Aggregation of Particulate Fillers: Factors, Determination, Properties

János Móczó[1,2], *Erika Fekete*[1,2], *Krisztina László*[3], *Béla Pukánszky*[1,2]*

[1]Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary
[2]Department of Plastics and Rubber Technology, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 92, Hungary
[3]Department of Physical Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 92, Hungary

Summary: The aggregation tendency of 11 different $CaCO_3$ fillers with widely differing particle sizes was studied in polypropylene (PP) composites. The fillers were characterized by different techniques in powder form and in suspension. Homogenization and sample preparation were carried out by extrusion and injection molding, or in an internal mixer and compression molding, respectively. Thin slices were prepared from the composites and the relative area of aggregates was determined by image analysis. Tensile and fracture properties were studied as a function of filler content. The results proved that the extent of aggregation increases with decreasing particle size and increasing filler content. Surprisingly, extruded and injection molded samples contained more aggregates than those prepared by homogenization in an internal mixer followed by compression molding. Good agreement was found between the powder properties of the fillers and their performance in the composites. Deviations from the general tendency indicate that some factors, which were not accounted for in the study, also influence aggregation and composite properties.

Introduction

Particulate filled composites are used in increasing quantities in many fields of application. Their characteristics are determined by component properties, composition, interfacial interaction and structure[1,2]. In most cases this latter is thought to be very simple, the homogeneous distribution of the particles is assumed in the polymer matrix. However, filler particles may aggregate in such composites leading to problems in processing, to decreasing aesthetic and deteriorating properties[2-6]. The understanding of the factors, which influence the aggregation tendency of fillers, offers the only possibility to decrease this phenomenon and to improve composite properties.

Two kinds of interaction exist in particulate filled composites. The polymer adheres to the surface of the particles forming an interphase with properties differing from those of

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the polymer matrix[7-11], on the one hand, while the particles may interact also with each other creating aggregates[1,3,6], on the other. Particulate filled composites are produced almost exclusively by the melt mixing of the components, when the shear stresses developing in the processing machine try to separate particles attached to each other[12]. The occurrence and extent of aggregation depend on the relative magnitude of adhesion and separating forces[13-15]. The former is determined by the surface tension of the filler and its particle size, while the latter depends on the level of shear forces. As a consequence, aggregation may be decreased by surface treatment and by increasing the particle size of the filler or shear forces[13]. Commercial grades of $CaCO_3$ usually have a wide particle size distribution. Consequently, a fraction of the small particles always aggregates, while large particles are distributed separately. The unambiguous determination of aggregation is difficult; various techniques can be used including measurements carried out on the dry filler, in suspension or on the composite itself[16-23].

Previous results have shown that aggregation always occurs below a certain particle size or above a certain specific surface area[14,15]. In PP composites, the critical value proved to be 5-7 m^2/g. Aggregation modifies stiffness only slightly[14], but strength and impact resistance depends very much on structure, both decreases with increasing extent of aggregation[14,15]. The mode of failure initiation also depends on particle size, debonding is the dominating deformation mechanism in composites containing large particles, while cracks are initiated inside large aggregates forming at small particles sizes[15]. Contradictory results were obtained concerning the effect of processing, injection molded specimens were not always more homogeneous than compression molded ones[15]. The main goals of this study were the quantitative characterization of the structure of the composites by optical microscopy, comparison the results obtained to mechanical properties and especially to fracture characteristics and the identification of the most important factors influencing aggregation. An attempt was made to resolve the contradiction concerning the effect of processing technology observed in our earlier study[15].

