Morphology and Properties of Particulate Filled Polymers

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Summary: Although the structure of particulate filled polymers is usually thought to be very simple, often structure related phenomena determine their properties. Segregation occurs only when long flow paths and large particles are used in production. The occurrence and extent of aggregation depend on the relative magnitude of attractive and separating forces, which prevail during the homogenization of the composite; the balance of adhesive and shear forces determines structure. Fillers of small particle size always aggregate, usually leading to decreased strength and especially low impact resistance. Anisotropic particles (talc, mica, short fibers) are orientated during processing. ESR is a relatively simple technique for the estimation of orientation and orientation distribution, which are determined by processing conditions, i.e. flow pattern, shear conditions, mold filling rates, cooling conditions, etc. The orientation of the particles strongly affects composite stiffness and strength. In practice, often several factors simultaneously influence the properties of products prepared from particulate filled polymers. Separation of the effects of the influencing factors is difficult, although such knowledge would help to control composite properties. The structure and properties of injection and compression moulded PP composites containing $CaCO_3$ or talc differs considerably from each other. The aggregation of $CaCO_3$, the nucleating effect and the orientation of talc affect product properties. The latter are also influenced by the skin-core structure developing during injection molding as well as by the orientation of the polymer. An example is discussed in this paper, which facilitates the identification of the effect of these factors with the help of a simple model and indicates a way in which product properties can be controlled.

Keywords: aggregation; crystalline structure; mechanical properties; orientation; particulate fillers; segregation; structure-property correlation

Introduction

The structure of semi-crystalline polymers, including polypropylene (PP), is relatively complicated. They can crystallize in different modifications. Their crystallinity and size, as well

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as size distribution of the crystalline units (lamellae, spherulites) vary over a wide range with changing sample preparation and processing conditions[1-4]. The introduction of a second component into PP usually further modifies morphology. Fillers may act as nucleating agents, changing thermodynamic and kinetic conditions of crystallization[5-8]. Crystal modification, the size of crystalline units and the amount of the crystalline phase can all change as a result[9]. The introduction of particulate fillers often leads to the development of specific morphology; anisotropic particles are usually orientated to different extents[10,11], while spherical fillers frequently form aggregates[12,13]

Because of the considerable number of factors influencing the structure and properties of particulate filled polypropylene, the views concerning their effects are often contradictory. In some cases the direct effect of a certain aspect of crystalline morphology is claimed to determine properties, in others such an influence is denied completely. Hutley and Darlington[14,15], for example, found a direct correlation between the crystallization temperature and impact strength of particulate filled PP, while Maiti et al.[16] observed linear dependence of some tensile characteristics on crystallinity. Kendall[17], on the other hand, denied the effect of matrix morphology on composite properties and emphasized the importance of interfacial interaction between the matrix and the dispersed phase.

Talc and $CaCO_3$ are used in large quantities for the modification of PP[18-20]. The two fillers have different particle geometry and a dissimilar effect on the crystalline structure of PP. $CaCO_3$ consists of more or less spherical particles and influences crystallization only slightly, while talc has plate-like geometry and a strong nucleation effect[9]. The properties of the composites prepared with the two fillers are also different; however, it is still debated whether the changing crystalline structure of the matrix, nucleation, or anisotropy and orientation of the filler cause the observed differences[21]. The goal of this paper is to give an overview of the factors influencing the properties of particulate filled polymers with special attention to the correlation of structure and properties. Structure-related phenomena occurring in particulate filled polymers are summarized briefly first, then a case study is presented, which shows the effect of various factors acting simultaneously in particulate filled PP and indicating a way how to separate these effects.

