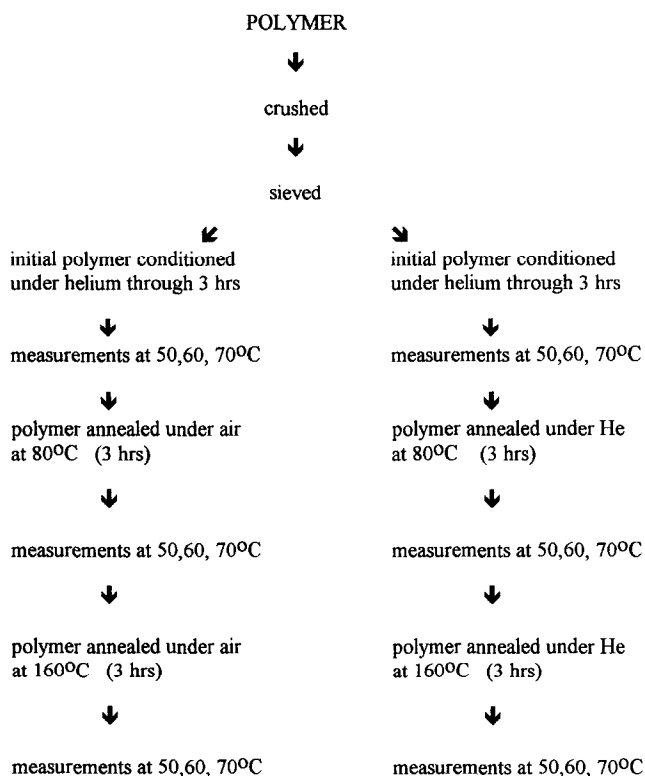
1. the dispersive component of the surface free energy γ_s^d , calculated from rearranged equation (7) and
2. Dong's $C'P_{DS}$ parameter, estimated from the slope of the linear relationship given by equation (10).

The polarizabilities of the test probes were calculated on the basis of their refractive indices.

RESULTS AND DISCUSSION

Dispersive properties of initial polymers

The dispersive properties of the initial polymers (before heat treatment) were estimated at 50°C, 60°C and 70°C after a short conditioning period under helium. Two probes for each polymer were examined. After the estimation of its properties the first probe was then successively annealed at two different temperatures under helium, while the



Scheme 1

second one was annealed under air; after each annealing step, retention data were collected (see Scheme 1). For characterization of the dispersive properties of the polymer, the dispersive component of the surface free energy γ_s^d and the $C'P_{DS}$ parameter proposed by Dong *et al.*²⁶ were used. The parameters for the initial polymers and those estimated after annealing of the polymers at elevated temperatures are given in Table 1. We found no differences in the dispersive parameters between the first (later heated under helium) and second (later heated under air) probes for the same polymer.

The values of the dispersive component of the surface free energy for the initial polymers are relatively low and lie in the range 24.8–39.8 mJ m⁻² at 50°C. They are comparable to those reported by Papirer *et al.*³¹ for silicas modified by grafting of perfluorinated silanes, but significantly lower than those found for untreated silica, i.e. 80 mJ m⁻². Chehimi *et al.*³² found the dispersive components of conducting polypyrroles to be in the 30–60 mJ m⁻² range at 50°C. An extremely low value of γ_s^d equal to 14.2 mJ m⁻² was found by Panzer and Schreiber⁴ for polycarbonates. They explained this unexpected result in terms of the elevated temperature of the experiment (80°C) and the chosen values of the molecular area.

In our work, the lowest value of γ_s^d at 50°C was found for the most polar polymer, P(BDM-co-MA) (24.8 mJ m⁻²), and the highest one for PNDM (39.8 mJ m⁻²). The studied polymers may be arranged according to increasing γ_s^d (see Figure 1) as P(BDM-co-MA) < PTEDM < POEDM < PBDM < PPDM < PMMA < PNDM. This order suggests that there exists a dependence of the γ_s^d value on the type and number of additional polar groups introduced into the

