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EFFECT OF PARTICLE TREATMENT OF COMPOSITE FILLER ON ITS INTERACTION COEFFICIENT

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SUMMARY

The effect of calcium carbonate treatment on its surface activity was studied by inverse gas chromatography, concentrating on the effect of water on the filler surface, the effect of coating the filler surface with stearic acid and the effect of the particle size of the filler. The surface activity was evaluated by determining the interaction coefficient, I_g .

Water on the filler surface decreases the surface activity, especially with untreated calcium carbonate. It also causes a levelling of the difference between the contributions of acid and/or base centres, which can be the cause of incorrect evaluation of their interaction contributions. Consequently, when establishing the filler surface properties, water on the calcium carbonate surface cannot be neglected and thermal conditioning of the filler surface prior to testing is therefore necessary. The dependence of the quality of calcium carbonate surface treatment on the means of adding stearic acid (directly during calcite grinding or from the solution after grinding) was established. The activity of the calcium carbonate surface was found to decrease with increasing particle diameter.

INTRODUCTION

Calcium carbonate is one of the most widely used fillers of polyolefinic composites. Prior to its application as a filler, natural calcium carbonate has to be ground in a ball-mill. The filler obtained has a wide distribution of particle diameters.

The dispersion of fillers in the polymer matrix and the mechanical properties of the filled polymers are influenced by surface interactions. In a non-polar polymer matrix, fillers whose surfaces show neither acid nor base characteristics¹ disperse more quickly (mechanically stronger composites are produced). Calcium carbonate shows very strong surface activity¹⁻⁴.

Prior to being added to a non-polar polymer, calcium carbonate is surface treated (the surface is deactivated) to fulfil the above-mentioned requirement of compatibility. The most common reagent in industrial manufacture is stearic acid, which is usually added to calcium carbonate at the grinding stage.

Different samples of the same filler and samples of different fillers may contain various amounts of water, depending on the sample treatment, its prior storage, the particle size, etc. So far, however, these facts have not been taken into account in the evaluation of the surface activity of fillers.

This paper is concerned with the effect of water present on the calcium carbonate surface on the surface activity of the filler. Also, the activity of the calcium carbonate surface was studied as functions of the method of treatment of the filler with stearic acid and of the particle diameter.

EXPERIMENTAL

The apparatus used was described in detail in a paper on the study of composite fillers by inverse gas chromatography⁴. The measurements were carried out using a Chrom gas chromatograph (Laboratory Instruments, Prague, Czechoslovakia) with a flame ionization detector. The chromatographic column is connected to the detector directly and to the injector with a 30 cm × 0.2 mm I.D. fused-silica capillary. A 0.02- μ l volume of the test solute was injected with a 0.5- μ l syringe (Scientific Glass Engineering, North Melbourne, Australia). An injector for capillary columns with a stream splitter was used. The splitting ratio of 200:1 permits only *ca.* $1 \cdot 10^{-7}$ g from the originally injected volume of 0.2 μ l of the test solute to enter the chromatographic column.

The filler sample (see Table I) was packed into a straight glass chromatographic column (10 cm × 0.3 cm I.D.). During mixing with the polymer (polypropylene), the

TABLE I
CHARACTERISTICS OF THE CALCIUM CARBONATE SAMPLES

| Sample No. | Type and supplier | Stearic acid (%) | Specific surface area (m ² /g) | Particle size distribution | |
|------------|----------------------------------------------------------------------------|------------------|-------------------------------------------|------------------------------------|------------------------------------|
| | | | | d_{50} (μ m) ^{***} | d_{97} (μ m) ^{***} |
| 1 | Durcal 2, OMYA, France | 0 | 3.3 | 3.0 | 10.0 |
| 2 | Precipitated, Heating Plant, Brno, Czechoslovakia | 0 | 2.6 | — | — |
| 3 | Pomezí near Jeseník, ÚNS Kutná Hora, Czechoslovakia | 0 | 4.3 | 2.3 | 6.2 |
| 4 | As 3 | 0.3 | 4.3 | 2.3 | 6.2 |
| 5 | As 3 | 0.5 | 4.3 | 2.3 | 6.2 |
| 6 | As 3 | 0.3* | 4.3 | 2.3 | 6.2 |
| 7 | As 3 | 0.5** | 4.3 | 2.3 | 6.2 |
| 8 | Pomezí near Jeseník, Chlumčanské Ceramic Works, Poběžovice, Chechoslovakia | 0.3 | 1.6 | — | — |
| 9 | As 8 | 0.31 | 4.6 | 3.0 | 10.0 |

* Sample 3 coated with 0.3% (w/w) of stearic acid from solution in *n*-pentane without thermal surface treatment.

