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Swelling parameter of polypropylene used in household appliances

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Samples of unfilled copolymer polypropylene were immersed in various solvents and the equilibrium swelling was recorded. Two-dimensional solubility maps of the Hildebrand parameter, δ, versus hydrogen bonding parameter, γ_c, and δ_h versus δ_v for polypropylene were plotted. Using the calculated percentage swell values and the solubility maps, the δ and δ_h values for detergent were postulated. No changes in the polypropylene backbone were revealed by mid- or far-infrared spectra, showing that the polypropylene polymer, when subjected to a number of different solvents, had not altered substantially.

1. Introduction

Polypropylene is being increasingly used as an engineering thermoplastic, particularly in domestic appliances [1] and examples of other applications are cited in the commercial literature [2]. Among these other applications, polypropylene is being used in parts of vacuum cleaners, towel dispensers and dishwashers [1, 2]. Thus, a proper understanding of its behaviour when subjected to various physical and chemical environments is necessary.

In recent years there has been a growth in the demand for polypropylene at a rate of 15% per annum [3]. This can be attributed to the low density, good impact resistance, colourability, good chemical resistance, and ease of moulding characteristics of this material [4].

Polypropylene is a semi-crystalline thermoplastic which is made in its homopolymer form by polymerizing the propylene monomer, using stereospecific catalysts, to form long-chain molecules. Stereospecific catalyst systems control the position of the side (methyl) group in each propene unit in the polymeric chain. Most commercial polypropylene is "isotactic", with the propene units arranged head to tail in the chain and all the methyl groups lying on the same side.

There have been studies investigating the effect of solvents on polymer materials [5–7] and these have mainly focused on developing guidelines that could be used for predicting solubility. A chemical will be a solvent for a polymer if the molecules of the two materials are compatible; i.e. they can coexist on the molecular scale and there is no tendency to separate. Molecules of two different species will be miscible on a molecular level if the force of attraction between different molecules is not less than the forces of attraction between two like molecules of either species. It is recognized that the solution process involves a breaking of the intermolecular bonds between the solute and the solvent molecules [8]. The most useful method of assessing the compatibilities of different chemical substances is the solubility parameter, δ, introduced by Hildebrand (see [9]). The solubility parameter (or solpar) is defined as the square root of the cohesive-energy density. The cohesive energy of the system is defined as the energy of vaporization per molar volume

$$\text{cohesive energy} = ([L - RT]/[M/D])^{1/2} \quad (1)$$

where L is the latent heat of vaporization, R is the universal gas constant, T is the absolute temperature, (L-RT) is defined as the energy of vaporization, M is the molecular weight and D is the density. The cohesive energy is expressed in Hildebrand units (H), or $\text{MPa}^{1/2}$.

The solubility of a polymer, in a given solvent, is favoured if the solubility parameter of the polymer and the solvent are equal to or within 2–3 $\text{MPa}^{1/2}$ [8]. Michaels *et al.* [5] measured the solubility parameter for semicrystalline isotactic polypropylene and reported a value of 16.8 $\text{MPa}^{1/2}$. In their study, the authors firstly measured the sorption levels of organic vapours in the polymer and secondly observed the "dissolution temperature" of polypropylene in various solvents. The dissolution temperature was obtained by immersing the film in excess solvent and noting the temperature at which the film disappears from view. By considering a number of simple molecules, Small (see [10]) was able to compile a list of molar attraction constants, G, for the various parts of a molecule. Using additive laws and elemental group contributions, the author calculated δ from the relationship

$$\delta = D\Sigma G/M \quad (2)$$

where G is Small's molar attraction constant, D the density and M the molecular weight of the polymer. Using Small's molar attraction constants, Seymour [11] estimated the solubility parameter for polypropylene, from Equation 2, to be 16.6 $\text{MPa}^{1/2}$. Brydson

0022-2461

[8] estimated the value of δ for a given polymer by immersing it in a range of solvents of known δ and recording the value at which equilibrium swelling occurred. The value for the polymer which caused the greatest equilibrium swelling was found to be within 2–3 MPa$^{1/2}$ of the solvent.

