PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 42, NO. 2, PP. 167-186 (1998)

AGGREGATION TENDENCY OF PARTICULATE FILLERS: DETERMINATION AND CONSEQUENCES

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Received: June 2, 1998

Abstract

The agglomeration tendency of 11 commercial $CaCO_3$ fillers with different particle size and specific surface area was investigated by means of various techniques. Some powder characteristics were measured and also the sedimentation of treated, as well as non-treated fillers were determined in water and toluene. Polypropylene (PP) composites containing 25 vol% filler were homogenized in an internal mixer. Melting and crystallization, as well as tensile properties were determined on compression molded plates. Unambiguous determination of aggregation is difficult, since it depends on interaction and experimental conditions. The extent of aggregation is always determined by the relative magnitude of attractive and separating forces under the given sample preparation and/or testing conditions. Observable aggregation begins at 5–7 m^2/g specific surface area for the studied fillers, but its extent depends also on their particle size distribution and on surface treatment. Composites with a larger number of aggregates possess inferior mechanical properties, however, the effect depends very much on the characteristics measured.

Keywords: aggregation, polypropylene composites, $CaCO_3$ fillers, characterization of aggregation tendency.

1. Introduction

The structure of particulate filled polymers is very often assumed to be a simple homogeneous dispersion of well defined particles in a polymer matrix. However, frequently a significant deviation of properties is observed from those predicted by models based on the assumption of such a structure. These deviations can be almost exclusively traced back to insufficient homogenization and generally to structure related phenomena. Numerous literature references are available proving that complicated structures can develop also in particulate filled polymers [1]–[3] and that structure/property correlations are of utmost importance in the determination of the properties of such materials.

Aggregation of filler particles is a crucial question during the preparation of filled polymers; it leads to inhomogeneous distribution of filler particles, processing problems, poor surface quality and deteriorated mechanical properties. The importance of particle/particle interactions is shown also by the fact that considerable effort is concentrated on the development of new surface treatment or processing technologies with the single goal of improving homogeneity [4], [5].

In spite of its importance, the possibility of aggregation is often disregarded, which has several reasons. Particle/particle interactions depend on numerous factors including composition and they affect all composite properties differently. Detection of aggregation is difficult and it is even more difficult to express it in quantitative terms. Various techniques were proposed in the literature for the study of aggregation: sedimentation of the particles [6], small angle light scattering [7], optothermal analysis [9], [10], particle size measurements [3], etc. However, the most often used technique is optical microscopy, sometimes combined with image analysis [2], [10], [11]. SVEHLOVA [11], for example, successfully used the area of aggregates to describe the extent of particle/particle interactions and found a good correlation between this quantity and the mechanical properties of particulate filled PP[11].

The goal of the present study was to compare the aggregation tendency of various commercial $CaCO_3$ fillers. The most diverse techniques were used for their characterization. Composites were also prepared with a given filler content and their various properties measured. An attempt was made to determine the most important factors leading to aggregation and the efficiency of various techniques to detect its occurrence.

2. Preliminary Considerations

Before the experimental data and their evaluation are presented, it is worth to consider the factors leading to the interaction or separation of filler particles in a composite. Numerous attractive forces can be identified, which might lead to aggregation. One of the most important of these is the adhesive force, which depends on the reversible work of adhesion (W_{AB}) and the radius of the particles (R), i.e.

$$F_a = \frac{3}{2}\pi W_{AB} R_e , \tag{1}$$

where, for particles with dissimilar size, $R_e = R_1R_2/(R_1 + R_2)$ an effective particle radius [12].

If particles are dispersed in a viscous liquid several forces can lead to attraction; the viscous force hinders the separation of particles. In a Newtonian fluid for particles of identical size, which are initially separated by a small distance (h_0) from each other, this can be expressed as [13]

$$F_v = 12\,\pi\,\eta\,2\,R^2\,\frac{\dot{h}}{2h_0}\,, \tag{2}$$

where η is the viscosity of the fluid and $\dot{h}$ the rate of separation. In the case of incomplete wetting, capillary forces act between particles connected by discrete liquid bridges. Capillary forces can be divided into two parts, one determined by surface tension, while the other is a hydrostatic component. The exact determination of these forces does not seem to be straightforward due to the geometric constants involved. Several forces may act between electrostatically charged particles [14], but these are small compared to those mentioned above.

The number of separating forces is smaller. Repulsion of particles having the same electrostatic charges may lead to separation [14], but the significance of these forces is limited here, too. Much more important is the hydrodynamic force acting on particles dispersed in a fluid [13], just like during the processing of polymer melts. The shear forces developing under such conditions can be expressed as

$$F_h = -6.12\,\eta\,2\,R^2\,\dot{\gamma}\,, \tag{3}$$

where $\dot{\gamma}$ is shear rate. Since the viscosity of polymer melts is usually high, this force may significantly hinder the development of aggregated structures.

Approximate calculations have been carried out and the estimated magnitude of various forces is summarized in *Table 1*. As the table shows, adhesive and hydrodynamic forces are the most important in polymer composites. Although the viscous force is relatively large as well, it is given for larger particles only; its value becomes even lower when the particle size decreases (see *Eq.* (2)). The above analysis clearly shows that aggregation is determined by the relative magnitudes of attractive and separating forces and the most important factors influencing the homogene2ity of polymer composites are the size of particles, their surface tension and the shear forces acting during their homogenization.