** Sample 3 coated with 0.3% (w/w) of stearic acid from solution in *n*-pentane after thermal surface treatment (3 h at 150°C).

*** The values of d_{50} (d_{97}) mean that 50% (97%) particles in the size distribution have diameters less than this value.

fillers were exposed to temperatures of about 200°C for 2 min. Therefore, the testing of the surface activity was carried out with the sample thermally conditioned at the temperature simulating the conditions of the commercial preparation of the composite. For this purpose the thermostat temperature was increased within 3 min from the laboratory temperature to 200°C, kept at this value for 2 min, then decreased to the test temperature. The testing of fillers was performed after 20 min.

The test temperature was 90°C, unless stated otherwise. The test solutes *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, dichloromethane, trichloromethane, benzene and furan were of analytical-reagent grade (Lachema, Brno, Czechoslovakia).

The activity of the calcium carbonate surface was evaluated by determining the interaction coefficient, I_g , which expresses the ratio of the specific interaction of the test solute with the filler surface to the non-specific interaction of a hypothetical *n*-alkane with the same vapour tension as the test solute⁵:

$$I_g = \frac{V_g(\text{test solute})}{V_g(\text{hypothetical } n\text{-alkane})} - 1$$

The test solutes were di- and trichloromethane, furan and benzene. The reproducibility of the retention times for one filler packing (sample 4) expressed in terms of the standard deviation of ten measurements was 1% for furan. The reproducibility of I_g for four independent measurements (four columns with the fillers each measured three times) was 5% for furan. Calcium carbonate was used non-sized, except in the study of the grain size effect. Sizing of calcium carbonate into individual fractions according to particle size was carried out with an Alpine 10 MZR apparatus (Alpine, Augsburg, F.R.G.). The surface area of calcium carbonate was measured by the dynamic desorption method⁶.

RESULTS AND DISCUSSION

Effect of surface water

Fig. 1 shows the specific retention volumes of the solutes as a function of the temperature of conditioning of calcium carbonate, either untreated or treated with 0.3% stearic acid. The fillers were heated in the column for 10 min at the given temperatures and then tested at a column temperature of 120°C. The retention volumes increase with increasing temperature of conditioning, especially for untreated calcium carbonate (Fig. 1a). At higher temperatures water is desorbed from the surface, the active centres on the sample surface are exposed and, consequently, the surface activity increases (Table II). For the calcium carbonate sample treated with stearic acid (Fig. 1b) the increase in retention is not so evident because the active centres are blocked by stearic acid molecules. The increase in the surface activity with increasing temperature of conditioning is less for the treated filler and above *ca.* 180°C it remains constant (Table II).

The dependence of the specific retention volumes of the tested solutes on the time of sample conditioning is shown in Fig. 2. The retention volumes of the solutes increase with increasing conditioning time, and to a greater extent with the untreated filler (Fig. 2a) than with treated calcium carbonate (Fig. 2b). For the filler treated with stearic acid and conditioned at the temperature used, the retention volume of the solutes is