Experimental

The trade name and most important characteristics of the fillers used in the study are listed in Table 1. Their particle size (d), consequently specific surface area (A_f) covers a wide range leading to very different aggregation tendencies. Besides particle size and

specific surface area, their bulk density, sedimentation rate and volume were also determined[14]. An injection molding grade PP homopolymer (Tipplen H 535, MFI = 4 g/10 min at 230 °C, 21.6 N) produced by TVK, Hungary was used for the preparation of the composites, which contained 10, 20 or 30 vol% filler. Two techniques were used for homogenization and sample preparation. A part of the composites were homogenized in a Brabender W 50 EH internal mixer at 190 °C, 50 rpm for 10 min, then compression molded (Fontijne SRA 100) at 190 °C into plates of 1 or 4 mm thickness. Continuous homogenization occurred in a Brabender DSK 42/7 twin-screw compounder with 190, 200 and 210 °C set temperatures at 50 rpm. The prepared pellets were injection molded into tensile bars using a Battenfeld BA 200 CD machine. All further testing was carried out on these bars.

Table 1 Characteristics of the studied fillers

Filler	Abbreviation	Source	A_f (m^2/g)	d (μm)
Omyacarb 130 GU	130 GU	Omya	0.3	130
Omyacarb 40 GU	40 GU	Omya	0.8	23
Omyacarb 15 GU	15 GU	Omya	2.0	12
Omyacarb 2 GU	2 GU	Omya	3.6	2.50
Polcarb	P	Imerys	5.0	1.30
Hydrocarb OG	HOG	Omya	6.0	1.90
Socal N2	SN2	Solvay	6.0	0.35
Socal N4	SN4	Solvay	9.0	0.25
Socal N6	SN6	Solvay	11.0	0.20
Setacarb OG	SOG	Omya	15.0	0.44
Socal U1	SU1	Solvay	20.0	0.08

Aggregation was characterized by the relative area of aggregates in the composites. Thin slices of 20 μm thickness were cut from the specimens and micrographs were taken from them by a Polaroid digital camera fitted to a Leitz Dialux 20 microscope. The micrographs were quantitatively analyzed by Image-Pro Plus software. Tensile properties, modulus (E), yield stress (σ_y) and strain (ε_y), as well as tensile strength (σ) and elongation-at-break (ε) were measured using a Zwick 1445 apparatus. Modulus was

measured at 0.5, while tensile properties at 5 mm/min cross-head speed and 50 mm gauge length. Linear elastic fracture mechanics (LEFM) was used for the characterization of the fracture resistance of the specimens. Instrumented impact testing was carried out at 2.9 m/s velocity; dynamic effects were damped by silicone rubber[24,25]. The specimens of 80 x 10 x 4 mm size were notched to different depths by a saw, then the notch was sharpened by an industrial razor blade to determine strain energy release rate (G_{Ic}) by the method of Plati and Williams[26,27]. Critical stress intensity factor (K_{Ic}) was calculated from the maximum force of the recorded load vs. deflection correlations.

Results

The results are presented in three sections. First the structure of the composites is analyzed quantitatively as a function of specific surface area, composition and processing technology. The dependence of composite properties on particle size and composition is presented the subsequent section, then structure-property correlations and the factors determining aggregation are discussed briefly in the final part of the paper.

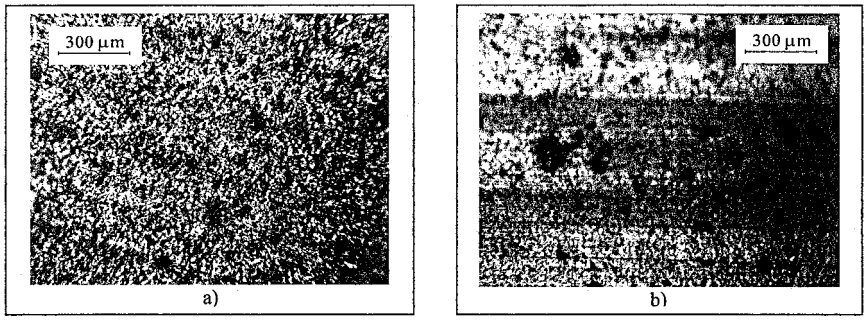

Fig. 1 *Structure of PP/$CaCO_3$ composites prepared by extrusion and injection molding. Filler content: 20 vol%. Particle size: a) 12, b) 0.25 µm.*