Solubility maps can be plotted, which usually show the maximum polymer concentration as a function of a Hildebrand parameter; however, they can be used to represent two or more parameters. Three-dimensional models, stereographs, sets of projections, and contours have all been used to present solubility parameters [10, 12]. In many cases, the solubility behaviour of a polymer can be adequately represented in two dimensions by δ and δ_h (the hydrogen bonding part of the solubility parameter), or δ and δ_p (the dispersion part of the solubility parameter). The most generally useful two-dimensional plots appear to be based on the subdivision of the Hildebrand parameter into a "volume dependent" part, δ_v, and a "residual" or a hydrogen bonding part, δ_R, where

$$\delta_v^2 \approx (\delta_d^2 + \delta_p^2) \qquad \delta_R^2 \approx \delta_h^2 \tag{3}$$

Two-dimensional solubility diagrams, using δ_v and δ_R values for several polymers, are cited in the literature [6,10,12–14].

The aim of the present investigation was to produce polymer–solvent interaction "spectra" or "maps" for polypropylene, to predict the solvents that are likely to have an effect on polypropylene.

2. Experimental procedure

2.1. Polymer material

Shell KMT polypropylene was used in this investigation. It has a typical melt index of 4.0 and is a medium flow, copolymer with high impact strength, designed for injection moulding. With these properties and its rigidity and creep resistance, KMT is particularly suited for the production of articles such as housewares, electrical appliances, components for domestic appliances and other related applications [4]. Samples of polypropylene Shell KMT copolymer, medium flow grade were injection moulded at 200 °C and formed into rectangular pieces.

2.2. Solvents

Twenty four solvents were used and their characteristics are listed in Table I. The Hildebrand solubility parameter is given by δ, while δ_d and δ_p are the dipolar and the dispersion components of the solubility parameter, respectively [10]. The hydrogen bonding parameter is given by γ_c. A number of different solvents was investigated with an emphasis placed on the likelihood of their contact with household appliances, although a number of other more "extreme" solvents were also tested. The δ values for the solvents ranged from 14–30 MPa$^{1/2}$. Two different concentrations (0.46% and 1.38% in aqueous solution) of added detergent (Finish™) were also examined.

Injection-moulded samples of approximate width 10.00 mm, thickness 1.00 mm and weight 0.2 g were totally submerged in each solvent, with ten control samples. All the samples were kept in a dark area at room temperature and periodically dried and weighed. After each sample had been numbered, the dimensions were recorded using a micrometer gauge. The weight of each sample was also recorded using a Mettler balance accurate to four decimal places.

2.3. Infrared spectra

Infrared spectra on a number of the polypropylene samples were run in the mid-infrared (4000–400 cm^{-1})

TABLE I Standard parameters, and swelling behaviour, of the solvents used to condition the polypropylene samples.

	δ_d (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_h (MPa$^{1/2}$)	δ_v (MPa$^{1/2}$)	δ (MPa$^{1/2}$)	Swell %	γ (MPa$^{1/2}$)
Toluene	17.9	1.1	2.1	17.93	18.2	21.041	4.5
Ethanol	15.8	8.8	19.2	18.09	26.5	0.969	18.7
Iso-octane	14.3	0	0	14.30	14	14.828	0
Cyclohexane	16.7	0	0	16.70	16.8	22.01	0
MEK	15.9	9.1	5.1	18.32	19	5.93	7.7
Acetone	15.5	10.4	7	18.67	20.5	1.948	9.7
Methylcyclohexane	16	0	0	16.00	16	21.978	0
p-xylene	17.3	0	4.7	17.30	17.9	16.96	4.5
n-butyl acetate	14.7	3.7	6.3	15.16	17.4	8.939	8.8
n-hexane	14.7	0	0	14.70	14.9	9.121	0
Dibutyl-ether				0	14.5	15.296	11
Methylene chloride	17.8	6.3	6.1	18.88	19.8	15.887	1.5
Cylohexanone	17.7	8.9	5.1	19.81	19.8	21.039	11.7
1,1,1 Trichloroethane	17	4.4	2.1	17.56	19.6	21.04	1.5
Ethyl acetate	15.8	5.3	7.2	16.67	18.6	3.862	8.4
Nitromethane	18.8	5.1	6.1	19.48	26	0.311	2.5
Methyl alchol	15.2	12.5	22.5	19.68	29.7	0	18.7
Ethylene glycol				0	20.2	– 0.005	13
Diethyl ether	14.5	2.9	5.1	14.79	15.1	9.082	13
Acetic acid	14.4	7.9	13.4	16.42	25.8	2.312	
Detergent (1)				0		2.847	
Detergent (2)				0		3.559	
Benzyldehyde				0		4.450	
Water	15.4	15.8	42.0	22.06	47.5	0	

on a Digilab FTS 40 spectrometer and in the far-infrared (700–50 cm^{-1}) on a Digilab FTS 40V spectrometer. Samples were run in the transmission mode, without any prior sample preparation.