3. Experimental

The most important characteristics of the fillers used i2n the experiments are compared in *Table 2*. Altogether 11 $CaCO_3$ fillers of different origin were used; four of them were precipitated products of Solvay (Socal), while the rest was ground type filler from two sources (Omya, ECC). Although the shape of the two types of filler were somewhat different – some ground types having sharp edges – their aspect ratio was approximately the same, around 1. As a consequence, particle shape was assumed to have a much

Table 1. Forces acting on 20 μm particles in polymer (PP) composites

Force			
Direction	Character	Type	Magnitude (N)
Adhesive	**Adhesive**		**10^{-4}**
	Viscous[a]		$10^{-5} - 10^{-6}$
	Capillary[a]	Surface tension	$10^{-5} - 10^{-6}$
		Hydrostatic	$10^{-5} - 10^{-6}$
	Electrostatic	Coulomb	10^{-7}
		Dipole	10^{-8}
		Image charge	10^{-7}
		Space charge	10^{-8}
Separating	**Hydrodynamic**		**10^{-3}**
	Electrostatic		10^{-8}

[a] For particles of 100 μm diameter [13]

smaller effect on aggregation than other characteristics, e.g. size, and it was disregarded in this study. Particle properties were characterized by various methods. Particle size (diameter, d) and size distribution were measured by an LSI Lasentec LAB-TEC 1000 apparatus, while specific surface area (A_f) was determined by single and five point BET measurements. During the subsequent analysis of the results, properties will be often presented as a function of specific surface area, since this quantity can be determined more accurately than particle size. Abbreviated names of the fillers are also listed in the table, and fillers with properties deviating from the general tendency will be marked by this in the figures. The pourability, bulk density (ρ_b) and the bulk density after compaction (vibration) (ρ_{bc}) were measured by means of the corresponding standard methods. Sedimentation measurements were carried out in water and toluene. Sedimentation rate (v_i) and the final volume of sedimentation (V_e) were determined in these experiments.

Polypropylene (Tipplen H501, TVK, Hungary, MFI = 4 g/10 min, 230 °C/21.6 N) composites containing 25 vol% of filler were homogenized in an internal mixer at 190 °C, 50 rpm for 10 min. The high filler content was specifically chosen to promote aggregation. The composite was compression molded into 1 mm thick plates at 190 °C; the plates were used in all subsequent studies. Melting and crystallization characteristics were deter-

Table 2. Characteristics of the investigated fillers

Trade name	Abbrev.	Source	A_f (m^2/g)	d (μm)	ρ_b (g/l)
Omyacarb 130 GU	130GU	Omya	0.3	130.00	1388
Omyacarb 40 GU	40GU	Omya	0.8	23.00	1016
Omyacarb 15 GU	15GU	Omya	2.0	12.00	926
Omyacarb 2 GU	2GU	Omya	3.6	2.50	677
Polcarb	P	ECC	5.0	1.30	538
Hydrocarb OG	HOG	Omya	6.0	1.90	627
Socal N2	SN2	Solvay	6.0	0.35	356
Socal N4	SN4	Solvay	9.0	0.25	273
Socal N6	SN6	Solvay	11.0	0.20	319
Setacarb OG	SOG	Omya	15.0	0.44	536
Socal U1	SU1	Solvay	20.0	0.08	285

mined in a DSC 30 cell of a Mettler TA 3000 thermo-analytical equipment at 10 °C/min heating and cooling rate. Two consecutive measurements were carried out on all samples, the results of the second run are reported here. Young's modulus (E) of the composites was measured at 0.5 mm/min (1% deformation rate), while other tensile properties at 5 mm/min cross-head speed. Yield stress (σ_y) and strain (ε_y), as well as tensile strength (σ) and elongation-at-break (ε) were derived from the measured force vs elongation correlations.

All fillers were treated with oleic acid to check the effect of decreased surface tension (reversible work of adhesion, see *Eq.* (1)). The amount of oleic acid used for the treatment was selected to give 100% surface coverage. This quantity was determined from the results of previous studies showing a linear correlation of A_f and the bonded fatty acid [15], [16]. Powder and sedimentation characteristics were also determined for the treated filler.

4. Results

The results are discussed in three sections dealing with powder properties, sedimentation and composite characteristics. During evaluation it must be always kept in mind that aggregation is determined by the relative magnitude of attractive and separating forces. Adhesion is basically the same under all conditions, it depends on the size of the particles and surface tension. However, the forces separating the particles depend on a number of factors including the presence of an eventual medium (fluid or melt), the mixing or shear forces, etc. When the filler is tested in powder form, the separating forces are determined mainly by gravitation, while in suspension stirring as well as solvation also influence the interaction of the particles. In the melt large shearing forces act leading to more efficient homogenization.

4.1. Powder properties

The bulk density of particulate materials is principally independent of their average particle size, since packing depends only on particle size distribution [17],[18]. However, it is influenced very much by the formation of higher order structures, i.e. by aggregation. The particle size distribution of the studied fillers is more or less similar, only a few fillers (Setacarb OG, Hydrocarb OG) have a different, relatively broad distribution. Although particle size distribution can be measured by various methods and instruments, because of the strong aggregation tendency of the above mentioned fillers the measured curves can be misleading. Even in spite of the effort to disintegrate aggregates by the application of surfactants and an ultrasonic bath, some of them prevail and behave like large particles biasing the distribution. In order to avoid presenting misleading information particle size distribution curves were omitted from this paper.

If aggregation occurs, bulk density decreases. Surface treatment reduces the surface tension of the filler, adhesion decreases between the particles, thus the extent of aggregation is expected to be smaller as well. This should lead to an increase in bulk density.

The bulk densities of the non-treated and treated fillers are plotted against their specific surface area in *Fig. 1*. In accordance with the above presented considerations, the bulk density strongly decreases with increasing specific surface area, indicating increasing aggregation of the fillers. Practically all fillers fall on the same line with the exception of Setacarb OG. The larger bulk density of this filler probably results from its wider particle size distribution, from the presence of a fraction with smaller particle size. The relatively sharp decrease of density at small specific surface areas slows down as the particle size of the filler decreases. The bulk density remains practically constant above 6–8 m^2/g specific surface area, the aggregation of the filler particles determines the measured density value. As expected, surface treatment increases bulk density in most cases, and decreased aggregation and improved pourability leads to the better compaction of the particles. The effect of treatment, however, is very slight indicating that mainly the particle size determines the relative magnitude of adhesive and separating forces.