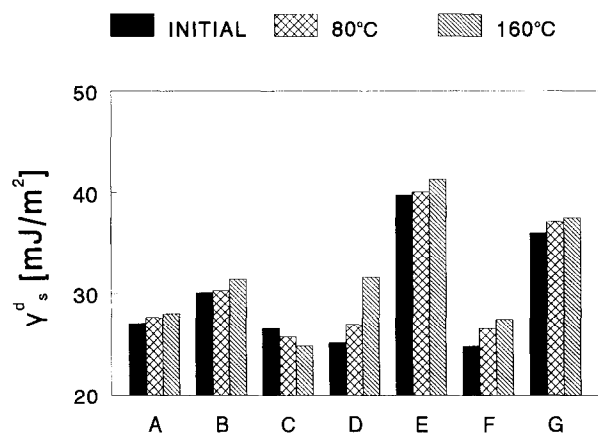


Figure 1 Initial and post-annealing (under helium) values of γ_s^d (50°C) for various polymers: (A) PBDM; (B) PPDM; (C) POEDM; (D) PTEDM; (E) PNDM; (F) P(BDM-co-MA); (G) PMMA

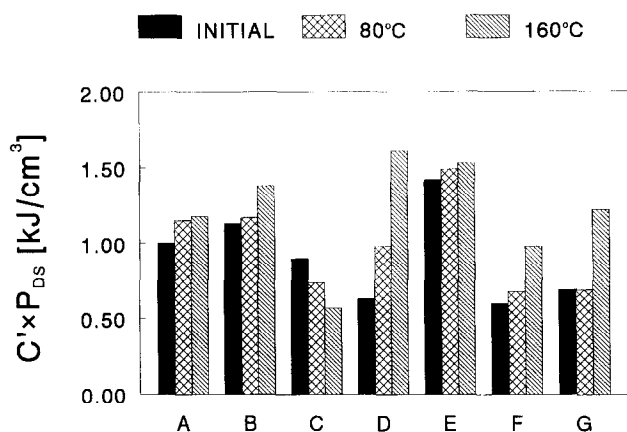


Figure 2 Initial and post-annealing (under helium) values of $C'P_{DS}$ (50°C) for various polymers: (A) PBDM; (B) PPDM; (C) POEDM; (D) PTEDM; (E) PNDM; (F) P(BDM-co-MA); (G) PMMA

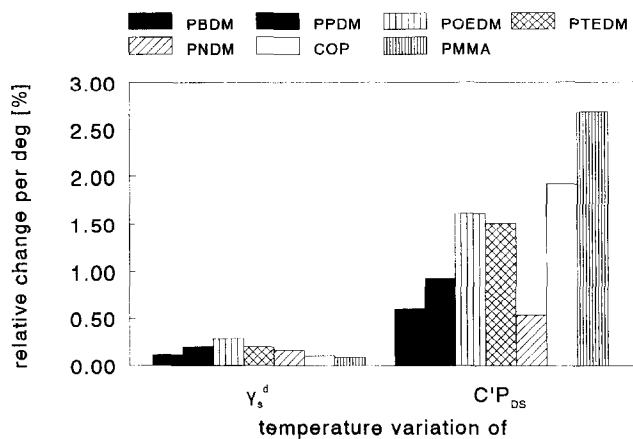


Figure 3 Relative temperature gradients of γ_s^d and $C'P_{DS}$ for the initial probes of the polymers

poly(dimethacrylate)s. The polymers possessing such groups seem to have lower γ_s^d values. However, PNDM does not fit such a scheme. The very high dispersive components of the surface free energy found for this polymer may be partially explained in terms of the screening of the nitrogen atom by the methyl group. Moreover, that PMMA has relatively high γ_s^d values may

Table 1 Dispersive properties of the studied polymers initially and after heat treatment