Structure

Two micrographs taken from composites prepared by extrusion and injection molding with fillers of different particle sizes are presented in Figs. 1a and 1b. According to the micrographs, large particles of 12 µm size are distributed homogeneously in the polymer matrix, aggregates do not form and cannot be detected in the composite (Fig. 1a). On the other hand, composites prepared under the same conditions from small particles

contain considerable number of aggregates as shown by Fig. 1b. These results are in accordance and strongly corroborate our earlier observations that aggregation depends on particle size and its extent increases with increasing specific surface area of the filler[14,15].

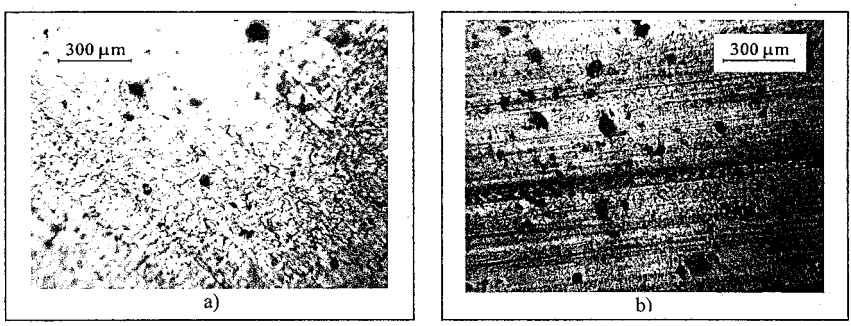

Fig. 2 *Effect of composition on the structure of PP/$CaCO_3$ composites. Processing: extrusion/injection molding. Particle size: 0.08 µm. Composition: a) 5, b) 20 vol%.*

According to the previous paragraph, fillers with small particle size has a strong tendency for aggregation. However, the extent of aggregation depends very much also on composition as shown by Fig. 2. The micrograph presented in Fig. 2a was taken from a composite containing 5 vol% Socal U1 filler. Several large aggregates can be clearly detected in the figure. The number of aggregates and the relative area occupied by them increases with filler content demonstrated well by Fig. 2b, which shows a composite containing the same filler, but in a different amount, in 20 vol%.

The relative area of the aggregates determined by image analysis of slices similar to those presented in Figs. 1 an 2 is plotted against the specific surface area of the fillers in Fig. 3. Aggregation becomes stronger with increasing surface area, i.e. with decreasing particle size, but also with composition. Obviously, dispersion becomes more and more difficult as the amount of filler increases in the composite. The tendency, which can be observed as a function of specific surface area is somewhat surprising, though. With decreasing particle size the relative area of aggregates seem to approach a saturation value at all filler contents. As an explanation one may assume that with increasing A_f, the contact surface between the filler and the polymer increases leading to larger viscosity, larger friction and less aggregation. This tentative explanation is corroborated by the increasing torque measured during the mixing or extrusion of the composites with

decreasing particle size, but further measurements and analysis is needed to prove it unambiguously.

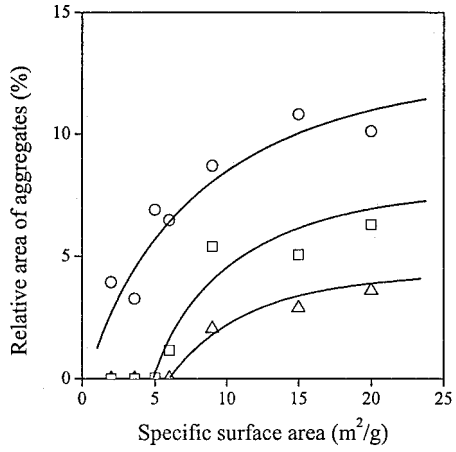

Fig. 3 *Effect of particle size and composition on the extent of aggregation. Extrusion and injection molding. Symbols:* (Δ) *5,* (□) *10,* (O) *20 vol%.*