The relative value of bulk density before and after compaction is presented in *Fig. 2* as a function of A_f. At the smallest specific surface area this value is relatively small and does not depend on surface treatment indicating that the large particles find optimum arrangement relatively easily. Larger

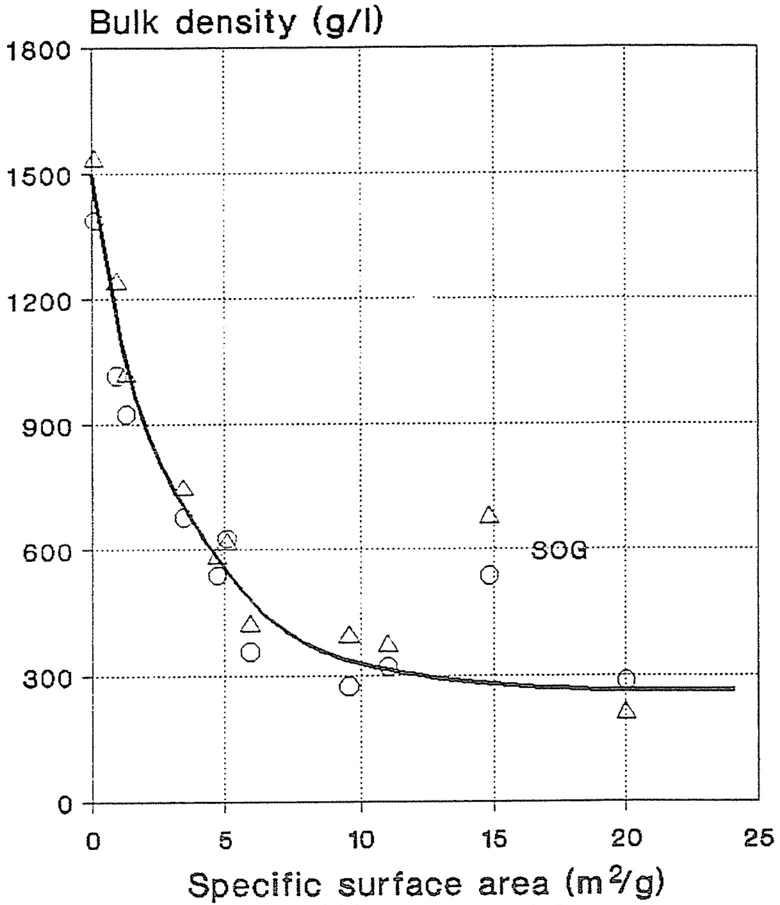

Fig. 1. Bulk density of non-treated (○) and treated (△) fillers as a function of their specific surface area

values are obtained at smaller particle sizes and the relative bulk density slightly decreases with increasing specific surface area. These results suggest that a closer packing of the particles is promoted by the application of external force (compaction). The effect of particle size is moderate on the relative bulk density. It is interesting to note the effect of surface treatment. At small A_f values, ρ_{brel} increases showing the beneficial effect of a decreased interaction on packing. Except for the filler with the largest particles, the values are significantly lower than without treatment indicating that aggregation takes place even at this low specific surface area, but it is efficiently decreased by surface treatment. The beneficial effect of treatment is shown also for the majority of fillers. The value of ρ_{brel} is relatively low indicating that for treated fillers compaction does not improve packing or decrease

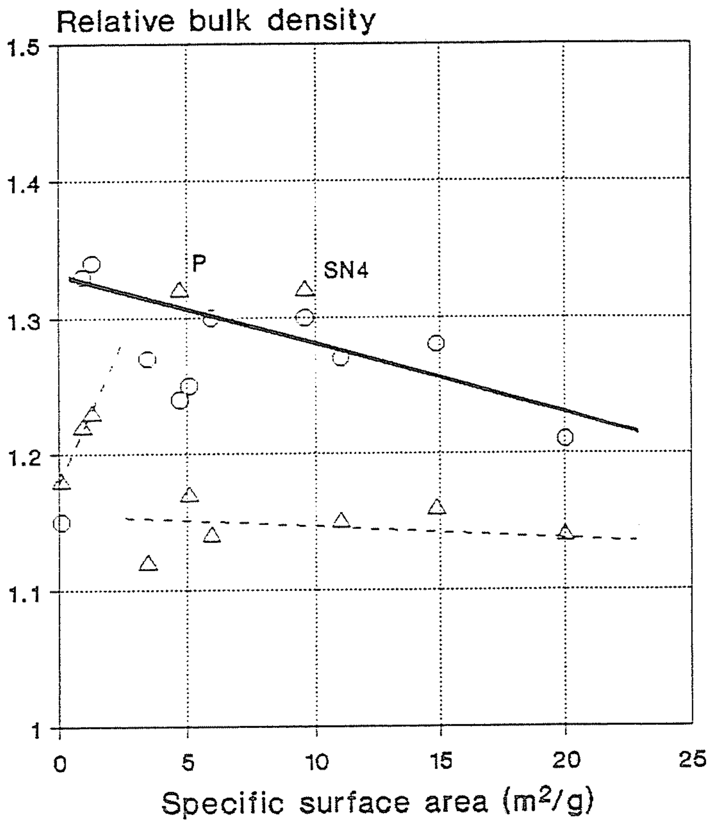

Fig. 2. Effect of compaction on the relative bulk density of treated (Δ) and non-treated (○) fillers

aggregation significantly. This complementary effect is also shown by the decreased slope of the straight lines connecting non-treated and treated fillers. Two of the treated fillers behave differently; in the case of Socal N4 and Polcarb both the treatment and compaction influence the bulk density. The results unambiguously show that the aggregation of filler particles increases with decreasing particle size, which is definitely the dominating factor, but particle size distribution also influences bulk density.

4.2. Sedimentation

The sedimentation of a filler in various solvents is also influenced by solid/liquid interaction. According to the Stokes equation the rate of sedimentation depends on the density difference of the particles and the liquid (Δ_ρ), the viscosity of the solvent (η_s) and on the size of the settling particles

$$V = \frac{2R^2\Delta\rho g}{9\eta_s}\,, \tag{4}$$

where g is the gravitational acceleration. It is well known, however, that the size of the settling particle differs from its real diameter, it depends also on the interaction of the components. Strong interaction decreases the flocculation of the particles, because a solvent layer is adsorbed on their surface. In the case of a weaker interaction, larger particles form a network enclosing numerous smaller ones and the aggregates sediment together. In such cases the rate of sedimentation increases and the equilibrium sedimentation volume (V_e) is larger than in solvents entering a strong interaction with the particles. V_e is of course strongly influenced by the particle size distribution of the fillers.