2.4. Swell values

Table I shows the percentage swell values, which were calculated from the change in weight of the sample after equilibrium had been reached (at a maximum time of 7 months). The δ_v values were calculated using Equation 4

$$\delta_v^2 = \delta_d^2 + \delta_p^2 \quad (4)$$

3. Results

The maps (δ, γ_c) and (δ_h, δ_v) are presented in Figs 1 and 2 respectively, for polypropylene. Fig. 1 shows a plot of the Hildebrand parameter, δ, versus hydrogen bonding parameter, γ_c, with various percentage swell contours. The figure shows three areas of swelling; the inner area corresponds to the most active solvents while the outer area corresponds to the least active solvents. The δ value for polypropylene is also shown. Fig. 2 shows a plot of δ_h versus δ_v for the polypropylene sample. Again three areas can be mapped; solvent damage, intermediate behaviour and full resistance. From Figs 1 and 2 it is apparent that the δ values between 16 and 17.5 $MPa^{1/2}$ have an effect on polypropylene, while δ_h values greater than 7 $MPa^{1/2}$ do not appear to affect the polypropylene sample.

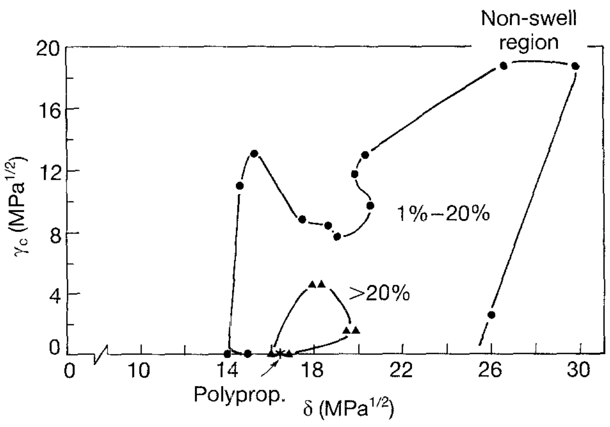

Figure 1 Hilderbrand parameter, δ, plotted against the hydrogei bonding parameter, γ_c, for polypropylene, with the percentage swel contours plotted.

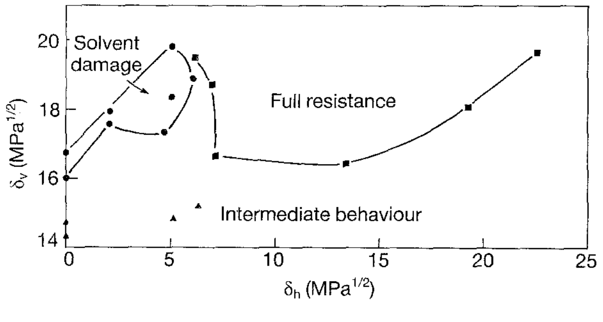

Figure 2 Solubility map showing δ_h against δ_v for the polypropylene sample, showing solvent damage behaviour.

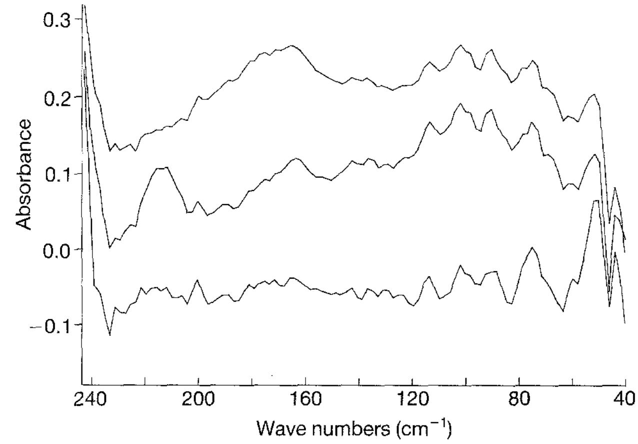

Figure 3 Far-infrared spectra for the polypropylene sample. The top spectrum shows the polypropylene after conditioning in toluene, the middle in ethanol and the bottom spectrum is a control sample.