Polymer	Parameter	Measurement temperature (°C)	Helium			Air			Parameter change after heating at 160°C	
			Initial polymer	80°C	160°C	Initial polymer	80°C	160°C	Helium	Air
PBDM	γ_s^d (mJ m ⁻²)	50	27.0	27.6	28.0	27.0	26.2	28.4	3.7	4.9
		60	26.8	26.7	27.5	26.8	26.0	28.2	2.6	5.2
		70	26.4	26.3	27.2	26.4	25.6	27.8	3.0	5.3
	$C'P_{DS}$ (kJ cm ⁻³)	50	1.00	1.15	1.18	1.00	0.82	1.26	18.0	26.0
		60	0.96	0.94	1.09	0.96	0.79	1.23	13.5	28.1
		70	0.88	0.86	1.04	0.88	0.73	1.15	18.2	30.0
PPDM	γ_s^d (mJ m ⁻²)	50	30.1	30.3	31.5	30.1	28.4	32.9	4.7	9.3
		60	29.6	30.2	30.7	29.6	28.2	31.4	3.7	6.1
		70	28.9	29.9	30.1	28.9	28.1	31.0	4.2	7.3
	$C'P_{DS}$ (kJ cm ⁻³)	50	1.13	1.17	1.38	1.13	0.83	1.63	22.1	44.0
		60	1.04	1.15	1.24	1.04	0.79	1.36	19.2	30.1
		70	0.92	1.10	1.13	0.92	0.77	1.29	22.8	40.2
POEDM	γ_s^d (mJ m ⁻²)	50	26.5	25.7	24.8	26.5	25.6	25.0	-6.4	-5.7
		60	25.7	24.8	24.2	25.7	24.8	24.5	-5.8	-4.7
		70	25.0	24.0	23.7	25.0	23.9	24.0	-5.2	-4.0
	$C'P_{DS}$ (kJ cm ⁻³)	50	0.90	0.74	0.57	0.90	0.73	0.61	-36.7	32.0
		60	0.75	0.57	0.46	0.75	0.57	0.52	-38.7	-30.1
		70	0.61	0.42	0.36	0.61	0.40	0.42	-41.0	-31.1
PTEDM	γ_s^d (mJ m ⁻²)	50	25.1	26.9	31.7	25.1	26.8	31.1	26.3	23.9
		60	24.7	26.0	31.0	24.7	26.1	30.4	25.5	23.1
		70	24.1	25.3	30.4	24.1	25.4	29.9	26.1	24.1
	$C'P_{DS}$ (kJ cm ⁻³)	50	0.63	0.98	1.61	0.63	0.96	1.49	155.6	136.5
		60	0.55	0.81	1.47	0.55	0.82	1.36	187.2	147.0
		70	0.44	0.61	1.36	0.44	0.69	1.26	209.1	186.4
PNDM	γ_s^d (mJ m ⁻²)	50	39.8	40.1	41.4	39.8	40.4	44.7	4.1	12.3
		60	38.9	39.1	40.1	38.8	40.3	43.3	3.1	11.6
		70	38.5	38.9	39.8	38.7	40.0	41.6	3.4	7.5
	$C'P_{DS}$ (kJ cm ⁻³)	50	1.42	1.49	1.53	1.42	1.51	1.61	7.7	13.4
		60	1.35	1.40	1.44	1.35	1.48	1.54	6.7	14.1
		70	1.27	1.34	1.38	1.27	1.37	1.45	8.7	14.2
P(BDM-co-MA)	γ_s^d (mJ m ⁻²)	50	24.8	26.5	27.4	24.8	25.8	26.3	10.5	6.0
		60	24.4	25.8	26.9	24.4	25.2	25.9	10.2	6.1
		70	24.3	25.5	26.6	24.3	24.9	25.5	9.5	4.9
	$C'P_{DS}$ (kJ cm ⁻³)	50	0.60	0.68	0.98	0.61	0.77	1.07	63.0	75.0
		60	0.48	0.55	0.77	0.42	0.76	0.99	60.4	135.7
		70	0.37	0.44	0.64	0.34	0.59	0.94	73.0	176.5
PMMA	γ_s^d (mJ m ⁻²)	50	36.1	37.2	37.6	36.1	37.0	37.4	4.2	3.6
		60	35.9	36.7	37.0	35.9	36.9	37.2	3.1	3.6
		70	35.5	36.3	36.6	35.5	36.6	36.9	3.1	3.9
	$C'P_{DS}$ (kJ cm ⁻³)	50	0.69	0.69	1.22	0.69	0.95	1.35	76.8	95.7
		60	0.47	0.58	0.81	0.47	0.61	0.88	72.3	87.2
		70	0.32	0.28	0.50	0.32	0.47	0.53	56.2	65.6

indicate that crosslinking lowers the dispersive component of the surface free energy.