The result of a typical sedimentation experiment is shown in *Fig. 3*. Sedimentation proceeds at a decreasing rate, an equilibrium volume is reached after a certain time. Sedimentation is relatively fast in this case, the time to reach equilibrium is about 15 min, because of the large particle size of the filler. The sedimentation curve can be described quantitatively by the following equation

$$V = V_e[1 - \exp(-a_1 t)]\,, \tag{5}$$

where a_1 is a rate constant. Good correlation was found between V_e and the sedimentation volume measured after 24 hours, as well as between a_1 and a rate value determined by the intersection of the straight lines fitted to the increasing and horizontal legs of the sedimentation curve (v_i).

Sedimentation rates (v_i) are plotted against the specific surface area of the filler in *Fig. 4*. The sedimentation of non-treated fillers was measured in water and toluene, while that of the treated ones only in toluene. The correlation is very similar to that of the bulk density, i.e. an equilibrium value seems to be reached at high A_f values. Aggregation is especially pronounced in the case of the surface treated fillers, which seems to be rather surprising at first. The two correlations, however, very well demonstrate the effect of the medium in which the measurement is made. The strong adsorption of water on the surface of the non-treated fillers leads to the formation of a solvate layer, which hinders aggregation, and the sedimentation of small particles is slower. We saw already that at high specific surface areas the effect of treatment is moderate, it cannot prohibit aggregation, the majority of the fillers sediment faster. In the case of fillers showing peculiar behaviour, a fraction of small particles must sediment slower than the bulk of the sample.

The sedimentation volume shows a more complicated picture (*Fig. 5*), V_e approaches an equilibrium value in all three cases. The relatively weak

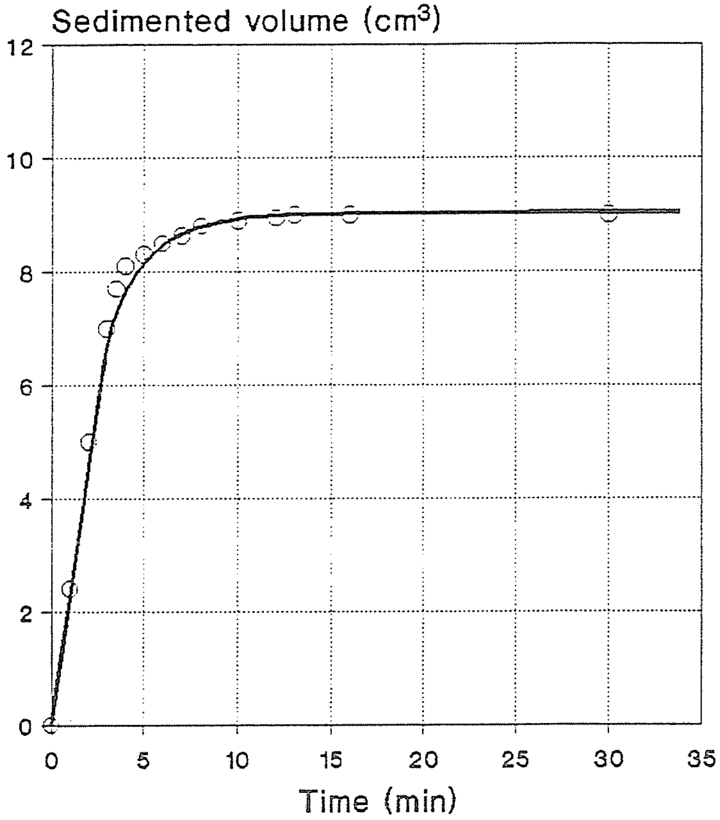

Fig. 3. Sedimentation of non-treated Omyacarb 15 GU in water

interaction of toluene and the non-treated filler leads to a fast increase in V_e. Above a certain specific surface area very small aggregated particles behave like larger ones, aggregation dominates, the sedimentation volume does not change any more. The strong interaction of water and the non-treated filler particles results in lower V_e values below 10 m^2/g specific surface area, but also in a continuous increase of aggregation. The saturation value seems to be higher, if this conclusion can be drawn from the single value of Socal U1 at all. Comparison of the two correlations indicates that the structure of the aggregated particles depends on the solvent used for the experiments, i.e. on interactions, its effect is much stronger on sedimentation than on the powder properties. Surface treatment has a much stronger effect on sedimentation volume than on the sedimentation rate or apparent bulk density, but the tendency is the same as in the case of the non-treated filler. If we compare these results to those presented in the previous section, it cannot

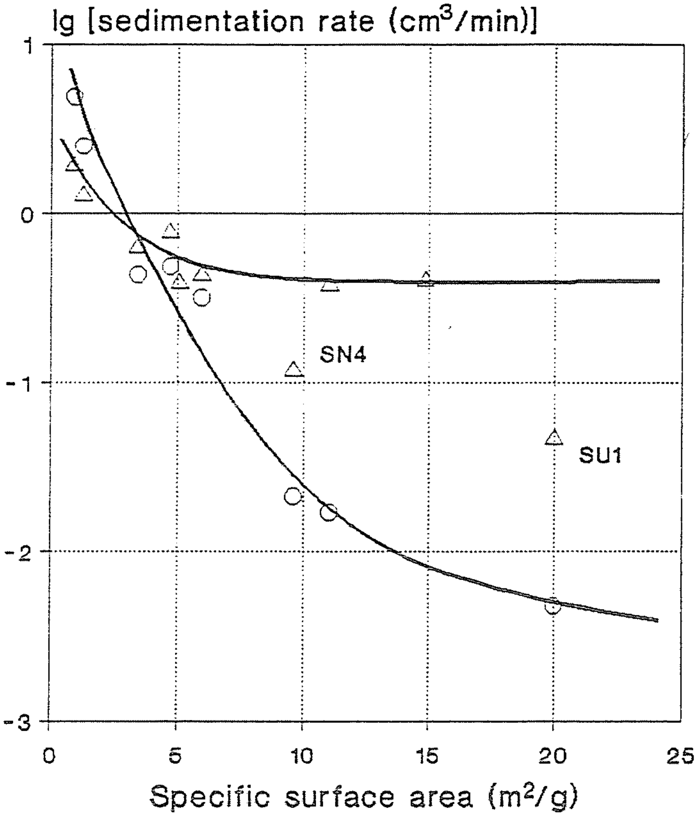

Fig. 4. Dependence of the rate of sedimentation on the specific surface area of the filler; (○) non-treated/water, (△) treated/toluene

be a coincidence that the maximum of V_e measured in toluene is around 8 m^2/g specific surface area.