The extent of aggregation is determined by the relative magnitude of adhesion and shear forces prevailing during processing, thus homogenization technology must have a large impact on it. It is generally accepted that in a twin-screw compounder and during injection molding higher shear forces develop in the melt than in an internal mixer or during compression molding. As a consequence, we expected less aggregation and a more homogeneous structure in the composites prepared by the former technology. The micrograph taken from a composite prepared by the second procedure, i.e. internal mixer and compression molding, is presented in Fig. 4. The structure of the composite is rather homogeneous, only one medium sized aggregate can be detected in it. If we compare the micrograph to Fig. 1b, which was taken from a composite of the same composition, but prepared by extrusion and injection molding, it becomes immediately clear that large differences exist in the homogeneity of the samples. In spite of our expectations, better dispersion is achieved in the internal mixer than in the twin-screw compounder. A plausible explanation is offered by the analysis of the homogenization and sample preparation procedure. Lower shear stresses developed in the extrusion/injection molding technology, because the twin screw compounder

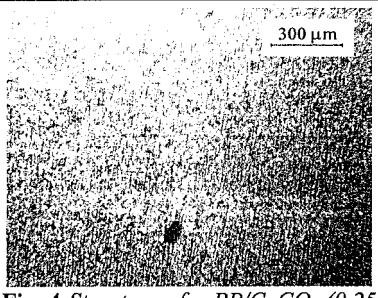

Fig. 4 *Structure of a PP/$CaCO_3$ (0.25 μm, 20 vol%) composite prepared by mixing and compression molding.*

has very deep channels, while the relative thick tensile bars were injection molded with a bar gate.

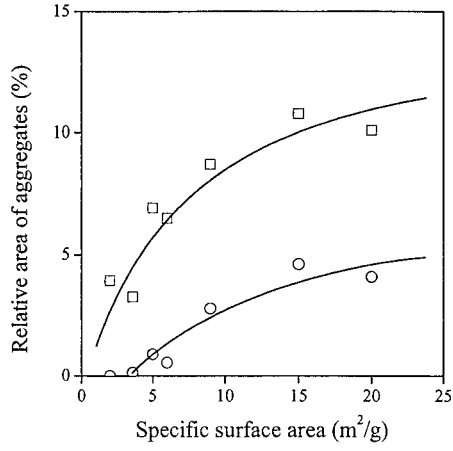

Fig. 5 *Effect of processing technology on the homogeneity of PP/$CaCO_3$ composites. Symbols:* (O) *mixer/compression,* (□) *extrusion/injection molding.*

The effect of processing technology on the structure of the composites can be compared quantitatively in Fig. 5, where the relative area of the aggregates is plotted against the specific surface area of the filler. All composites contained 20 vol% filler. The tendency is the same as in Fig. 3. Depending on the intensity of shearing provided by the technology, the filler does not aggregate above a certain particle size and the relative area of aggregates approaches towards a saturation value as a function of specific surface area. The large difference in the efficiency of homogenization is very obvious in the figure, much larger shear forces must develop in the internal mixer than during extrusion and injection molding. The results presented in this section clearly prove that parti-

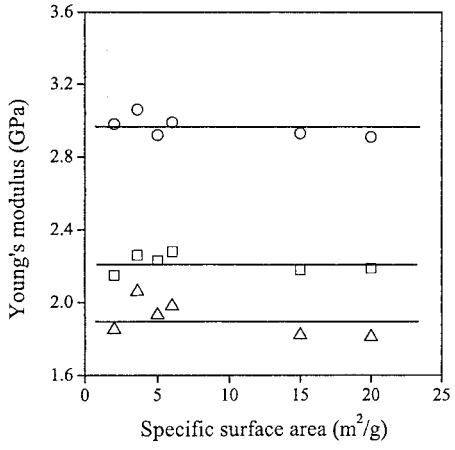

Fig. 6 *Effect of particle size on the stiffness of PP composites. Symbols:* (Δ) *5,* (□) *10,* (O) *20 vol%.*

cle size, composition and the relative magnitude of shear forces strongly influence the structure of particulate filled composites. Shear forces are determined by the geometry of the processing equipment and the technological parameters used.