The $C'P_{DS}$ parameter for all the polymers varies from 0.60 to 1.42 kJ cm⁻³ at 50°C (Figure 2). The $C'P_{DS}$ values reported by Dong *et al.*²⁶ for carbon fibres and graphite powders were 0.7–1.0 kJ cm⁻³ and 1.0–1.2 kJ cm⁻³, respectively. For our group of polymers, once again the lowest value was found for P(BDM-co-MA) and the highest one for PNDM. The arrangement of the polymers according to increasing values of $C'P_{DS}$ is similar to the case of γ_s^d , one exception being the position of PMMA. $C'P_{DS}$ values for this polymer are close to those of P(BDM-co-MA).

Intermolecular interactions decrease with temperature rise, and so does the dispersive component of the surface free energy. The temperature gradient of γ_s^d characterizes the ability of the surface to change reversibly its dispersive

properties. The influence of the temperature of the i.g.c. experiment was quantified using the relative temperature gradients of γ_s^d and $C'P_{DS}$ expressed as percentage

$$-(d\gamma_s^d/dT)/\gamma_s^d(50^\circ\text{C}) \quad (12)$$

where $d\gamma_s^d/dT$ is the slope of the linear relationship between γ_s^d and the temperature of the gas chromatographic column and $\gamma_s^d(50^\circ\text{C})$ is the dispersive component of the surface free energy determined at 50°C, and

$$-(dC'P_{DS}/dT)/C'P_{DS}(50^\circ\text{C}) \quad (13)$$

where $dC'P_{DS}/dT$ is the slope of the linear relationship between $C'P_{DS}$ and the temperature of the gas chromatographic column and $C'P_{DS}(50^\circ\text{C})$ is Dong's parameter determined at 50°C.

The temperature gradients for the initial probes of the polymers are presented in Figure 3. The relative

Table 2 Relative temperature gradients of the dispersive force parameters

Polymer	Parameter	Annealing conditions			
		80°C in helium	80°C in air	160°C in helium	160°C in air
PBDM	$-(d\gamma_s^d/dT)/\gamma_s^d(50^\circ\text{C})$ (%)	0.24	0.11	0.14	0.11
	$-dC'P_{DS}/dT)/C'P_{DS}(50^\circ\text{C})$ (%)	1.26	0.55	0.59	0.44
PPDM	$-(d\gamma_s^d/dT)/\gamma_s^d(50^\circ\text{C})$ (%)	0.07	0.05	0.22	0.29
	$-dC'P_{DS}/dT)/C'P_{DS}(50^\circ\text{C})$ (%)	0.30	0.36	0.91	1.04
POEDM	$-(d\gamma_s^d/dT)/\gamma_s^d(50^\circ\text{C})$ (%)	0.33	0.33	0.22	0.20
	$-dC'P_{DS}/dT)/C'P_{DS}(50^\circ\text{C})$ (%)	2.16	2.26	1.84	1.56
PTEDM	$-(d\gamma_s^d/dT)/\gamma_s^d(50^\circ\text{C})$ (%)	0.30	0.26	0.21	0.19
	$-dC'P_{DS}/dT)/C'P_{DS}(50^\circ\text{C})$ (%)	1.89	1.41	0.78	0.77
PNDM	$-(d\gamma_s^d/dT)/\gamma_s^d(50^\circ\text{C})$ (%)	0.15	0.05	0.19	0.35
	$-dC'P_{DS}/dT)/C'P_{DS}(50^\circ\text{C})$ (%)	0.50	0.46	0.49	0.50
P(BDM-co-MA)	$-(d\gamma_s^d/dT)/\gamma_s^d(50^\circ\text{C})$ (%)	0.19	0.17	0.17	0.15
	$-dC'P_{DS}/dT)/C'P_{DS}(50^\circ\text{C})$ (%)	1.76	1.17	1.73	0.61
PMMA	$-(d\gamma_s^d/dT)/\gamma_s^d(50^\circ\text{C})$ (%)	0.12	0.05	0.13	0.07
	$-dC'P_{DS}/dT)/C'P_{DS}(50^\circ\text{C})$ (%)	2.97	2.53	2.95	3.04