4.3. Composite Properties

Particulate filled polymers are prepared almost exclusively by the homogenization of the polymer melt with the filler particles [19]. In the melt adhesive forces keep the particles together, while hydrodynamic forces (shear) separate them. By using *Eqs.* (1) and (3), model calculations were carried out to determine these forces in PP/$CaCO_3$ composites. The results are plotted in *Fig. 6* showing that below a certain particle size adhesion is larger than

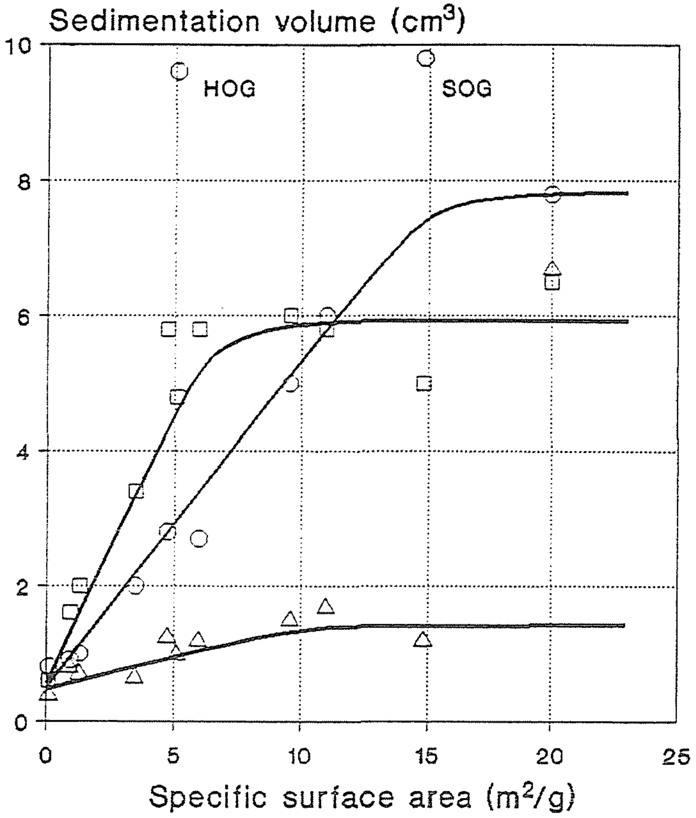

Fig. 5. Correlation of equilibrium sedimentation volume and the specific surface area of the filler; (○) non-treated/water, (□) non-treated/toluene, (△) treated/toluene

the hydrodynamic forces, and aggregation takes place. The particle size where this occurs corresponds to a specific surface area of about 6 m^2/g. Attention must be called here to the fact, though, that uniform particle size was used in the calculations, both the particle size distribution and the complicated shear field prevailing in the internal mixer were neglected. Nevertheless, the correlations agree well with expectations and the obtained critical value corresponds to those derived from other measurements.

Aggregation has a pronounced effect on the crystallization and melting behavior of PP. It has been observed earlier that occasionally crystallization exotherms split into two parts; aggregation seems to initiate the crystallization of polypropylene. A typical crystallization exotherm is presented in

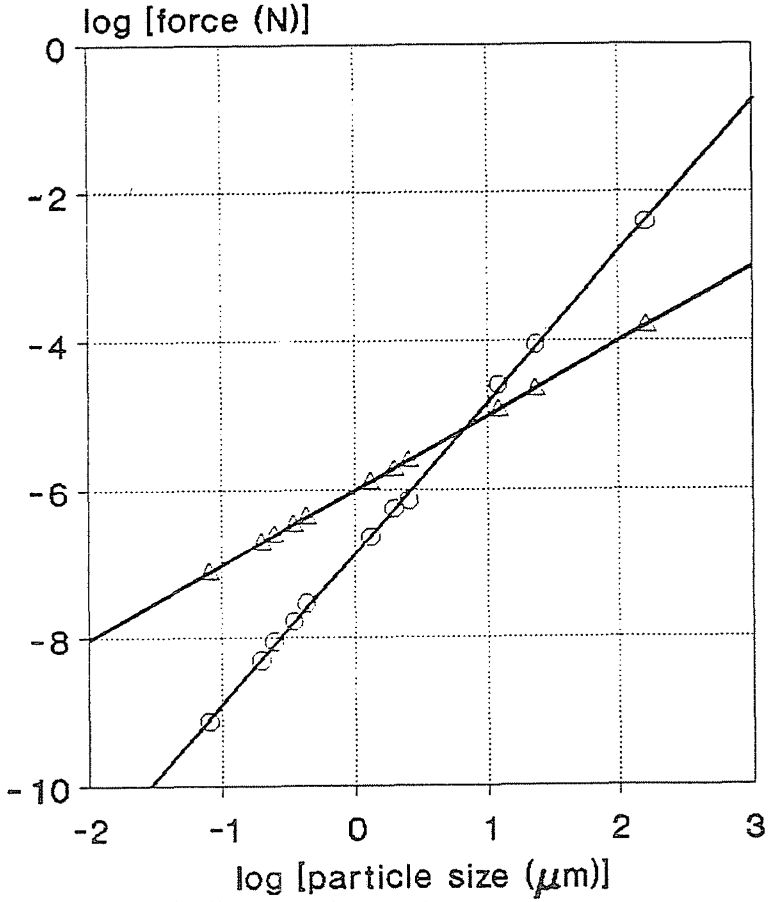

Fig. 6. Dependence of adhesive and hydrodynamic forces during homogenization on the size of the particles; (Δ) adhesion, (○) shear

Fig. 7, the crystallization temperature at the first peak is 135.2 °C which indicates a very strong nucleation effect. The effect depends very strongly on the specific surface area of the filler and on composition, it appears more often at high surface areas [3].