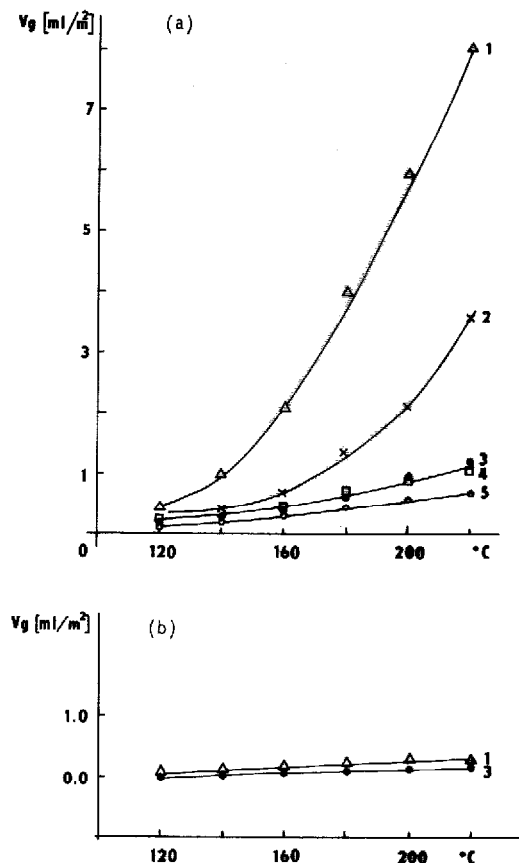


Fig. 1. Dependence of the specific retention volumes of the test solutes (V_g) on the temperature of calcium carbonate conditioning. (a) Sample 3; (b) sample 4 (see Table I). 1 = Furan; 2 = benzene; 3 = *n*-octane; 4 = trichloromethane; 5 = dichloromethane.

constant after *ca.* 3 h. For untreated calcium carbonate, a stable state was not reached even after 5 h of conditioning. The surface activity increases again with the time of conditioning, within 3 h for untreated and within 1 h for treated calcium carbonate (Table III).

It is evident that water has a decisive effect on the surface activity especially of the untreated fillers and it cannot be neglected when establishing the filler surface activity. Fig. 3 shows the values of the interaction coefficient (I_g) for the thermally unconditioned surface of calcium carbonate of different origins at a column temperature of 30 $^{\circ}\text{C}$. Differences in I_g between individual fillers are not very large. Fig. 4 shows the values of I_g after thermal conditioning of the fillers. It is evident that in the latter instance the differences in I_g are substantially higher, the surface activity increasing several fold. For example, I_g of furan for sample 3 is *ca.* 20 times higher for the conditioned fillers even if the testing temperature is 90 $^{\circ}\text{C}$, *i.e.*, 60 $^{\circ}\text{C}$ higher than the

TABLE II

DEPENDENCE OF INTERACTION COEFFICIENT (I_g) ON THE TEMPERATURE OF CONDITIONING

Column temperature, 120°C.

| Calcium carbonate | Temperature (°C) | I_g | | | |
|----------------------------------------------------|------------------|-----------------|------------------|-------|---------|
| | | Dichloromethane | Trichloromethane | Furan | Benzene |
| Untreated (sample 3) | 120 | 4.9 | 5.0 | 36.2 | 3.2 |
| | 140 | 7.5 | 5.8 | 40.7 | 2.7 |
| | 160 | 5.8 | 4.9 | 60.6 | 4.6 |
| | 180 | 6.9 | 5.8 | 90.2 | 6.6 |
| | 200 | 7.9 | 6.1 | 119.2 | 8.1 |
| | 220 | 8.8 | 6.4 | 157.5 | 12.8 |
| Treated with 0.3% (w/w) of stearic acid (sample 4) | 120 | 0.9 | 1.0 | 3.8 | 0.5 |
| | 140 | 1.1 | 1.4 | 5.3 | 0.5 |
| | 160 | 2.1 | 1.9 | 9.9 | 0.6 |
| | 180 | 2.8 | 2.4 | 16.0 | 0.7 |
| | 200 | 2.2 | 2.2 | 14.7 | 0.6 |
| | 220 | 1.6 | 1.7 | 12.2 | 0.4 |