Properties

The presence of aggregates influences the various properties of particulate filled composites differently. Modulus usually does not depend very strongly on structure, an experience that is supported also by Fig. 6, where the Young's modulus of the composites is plotted against the specific surface area of the filler. Stiffness increases with filler content as expected, but it is practically independent of A_f. This independence can be explained by the low deformations developing during the measurement of modulus.

Contrary to stiffness, tensile properties measured at larger deformation change strongly as a function of particle size and they depend also on the degree of aggregation. The tensile yield stress of the composites is plotted against the specific surface area of the fillers in Fig. 7. The correlation can be described by two straight lines. Yield stress increases with increasing A_f first, then at a certain value it starts to decrease. The linear dependence of the first section can be explained by a simple theory developed for the description of the composition dependence of yield stress and tensile strength[28,29]. After the critical point the correlation is not necessarily linear, but we do not have enough experimental data in this range to determine the correct function. Yield stress is decreased by aggregation.

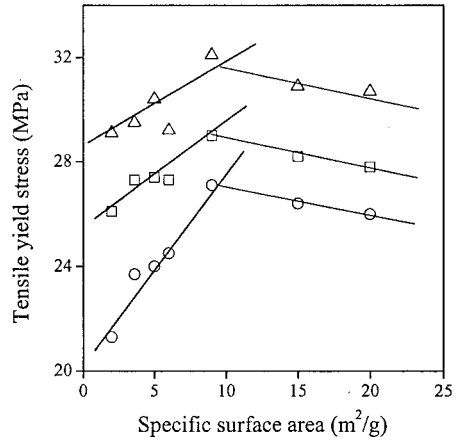

Fig. 7 *Composition and A_f dependence of tensile yield stress of composites prepared by extrusion and injection molding. Symbols are the same as in Fig. 3.*

Large aggregates may behave like large particles for which debonding is easy leading to lower yield stress or their strength might be low, they may rupture during deformation with a similar result[33,34]. Quantitative evaluation of the yield stress of the composites offers another approach for the determination of the critical A_f value (or particle size) where considerable aggregation starts at a given processing technology as described in a previous paper[15]. The dependence of tensile strength on particle characteristics and composition is very similar to that of yield stress (see Fig. 7) thus we avoid its discussion in order to save space.

The effect of processing technology on the tensile strength of the composites is presented in Fig. 8. In accordance with the results presented in the previous section, the more homogeneous structure of the composites prepared in the internal mixer leads to better properties, to higher tensile strength. Both the actual strength values and the critical surface area where significant aggregation occurs are larger for these composites proving that structure determines properties, indeed. The critical stress intensity factor of the composites depends on particle characteristics and composition in a much more complex way (Fig. 9). The very large scatter of the points is not justified by the large standard deviation of the measurement. We should like to call attention here to the experimental value measured at 20 vol% for the filler which has 15 m^2/g specific surface area (indicated by a circle). The fracture toughness of the composite containing this filler is much larger than predicted by the general tendency. Obviously, specific surface area does not completely describes the effect of the filler, this single characteristics is unable to predict its

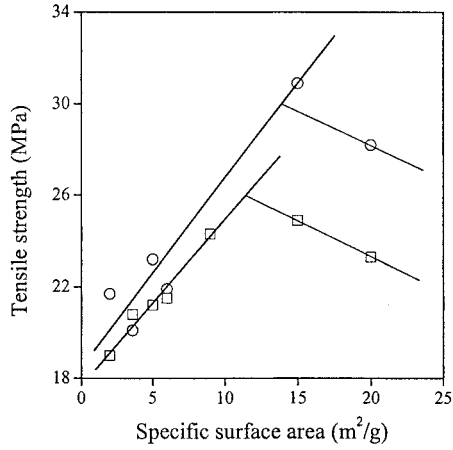

Fig. 8 *Effect of processing technology on the aggregation tendency of $CaCO_3$ fillers in PP composites at 20 vol% filler content. Symbols are the same as in Fig. 5.*