The above mentioned nucleation effect is demonstrated well in *Fig. 8*, where crystallization peak temperatures are plotted against the specific surface area of the filler. The figure proves that, indeed, strong interaction appears more frequently at large specific surface areas, but obviously A_f is not the only and maybe not even the dominating factor shown by the behaviour of Polcarb and Hydrocarb OG. In all probability, the small particle fractions of these fillers form aggregates, which nucleate the crystallization of PP. The four fillers specifically indicated in the figure have shown irregular

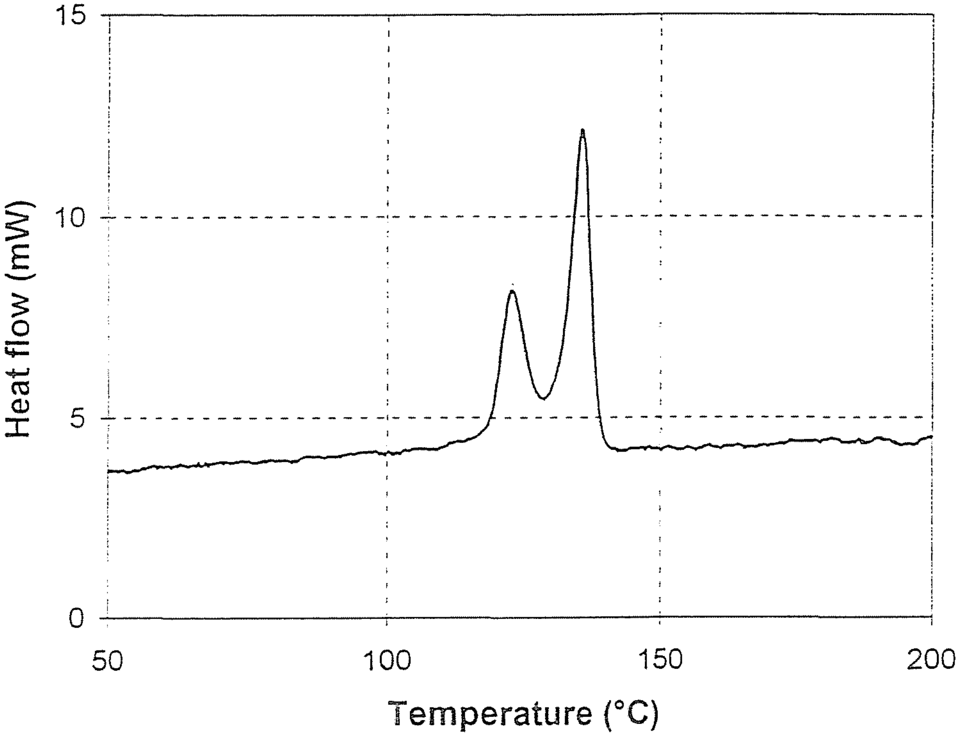

Fig. 7. Crystallization exotherm of a PP composite containing 0.25 v% Polcarb

behaviour before (see *Figs. 1, 2, 4* and *5*). The intensity of the nucleating effect can be deduced from the dependence of the heat of crystallization (ΔH_c) on A_f. The total value of ΔH_c is independent of the specific surface area of the filler (*Fig. 9*). The crystallization exotherm can be divided into two parts for fillers having a strong nucleating effect. ΔH_{c1} is proportional to the amount of PP crystallizing according to the normal nucleation process with a peak temperature corresponding in most cases to the straight line of *Fig. 8*, while ΔH_{c2} indicates the amount influenced by the strong nucleation effect of the aggregates. *Fig. 9* shows that in the case of HOG and SU1 especially strong nucleation is observed. These results indicate that in PP composites the presence of aggregates can be very sensitively detected by thermal analysis.

The mechanical properties of particulate filled composites are expected to be strongly influenced by aggregation. The different properties, however,

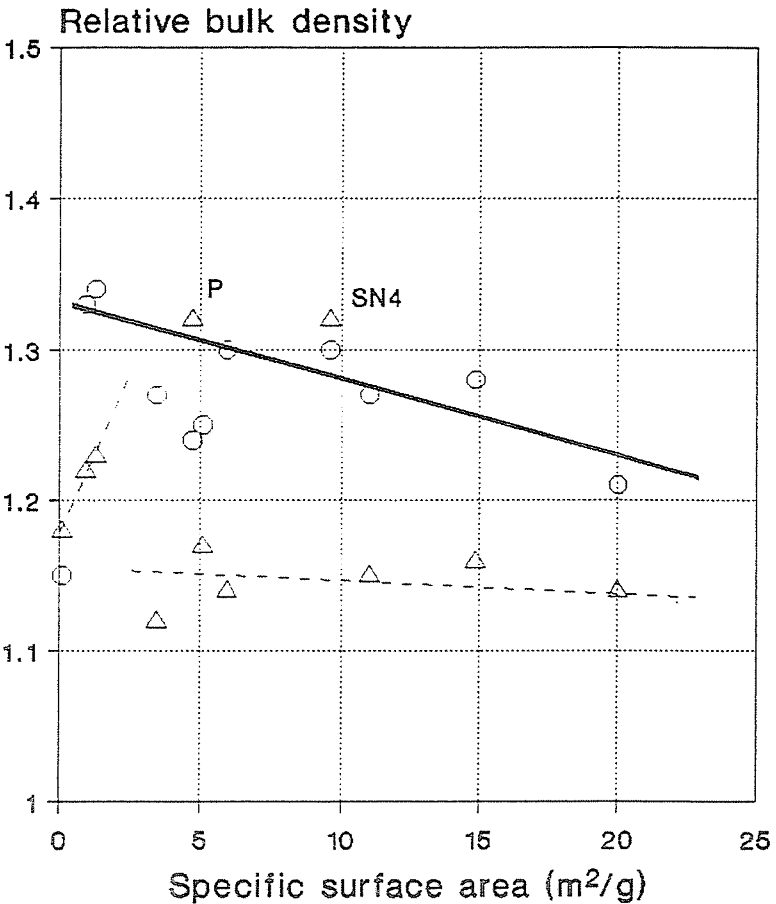

Fig. 8. Crystallization peak temperatures of PP in the presence of $CaCO_3$ fillers with various specific surface areas; (○) low, (△) high peak temperature