TABLE III

DEPENDENCE OF INTERACTION COEFFICIENT (I_g) ON THE TIME OF COLUMN CONDITIONING AT 120°C

| Calcium carbonate | Column temperature (°C) | Time (min) | I_g | | | |
|----------------------|-------------------------|----------------------------------------------------|------------------|-------------------|-------|---------|
| | | | Dichloro-methane | Trichloro-methane | Furan | Benzene |
| Untreated (sample 3) | 120 | 20 | 2.7 | 2.9 | 13.8 | 1.3 |
| | | 50 | 2.8 | 3.1 | 18.5 | 2.1 |
| | | 80 | 4.4 | 4.3 | 27.2 | 3.3 |
| | | 130 | 4.3 | 4.0 | 30.3 | 2.5 |
| | | 160 | 4.3 | 4.1 | 35.3 | 2.7 |
| | | 190 | 4.5 | 4.5 | 37.0 | 2.9 |
| | | 230 | 4.6 | 4.4 | 38.8 | 3.0 |
| | | 270 | 4.0 | 4.0 | 34.5 | 2.8 |
| | | 320 | 3.4 | 3.4 | 28.5 | 2.4 |
| | | Treated with 0.3% (w/w) of stearic acid (sample 4) | 90 | 20 | 1.8 | 2.0 |
| 50 | 2.4 | | | 2.4 | 15.6 | 0.9 |
| 80 | 2.6 | | | 2.6 | 19.0 | 1.0 |
| 120 | 2.6 | | | 2.6 | 19.0 | 1.0 |
| 180 | 2.2 | | | 2.3 | 17.2 | 0.8 |
| 240 | 2.4 | | | 2.4 | 18.0 | 0.8 |
| 300 | 2.3 | | | 2.3 | 17.6 | 0.8 |

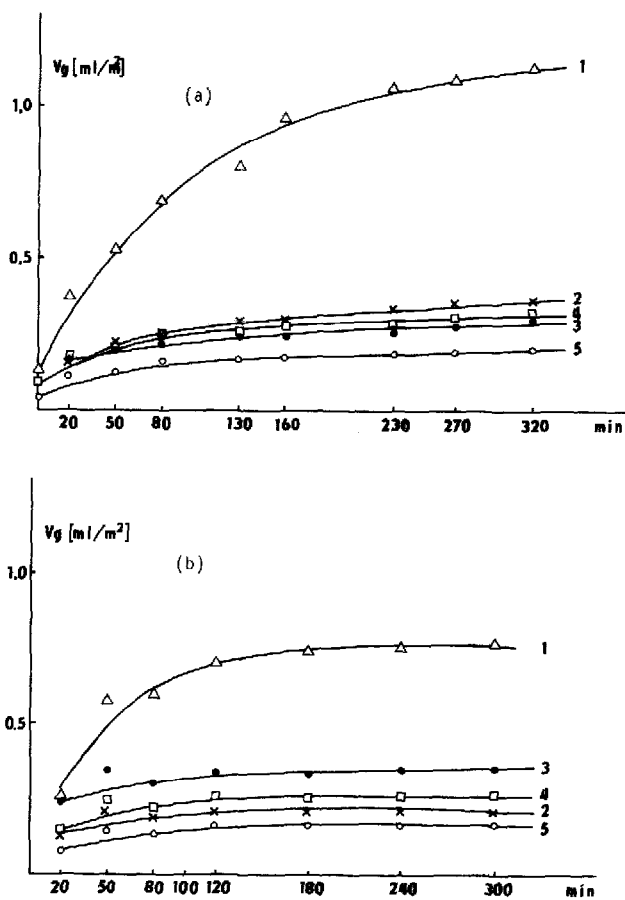


Fig. 2. Dependence of the specific retention volumes of the test solutes (V_g) on the time of calcium carbonate conditioning. (a) Sample 3, column temperature 120°C ; (b) sample 4, column temperature 90°C . Lines 1–5 as in Fig. 1.

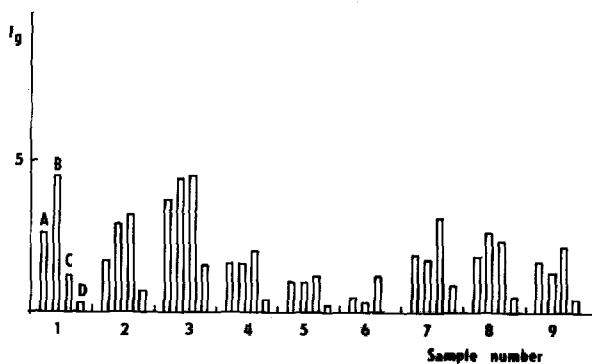


Fig. 3. Values of interaction coefficients (I_g) without prior thermal conditioning of calcium carbonate. A = Dichloromethane; B = trichloromethane; C = furan; D = benzene. For samples 1–9, see Table I. Column temperature, 30°C .