aggregation tendency. Strain energy release rate (G_{Ic}) shows an even larger scatter if we plot it as a function of A_f. Hopefully, the direct comparison of the relative area of aggregates with the mechanical properties and especially with the fracture resistance of the composites yields better correlations and gives us more information about the factors determining the aggregation tendency of particulate fillers.

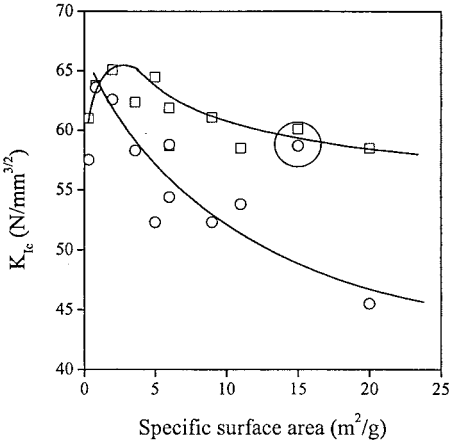

Fig. 9 *Dependence of fracture toughness on particle characteristics and composition. Extrusion and injection molding. Symbols are the same as in Fig. 3.*

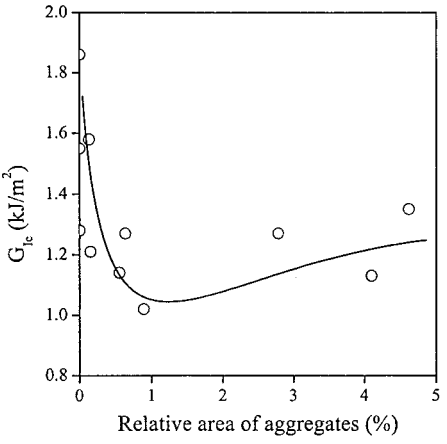

Fig. 10 *Correlation between aggregation and fracture resistance. 20 vol%, extrusion and injection molding.*

Discussion

The correlation mentioned at the end of the previous paragraph is presented in Fig. 10. The drastic decrease of fracture resistance with increasing extent of aggregation is clear and unambiguous. However, the deviation of several points from the general tendency, especially at large A_f values, indicates that similarly to the

specific surface area of the filler, the relative area of aggregates is not the sole parameter that determines this property of the composites. Earlier results indicated that several characteristics of the fillers and some properties of the composites depend on A_f in a similar way. For example the bulk density of the fillers is plotted against their specific surface area in Fig. 11. A rather close correlation is obtained with the single deviating value of Setacarb OG. Rather surprisingly, the plot of G_{Ic} against A_f resembles very much to the previous correlation, the value of SOG deviates again from the general tendency (Fig. 12). Although the scatter of the measured values is larger for G_{Ic} than for bulk density, the tendency is unambiguous as well as the position of the filler mentioned above. These results indicate that the distribution and performance of the filler is determined by the same fac-

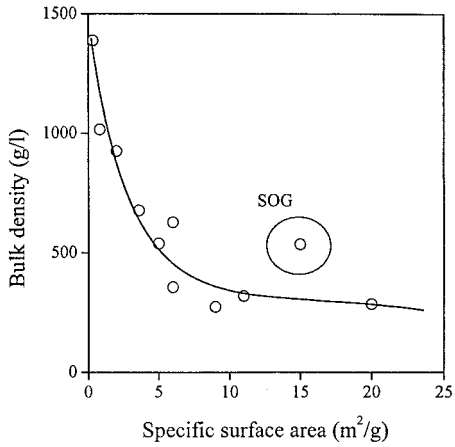

Fig. 11 *Correlation of some characteristics of the investigated $CaCO_3$ fillers.*