Segregation

The segregation of a second phase during processing is observed in some heterogeneous polymer systems[22,23]. Kubát and Szalánczi[22] investigated the separation of phases during the injection molding of polyethylene and polyamide using the spiral test. The two polymers contained large glass spheres of 50-100 μm particle size and extremely long flow paths of up to 1.6 m. They found that considerable segregation took place along the flow path; the glass content of a composite containing 25 wt% filler exceeded 40 % locally, at the end of the mold. Occasionally segregation was also observed across the cross-section of the sample; the local amount of filler was higher in the core than at the walls. Segregation depended on filler content and it became more pronounced with increasing size of the particles. Karger and Csikai[23] observed the segregation of the dispersed phase in elastomer modified PP. They also found an increased amount of the dispersed phase in the center of the specimen.

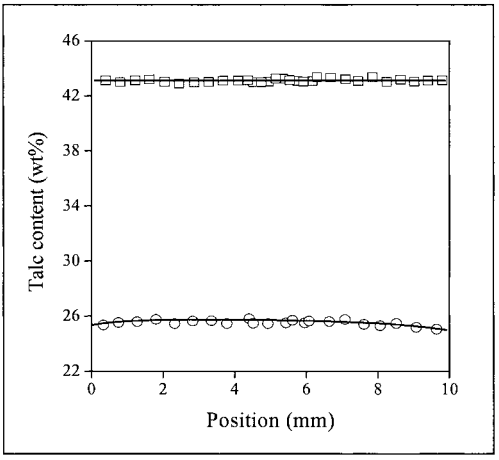

Figure 1. Distribution of talc across the width of injection moulded PP specimens. (o) 10 vol%, (□) 20 vol% talc content.

The possible segregation of talc particles dispersed in a PP matrix was investigated in injection-moulded specimens of 4 x 10 x 150 mm dimensions. Filler content was measured across the cross-section of the specimens by thermogravimetric analysis. As Figure 1 shows, no differences in filler content were detected as a function of position; the particles were homogeneously distributed in the PP matrix, independent of the average filler content. These and other results indicate that under practical conditions (small particles, relatively high filler content, normal flow path) segregation is of secondary importance, and we may assume the homogeneous distribution of the dispersed phase in the matrix polymer.

Aggregation

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[24]. The occurrence and extent of aggregation depend on the relative magnitude of adhesion and separating forces[25-27]. The former is determined by the surface tension of the filler and its particle size, while the latter also depends on particle size as well as on the level of shear forces. As a consequence, aggregation may be decreased by surface treatment, by increasing the particle size of the filler or shear forces[25]. Commercial grades of $CaCO_3$ usually have a wide particle size distribution, thus 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[28-33].

Previous results have shown that aggregation always occurs below a certain particle size or above a certain specific surface area[26,27]. In PP composites, the critical value was 5-7 m^2/g. Aggregation modifies stiffness only slightly[26], but strength and impact resistance depend very much on structure, both decrease with increasing extent of aggregation[26,27]. The mode of failure initiation depends also on particle size. Debonding is the dominat deformation mechanism in composites containing large particles, while cracks are initiated inside aggregates forming at smaller particles sizes[27]. Contradictory results were obtained on the effect of processing technology; injection-moulded specimens did not appear to be always more homogeneous than

compression moulded ones[27]. However, a detailed analysis of actual processing conditions and the determination of the number of aggregates proved that properties can be related to the extent of aggregation[34]. On the other hand, deviations from the general tendency indicated that some factors also influence properties, which had not been taken into account during the analysis.

One of these factors is the strength of the aggregates. The strength of agglomerates is of considerable importance in a number of industries, i.e. in the granulating of powders, briquetting, pelletizing, etc. As a consequence, several theories were developed for the prediction of agglomerate strength. Manas-Zloczower[35] gives a brief overview of them in a monograph focusing on the mixing and compounding of polymers. Rumpf[36] proposed one of the first equations for the calculation of the tensile strength of aggregates:

$$T = \frac{9}{8}\frac{1-\varepsilon}{\pi d^2} c F \tag{1}$$

where T is the tensile strength of the aggregate, d is the diameter of the spherical particles in it, ε is the void volume fraction within the total volume, c is the mean coordination number and F is the mean interparticle force. According to the model the tensile strength of aggregates depends mainly on the particle size of the filler, and it increases with decreasing particle diameter. Cheng[37,38] suggested a somewhat different relationship for T:

$$T = \frac{3}{4} H^0 \frac{\bar{d}\,\bar{s}}{\bar{v}} \frac{\rho/\rho_s}{1-\rho/\rho_s} F_{pp}^0 \tag{2}$$

where H^0 is the effective surface separation distance of zero tensile strength; $\bar{d}$, $\bar{s}$, and $\bar{v}$ are the mean diameter, surface area and volume of the particles, ρ is bulk density and ρ_s the density of the particles, while F_{pp}^0 is the interparticle force per unit fracture area. Kendall[39] strongly criticized the approach of Rumpf[36] and followed a completely different approach; he proposed a model for aggregate strength, which is based on fracture mechanics:

$$T = 15.6\,\phi^4\,\Gamma_c^{5/6}\,\Gamma^{1/6}(d\,c)^{-1/2} \tag{3}$$

where ϕ is the volume fraction of the filler, Γ_c the fracture energy of the agglomerate, Γ the interfacial energy between the particles with a diameter of d, and c is the length of a macroscopic flaw in the aggregate. The validity of all three models was checked on agglomerated particulate material and good agreement was found between prediction and the experimental results obtained.

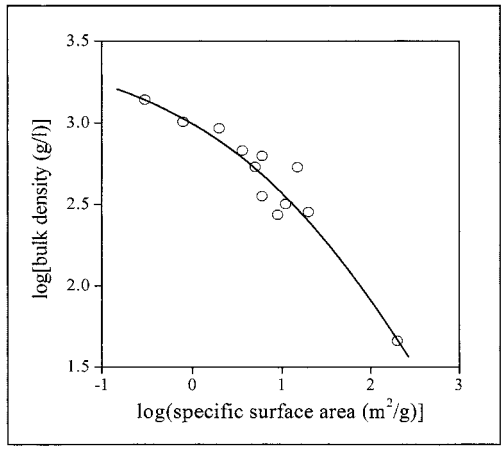

Figure 2. Correlation of the bulk density and specific surface area of various commercial $CaCO_3$ fillers.

Although Manas-Zloczower[35] suggests the use of the same or similar correlation for the prediction of aggregate strength in a polymer matrix, very limited experimental evidence exists to support such an approach. Nevertheless, we may consider the effect of some of the parameters included in Eqs. 1 and 2 on aggregate strength. The bulk density of the filler can be measured and, according to Eq. 2, the tensile strength of the aggregates should become smaller with decreasing bulk density. In Figure 2, the bulk densities of 11 $CaCO_3$ fillers[26] with a wide range of particle characteristics are plotted against their specific surface areas on a logarithmic scale. We can see that with increasing surface area, i.e. decreasing particle size, the bulk density of the filler decreases significantly, indicating strongly decreasing tensile strength of the aggregates. The other important parameter, which appears in all equations, is the size of the filler particles. According to Eq. 1, the tensile strength of the aggregates is proportional to the reciprocal square

of particle diameter. We plotted this quantity as a function of the specific surface area of the fillers in Figure 3. The $1/d^2$ value covers more then 10 orders of magnitude, which indicates that this parameter has indeed a strong influence on aggregate strength. If Eq. 1 is valid, the tensile strength of the aggregates should increase drastically with decreasing particle size.

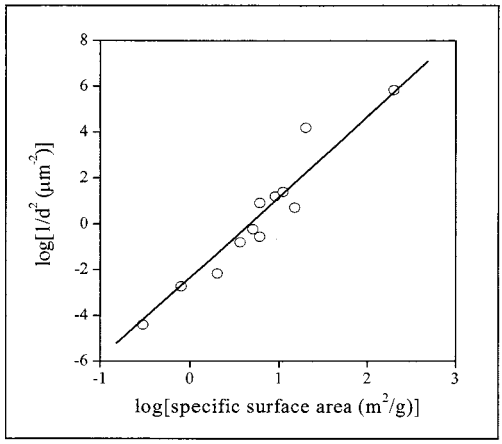

Figure 3. Dependence of aggregate strength on the particle size of the filler for various $CaCO_3$ fillers.