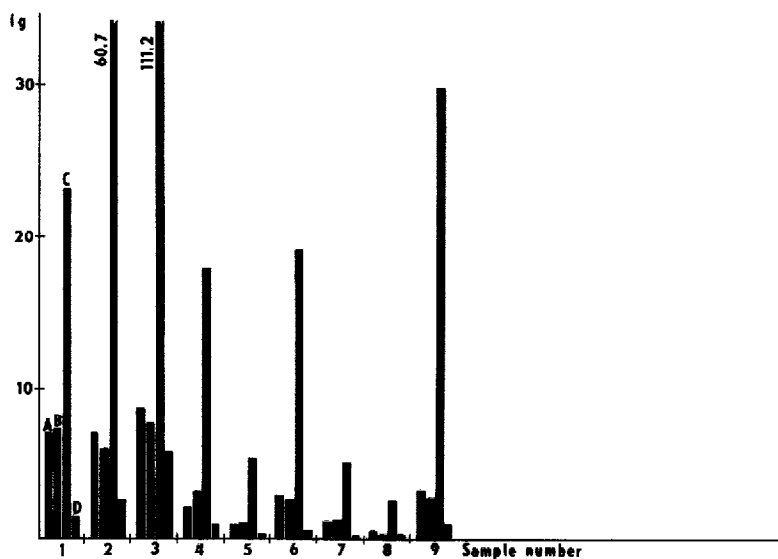


Fig. 4. Values of interaction coefficients (I_g) with calcium carbonate thermally conditioned. A–D as in Fig. 3 and samples 1–9 as in Table I. Column temperature, 90°C.

testing temperature for the same unconditioned fillers. At a testing temperature of 30°C the retention times of the conditioned fillers are very long. Moreover, the molecules of water on the surface of calcium carbonate cause a levelling of the difference between the contributions of acid and/or base centres and, consequently, the I_g for all four test solutes are comparable (see, *e.g.*, sample 3). After conditioning, especially the contribution of acidic centres on the filler surface increases.

The effect of water is also reflected in the fact that the interaction coefficient depends on the testing temperature (Table IV). These changes are so important that they cannot be caused by fortuitous different dependences of the retention volumes of *n*-alkanes and the tested solutes on the temperature of the chromatographic column. At a higher chromatographic temperature the filler sample is, in fact, always conditioned prior to the surface activity measurement.

TABLE IV

EFFECT OF TESTING TEMPERATURE ON INTERACTION COEFFICIENT (I_g)

Sample 3 (see Table I) without thermal conditioning.

| Solute | I_g | | |
|------------------|-------|------|-------|
| | 30°C | 90°C | 120°C |
| Dichloromethane | 4.0 | 4.8 | 6.4 |
| Trichloromethane | 4.2 | 5.0 | 5.8 |
| Furan | 5.2 | 16.0 | 35.7 |
| Benzene | 1.8 | 1.8 | 2.8 |

Effect of filler surface treatment with stearic acid

As a consequence of the wide distribution of particle diameters of ground calcium carbonate and because stearic acid is added to the filler only mechanically by pouring during grinding, it seems likely that the surface coating of calcium carbonate with stearic acid is not uniform in this instance.

The values of I_g for the calcium carbonate samples both untreated and treated during grinding of the original material with 0.3 and 0.5 wt.-% of stearic acid (Fig. 4, samples 3–5) show that the filler surface activity decreases with increasing amount of stearic acid, which corresponds with the results obtained previously³.