react dissimilarly to the presence of aggregates, the impact properties indicate it the most sensitively. *Fig. 10* presents the dependence of the Young's modulus of the composites on the specific surface area of the fillers. Aggregation does not seem to influence this quantity at all. Only one deviating point is observed, the one belonging to the composite containing the filler with the largest particles. The obvious reason for the small E value is the easy debonding of the particles even under the effect of the very small stress developing in the test. The increase of Young's modulus with increasing A_f is due to the development of an interphase with properties different both from those of the filler and the matrix polymer [20], [21]. Obviously the volume of the polymer bonded in the interphase increases with A_f. The slope of the E vs A_f correlation depends on the extent of deformation used in the

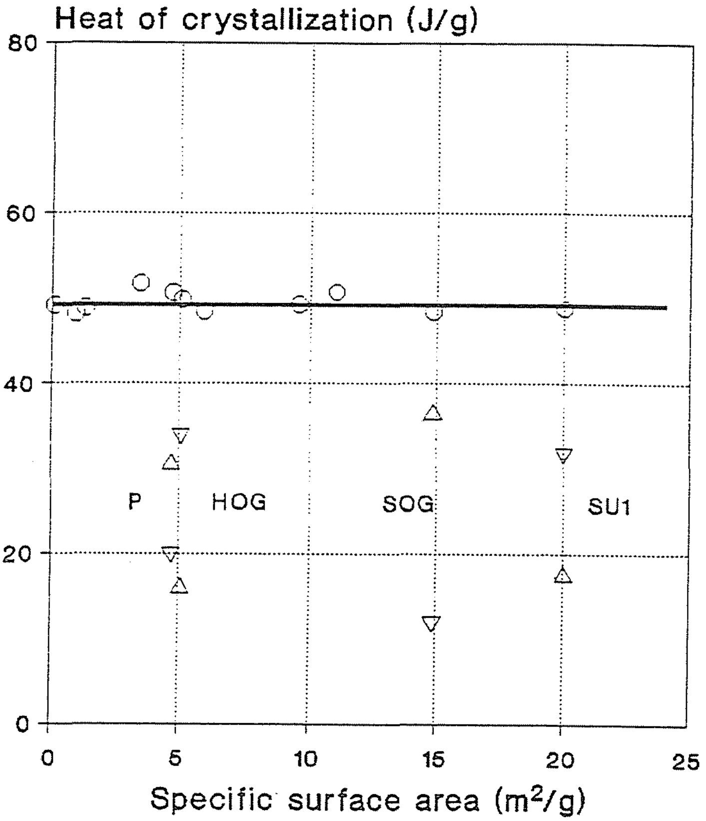

Fig. 9. Effect of A_f on the amount of crystalline PP in the composites; (○) total crystallinity, (△) low, (◇) high temperature peak

experiment, it would increase at larger deformations. The results completely correspond to the expectation and prove that the structure, including aggregation, influences only slightly the properties measured at low deformations [22], [23]. Indeed, the elongation-at-break values show a completely different dependence on A_f (*Fig. 11*). The fillers can be classified into two groups; Omyacarb 2GU is obviously not fitting into either category. The reason for this unexpected behaviour is not known for the moment. The increase in ε at low specific surface areas is a consequence of increasing debonding stress with decreasing particle size. In the case of large particles numerous large holes are formed even at low deformations because of debonding. During further deformation these rapidly merge into cracks leading to premature failure. Above a certain specific surface area, the role of the polymer bonded

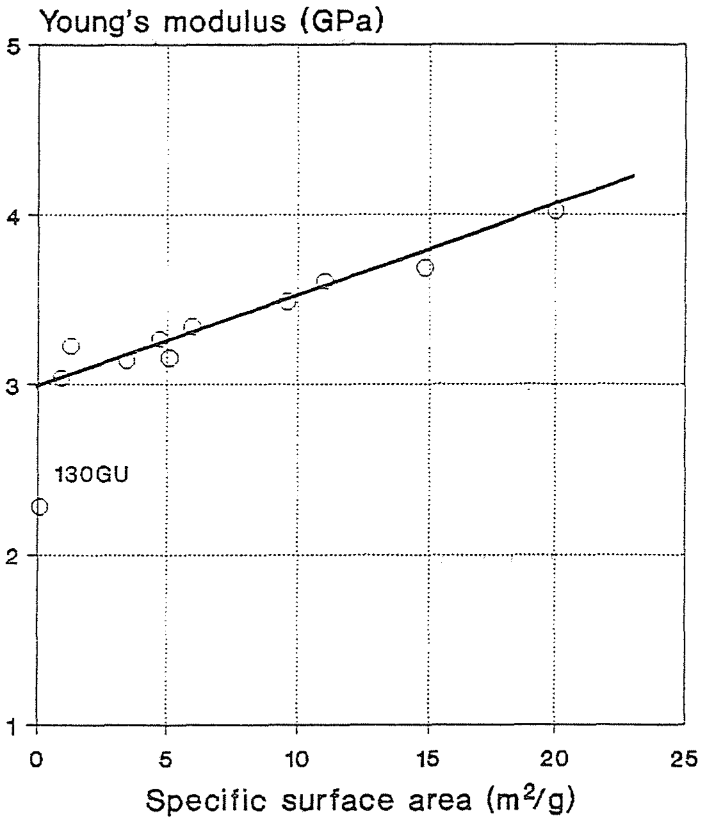

Fig. 10. Young's modulus of PP/$CaCO_3$ composites plotted against the specific surface area of the filler

in the interphase becomes significant, the debonding stress increases, brittle failure occurs. As a consequence elongation does not change much, it decreases slightly with increasing A_f.