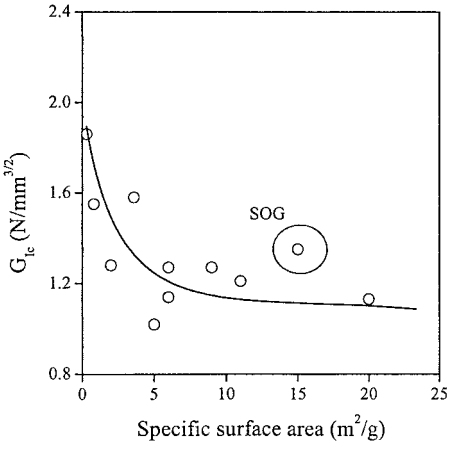

Fig. 12 *Particle size dependence of fracture resistance. 20 vol%, extrusion and injection molding.*

tors in powder form and in the composite. One factor, which has not been studied yet and might influence properties is the particle size distribution of the filler, which is somewhat different for SOG than for the other fillers. Further study must be carried out in the future to determine its effect on aggregation and on the properties of the composites.

To check the correlation of the two quantities, i.e. G_{Ic} and bulk density, they are plotted against each other in Fig. 13. A linear correlation is obtained, which indicates that the two quantities are determined by the same or similar factors, indeed. The behavior of Setacarb OG also corresponds to the general tendency. However, three other fillers behave differently, the corresponding values are situated well below the straight line representing the behavior of the majority of the fillers. This result calls attention again to the fact that a single parameter cannot describe the aggregation tendency of particulate fillers and the properties of composites prepared from them. Moreover, although the different particle size distribution of Setacarb HOG may be a convenient explanation for its different behavior, it is still not clear why this difference is not reflected in the relative area of aggregates (see Figs. 3 and 5). Since large aggregates fracture relatively easily and cracks are often initiated inside them[15], their strength might also influence the fracture resistance of the composite[33,34]. However, the low G_{Ic} value of the composite containing Omyacarb 15 GU cannot be explained this way, since the large particles of this filler do not form aggregates. The composites containing the three fillers might deform according to different mechanisms than the others, e.g. easier debonding of large particles or aggre-

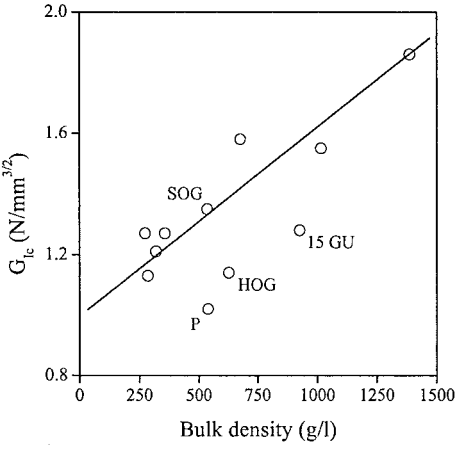

Fig. 13 *Similarity of powder characteristics and composite porperties. 20 vol %, extrusion and injection molding.*

gates[30-32], but this assumption must be also verified by experiments. Obviously further study must be carried out to identify all the factors, which determine the aggregation tendency of fillers and the properties of particulate filled composites.

Conclusion

The experiments carried out on PP composites prepared with 11 different $CaCO_3$ fillers proved that most commercial fillers form aggregates under processing conditions used in everyday practice. The extent of aggregation increases with decreasing particle size and increasing filler content. Processing conditions determine the prevailing shear forces thus also the number of aggregates formed. Optical microscopy combined with image analysis is a useful way to characterize the structure of particulate filled polymers, but the relative area of aggregates is not the only factor which determines composite properties. Fillers behave similarly in all media, in bulk, suspension or in the composite. Numerous factors, including the particle size distribution of the filler, influence the extent of aggregation. Composite properties may depend also on the internal structure and strength of the aggregates. Further study must be carried out to identify all the factors determining aggregation and the properties of the composites.

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