The original sample of surface-untreated calcium carbonate (sample 3) was treated, before testing, with 0.3 wt.-% of stearic acid from a solution in *n*-pentane in the same manner as used for coating the chromatographic support with a stationary phase, *i.e.*, by gradual evaporation of the solvent (samples 6 and 7). Sample 6 was treated with stearic acid without prior thermal conditioning and sample 7 was conditioned prior to treatment at 150°C for 3 h. This method of filler treatment should make the filler surface coating with stearic acid much more uniform than the treatment directly during grinding. The measured surface activity verified this assumption. The I_g of sample 7 for a 0.3% coating from the solution is close to the values for a 0.5% surface coating during calcium carbonate grinding (sample 5). Again, however, water present on the surface proves to be an important factor. The activity of sample 6 (unconditioned) is comparable to that of sample 4 (0.3% of stearic acid during grinding). This agreement is due to the presence of water on the untreated filler surface prior to its treatment with stearic acid from the solution, which causes imperfect surface coating. Hence, the filler coating with stearic acid by gradual evaporation of the solvent without prior thermal treatment (sample 6) has approximately the same effect on the decrease in surface activity as deactivation with the acid directly during grinding, *i.e.*, when calcium carbonate is treated while the water content on the surface is still low.

Effect of the filler particle size

Untreated calcium carbonate (sample 3) was sized into four fractions: 4.3–6.1, 2.3–3.9, 1.4–2.2 and below 1.4 μm , while the dust (particles below 1 μm) was blown away during sizing. The I_g values for all the four fractions (Table V) are evidently lower

TABLE V
VALUES OF INTERACTION COEFFICIENT (I_g) FOR SIZED UNTREATED CALCIUM CARBONATE

Individual fractions were prepared from sample 3 (see Table I).

| Particle size distribution (μm) | Specific surface area (m^2/g) | I_g | | | |
|----------------------------------------------|-------------------------------------------------|-----------------|------------------|-------|---------|
| | | Dichloromethane | Trichloromethane | Furan | Benzene |
| <1.4 | 6.8 | 6.4 | 6.4 | 73.1 | 4.3 |
| 1.4–2.2 | 3.5 | 7.3 | 7.1 | 80.0 | 4.6 |
| 2.3–3.9 | 3.0 | 5.8 | 5.4 | 60.8 | 2.3 |
| 4.3–6.1 | 2.1 | 5.1 | 4.7 | 49.6 | 2.1 |

in comparison with the original non-sized sample (*cf.*, Fig. 4). In spite of the relatively high dispersion of I_g values for different columns with the same filler⁴ (the greatest relative error was found for dichloromethane and was 20% for the 2.3–3.9 μm fraction), the trend of decreasing I_g with increasing particle diameter can be seen clearly in Table V. The fact that the I_g values for the non-sized calcium carbonate are higher than those for all the sized fractions can be explained by the blowing away of the dust particles (these particles remain in the filter of the sizing device and so they could not be measured). The changes in I_g values as a function of the particle diameter cannot be explained by the available physico-chemical data. The changes are not related to the content of aluminosilicates.

Sizing of the filler to a fraction with a narrower particle distribution is also important for the chromatographic testing of the surface activity. A chromatographic column packed with the sized material has, at the same flow-rate of the carrier gas, a much lower inlet pressure. This enables carrier gas flow-rates higher than 5 ml/min (the maximum obtainable flow-rate for the column with the non-sized calcium carbonate) to be used, which shortens the time of testing and improves the separation efficiency of the chromatographic column.

CONCLUSIONS

Water present on the filler surface has a great effect on the filler activity. It is therefore necessary to condition the filler thermally prior to testing the activity. To be able to compare the activities of different fillers, it is necessary to condition and measure the fillers at the same temperature.

The method of filler treatment with stearic acid influences the surface activity of the final filler. A more uniform coating of the surface with the acid results in a lower surface activity. Filler treatment in which the surface coating with stearic acid (or other material) is more uniform than is given by simple mixing of the filler and the acid during grinding is, therefore, more suitable for the final composite.

The filler surface activity depends on the particle diameter. Sizing of the original material to a fraction with a narrow particle size distribution with simultaneous removal of the particles having very small diameters (dust) should improve the filler quality. The use of a sized fraction for testing of the filler surface activity is, moreover, more suitable when using inverse gas chromatography.

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