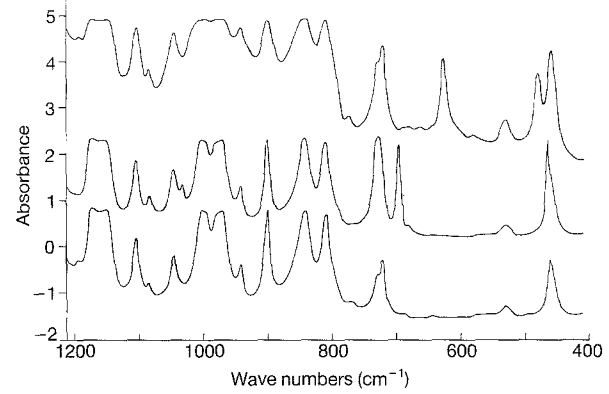

Figure 4 Mid-infrared spectra for the polypropylene samples. The top spectrum shows the polypropylene after conditioning in toluene, the middle in ethanol and the bottom spectrum is a control sample.

Fig. 3 shows far-infrared spectra for the polypropylene samples after conditioning in toluene and ethanol and a control sample, between 240 and 60 cm^{-1}. Fig. 4 shows mid-infrared spectra for the same samples between 1200 and 400 cm^{-1}.

4. Discussion

From the results it is evident that a model solely considering the solubility parameter of solvents and polymer is inadequate to explain the behaviour. It is necessary to take account of other properties of the liquid. One such property would be the strength of the hydrogen bonds between the solvent molecules themselves and the molecules of the liquid and polymer. Pimental and McClellan [15] classify solvents by the manner in which they contribute to hydrogen bond formation:

1. solvents which can act as proton donors (e.g. chloroform);
2. solvents which can act as proton acceptors (e.g. ketones, esters, ethers and aromatic hydrocarbons);

3. solvents which can act simultaneously as proton donors and acceptors (e.g. alcohols, carboxylic acids and secondary amines);

4. solvents which do not hydrogen bond (e.g. paraffins).

From the results of this work, weakly hydrogen bonded solvents having hydrogen bonding parameters less than 1.5 $MPa^{1/2}$ cause the greatest amount of swelling and could be considered as solvents for polypropylene. However, for very strongly bonded solvents of hydrogen bonding greater than 18 $MPa^{1/2}$, little or no swelling is observed.

It is interesting to note that Vincent and Raha [13] found that for PMMA and PVC, weakly hydrogen bonded liquids of bonding parameters less than 1.5 are not solvents.

In Fig. 1, the 1–20% swelling region can be divided into two areas; a low-swelling area which appears to be on the right-hand side of the curve, and a high-swelling region which is found to the left. From Table I it is evident that the swelling of samples immersed in the aqueous detergent samples is between 4% and 5%. From the results of this work it can be postulated that the δ value for the detergent would lie between 20 and 28 $MPa^{1/2}$ and the δ_h value would lie between 0 and 20 $MPa^{1/2}$. More research is currently underway to establish values for δ and δ_h for the detergent. The $\delta(47.5)$ and $\delta_h(42)$ values for distilled water lie in the theoretical non-swell region of the curve in Fig. 1 and this has been reinforced by a 0% swelling in this solvent.

Infrared spectroscopy was used to compare a number of polypropylene samples that had been subjected to the solvents as discussed above. The polypropylene samples that had been subjected to toluene (the region of damage), ethanol ($<$ 1% swell) and distilled water (full resistance) were studied in detail with a standard polypropylene control. Changes in the polypropylene backbone would be revealed by band shifts or absences in the mid-infrared for chemical alteration and in the far-infrared for alteration in polypropylene crystallinity [16]. In both spectral regions, shown in Figs 3 and 4, the bands in the polypropylene samples were retained, showing that the polypropylene polymer had not been substantially altered by these solvents. Additional features were found in the ethanol/polypropylene sample (350, 694, 1030, 1496, 1605 and 3087 cm^{-1}) and in the toluene/polypropylene sample (350, 479, 625, 1592 and 1712 cm^{-1}), which do not correlate directly with the neat solvent spectra. Work is proceeding on the identification of these features.

5. Conclusion

The solubility parameter alone does not adequately describe all the intramolecular forces present in a solution. Dispersion, polar and hydrogen bonding interactions must be considered separately in order to predict adequately polymer solubility. Constructing solubility maps, for polypropylene in various solvents, provides a way of examining its behaviour in the presence of liquid environments.

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