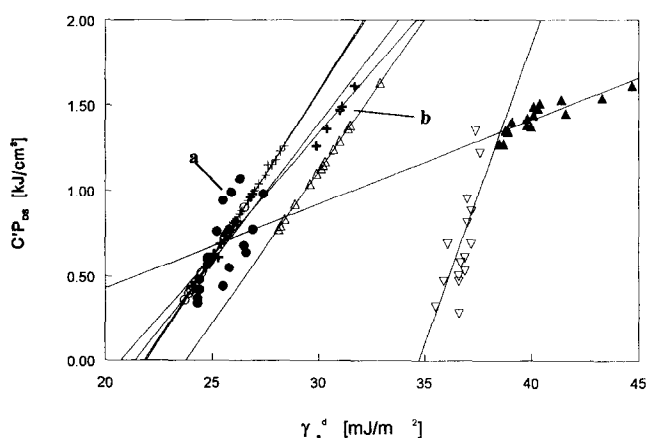


Figure 4 Relationships between γ_s^d and $C'P_{DS}$ for various polymers: (+) PBDM; (Δ) PPDM; (\circ) POEDM; (+) PTEDM; (\blacktriangle) PNDM; (\bullet) P(BDM-co-MA); (∇) PMMA

temperature gradients of γ_s^d seem to be somewhat higher for heteroatom-containing polymers. They are often one order lower than the corresponding temperature gradients of $C'P_{DS}$ and never exceed 0.5%. The lowest temperature gradients of γ_s^d were found for PBDM (0.11%), P(BDM-co-MA) (0.1%) and PMMA (0.08%). In comparison, the lowest temperature gradients of $C'P_{DS}$ we observed for PBDM (0.6%) and PNDM (0.53%). However, the temperature gradients of Dong's parameter for P(BDM-co-MA) and PMMA are surprisingly high and equal to 1.92% and 2.68%, respectively. Judging by these relative temperature gradients, PBDM and PNDM ($-(d\gamma_s^d/dT)/\gamma_s^d(50^\circ\text{C})$ for PNDM is 0.16%) may be selected as the polymers for which the smallest changes in dispersive surface properties under varying measurement temperature occur.

The influence of polymer heating on dispersive properties

In this part of the investigation we tried to discover whether the heat treatment of the polymer under chosen conditions affects irreversibly the polymer surface; this topic relates to polymer stability. We found that when samples of the initial polymers were heated at elevated temperature under helium or air, significant changes in dispersive surface properties occurred. The general trend was an increase in both γ_s^d and $C'P_{DS}$ with increasing

annealing temperature (Table 1, Figures 1 and 2). Usually, the changes caused by heating under air were larger than those occurring under helium. The changes in γ_s^d at 160°C relative to the initial polymers (Table 1, last two columns) were of the order of several per cent and generally did not exceed 13% at all temperatures of measurement. The changes in $C'P_{DS}$ were markedly higher. A deviation from typical behaviour was found for the sulfur-containing polymer, the dispersive parameters of which increased after heat treatment to a much higher degree than for the other polymers (23–26% for γ_s^d and 130–21% for $C'P_{DS}$). Moreover, the changes in dispersive surface parameters for this polymer were somewhat higher under helium than under air.

POEDM shows exceptional behaviour. In contrast to all the other polymers studied here, the parameters describing its dispersive properties decrease with rising annealing temperature. Also in this case, the changes in γ_s^d and $C'P_{DS}$ are higher after heating in helium than in air. However, for the present we are not able to explain the exceptional behaviour of POEDM.

The results presented in this subsection indicate that heat treatment causes an irreversible modification of the polymer surface. The modified surface possesses different properties which may be manifested not only by changes in γ_s^d and $C'P_{DS}$ but also by variations in the relative temperature gradients during i.g.c. measurements. Such variations are presented in Table 2.