The tensile strength of the composites is plotted against A_f in *Fig. 11.5.* Up to a certain specific surface area, strength increases linearly with A_f, which can be easily explained by the reinforcing effect of the filler and the formation of an interphase [23]–[25]. In the absence of structural effects, e.g. aggregation, the yield stress and tensile strength of particulate filled polymers are determined by component properties, composition and interfacial interaction. The first two factors are constant here. The effect of interaction depends on the size of the interface (specific surface area) and the strength of the interaction. Having the same components, i.e. PP and $CaCO_3$, the strength of interaction is the same in all composites, but the

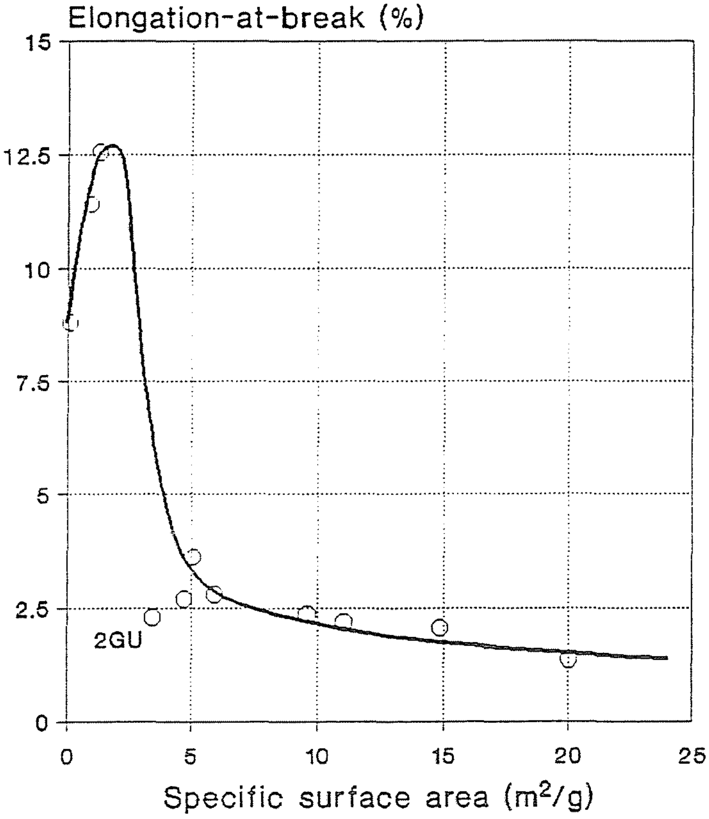

Fig. 11. Dependence of the elongation-at-break of PP/$CaCO_3$ composites on A_f

specific surface area of the filler changes. Since, as an effect of interaction, usually a hard interlayer is formed, the filler reinforces the polymer, and the tensile strength increases with increasing A_f. The correlation changes at a critical A_f value of about 6 m^2/g. Above this value tensile strength decreases continuously due to the development of an internal structure, i. e. aggregation. The results prove that in fact aggregates act as fracture initiation sites. The impact resistance reflects the existence of aggregates and differentiates fillers even better [11], [26].

5. Conclusions

The results of the experiments carried out with 11 $CaCO_3$ fillers prove that the extent of aggregation is always determined by the relative magnitude

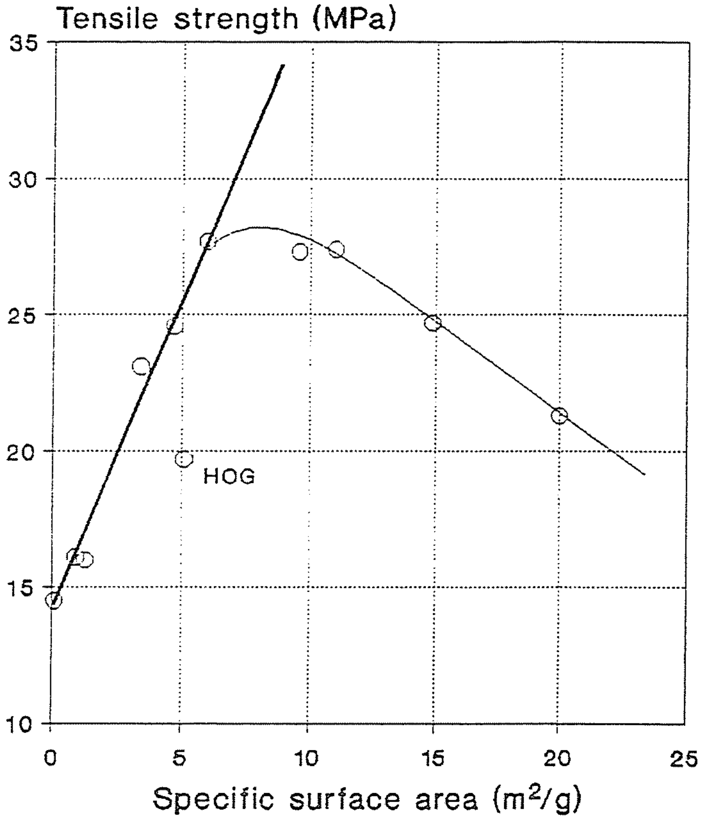

Fig. 12. Correlation between the tensile strength of PP/$CaCO_3$ composites and the specific surface area of the fillers

of attractive and separating forces. In polymer composites the most important attractive force is adhesion, while hydrodynamic forces, i.e. shear, lead to the separation of the particles. The aggregation of fillers is strongly influenced by their particle characteristics (particle size, surface tension). Although the specific surface area gives a good indication about the aggregation tendency of the filler, the particle size distribution is more important, since individual particles interact with each other. According to the results, also powder and suspension properties may yield valuable indirect information about aggregation. The extent of aggregation is system specific, since both the adhesive, but especially separating forces depend very much on the type of the polymer and filler, as well as on processing conditions. Aggregation usually deteriorates composite properties, but the effect is different for all properties. The extent of aggregation may be decreased by non-reactive surface treatment and increased shear. Although the results presented here are unambiguous, further verification is needed by the direct measurement of aggregation.

Acknowledgement

The authors are indebted to Judit Magyar for carrying out some of the measurements and to the National Scientific Research Fund (Grant No. 016500) for financial support.

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