Generally, as for the initial polymers, the relative temperature gradients of γ_s^d are almost one order lower than those observed for Dong's parameter. We cannot propose a general rule which will describe the influence of polymer annealing on the relative temperature gradients. The heat treatment does not affect both relative temperature gradients in the same way. The direction and magnitude of the changes seem to be unique for each polymer and vary with annealing temperature and atmosphere. The relative temperature gradients most often slightly increase for heat-treated surfaces, but this change depends on the polymer type and heating conditions.

Relationships between parameters used for characterization of dispersive properties of polymers

According to Dong *et al.*²⁶, $C'P_{DS}$ should be proportional to the ability of the solid surface to participate in

dispersive interactions, and in this way should be proportional to the dispersive component of the surface free energy γ_s^d . Thus, the relationship between these two quantities should be linear.

Indeed, Dong *et al.*²⁶ found the same linear relationship between γ_s^d and $C'P_{DS}$ for carbon fibres and graphite powders. In our case, the attempt to find one general linear relationship did not give satisfactory results (Figure 4). Several straight lines were found, and each polymer seems to show a unique γ_s^d versus $C'P_{DS}$ plot. Excellent linear relationships exist between γ_s^d and $C'P_{DS}$ for PBDM, PPDM, POEDM and PTEDM. Poorer straight lines were obtained for PNDM, P(BDM-co-MA) and surprisingly, PMMA. The plots for PNDM and PMMA substantially differ from those for the other polymers. Deviations from linearity were very often observed for data points derived at elevated temperature (160°C) both under helium and air. Note the points labelled 'a' for P(BDM-co-MA) (Figure 4). These points and five others for PTEDM (labelled 'b' in Figure 4), corresponding to polymer probes annealed under helium and air at 160°C, deviate from the straight line which might be common for PBDM, POEDM and, in part, PTEDM and P(BDM-co-MA). The $C'P_{DS}$ values for these points are lower than the hypothetical ones, i.e. for all points on the straight line. The most substantial deviations from the straight line are found for PNDM, where the points form three groups randomly distributed around the best statistical fit. In our opinion, all the observed deviations from the straight line of γ_s^d versus $C'P_{DS}$ for a given polymer may result from the significant changes in surface character that result from heating the polymer at elevated temperatures.

CONCLUSIONS

Dispersive properties characterize the ability of a surface to interact with another substance through non-polar intermolecular interactions. Examination of these properties by i.g.c. has led us to the following conclusions. (1) Polymers with very similar chemical structures (e.g. PPDM and PBDM) exhibit different surface dispersive properties as quantified by γ_s^d and $C'P_{DS}$. (2) Cross-linking influences the dispersive force parameters (compare PBDM with PMMA). (3) There exists a temperature gradient effect on the dispersive parameters which is observed during the temperature rise in the i.g.c. experiment. This effect results mainly from the reduction in intermolecular interactions due to thermal motion, but its magnitude depends on the surface type and is not related to the initial value of the dispersive parameter. (4) An increase in the number of polar functional groups reduces the values of both dispersive parameters. (5) Heat treatment modifies markedly the properties of the polymer surface. The magnitude and direction of the observed changes are unique to each polymer. (6) The modification of the surface is irreversible, e.g. the parameter measured at 50°C after annealing at 160°C shows a different value from that before heating. Progressive modification results in various relative temperature gradients observed after each step of annealing. (7) $C'P_{DS}$ is more sensitive to polymer annealing and the temperature of the i.g.c. experiment than is γ_s^d . (8) The increase in dispersive parameters after heat treatment of the polymer sample may suggest

an increase in the non-polar character of the surface, i.e. the disappearance of polar groups.

The dispersive parameters describe the weak intermolecular interactions, which contribute to the resulting surface properties to a lesser degree than acid-base interactions. In spite of this, dispersive parameters are able to describe the differences between the surfaces of chemically similar polymers and the change occurring on such surfaces under the influence of various physical factors.

To fulfil the characterization of the surface properties of the examined polymers, the dispersive force parameter data should be complemented by data representing acid-base interactions. The discussion of the acid-base properties of the same group of polymers will be presented in the second paper of this series.

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