Unfortunately we could not check the effect of bulk density and particle size on aggregate strength directly, but we could obtain some information about it from the analysis of composite properties. The tensile strength of PP composites is plotted against filler content in Figure 4. We know that under the effect of external load large particles easily debond from the matrix, which leads to a continuous decrease in tensile strength with increasing filler content. With decreasing particle size the effect of interfacial interactions become more important and tensile strength increases as an effect of the formation of a hard interlayer[25].

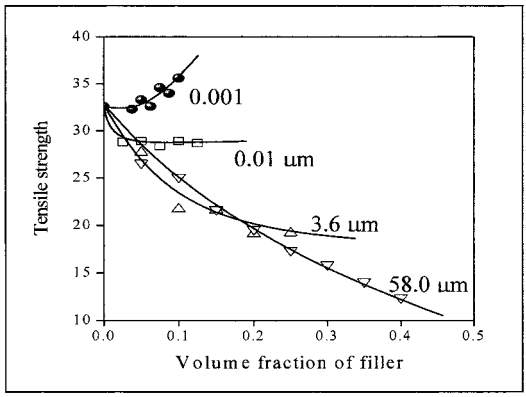

Figure 4. Effect of filler particle size and composition on the tensile strength of PP composites.

At particle sizes smaller than 1.0 μm aggregation becomes noticeable, but the strength of the aggregates is low[27]. However, the tensile strength of composites containing very small particles increases with filler content, indicating that debonding is no longer the dominating deformation mechanism. Moreover, the bulk density of this filler is 46 g/l, compared to the ~1400 g/l of the largest particles, which proves that Eq. 1 predicts aggregate properties better than Eq. 2 does. Although aggregate characteristics must still be studied in more detail in the future, aggregate strength may indeed influence composite properties. We must mention here, though, that PP composites containing 0.001 μm large particles are very stiff and brittle, thus their practical relevance is relatively small.

Orientation

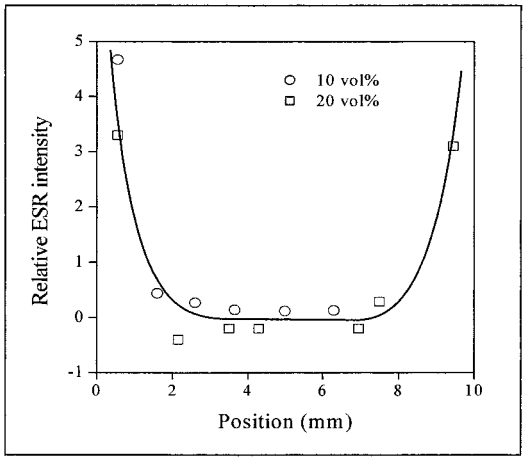

Figure 5. Orientation of talc particles across specimen thickness in injection moulded PP composites of different filler contents.

The orientation of anisotropic filler particles occurs in all processing operations, and orientation, as well as orientation distribution was shown to drastically influence composite properties. Orientation in extruded and compression-moulded products is relatively homogeneous, while it changes across the thickness and width of injection moulded parts according to the flow pattern developing during mold filling. Several methods are available for the determination of particle orientation, but most of them are rather tedious. ESR spectroscopy is a relatively simple technique which can be used for the determination of local and average orientation[40,41]. It uses the signal of transition metal contamination found in every mineral for the determination of orientation. The shape and the intensity of the signal depend on the relative orientation of the crystal planes and the magnetic field. A comparison of the spectrum of the powder and that of the oriented specimens offers a way to estimate the relative orientation of the particles. Further details of the technique can be found elsewhere[40,41]. Figure 5 shows the orientation distribution of talc particles in a specimen of 4 x 10 mm cross-section, injection moulded from a PP/talc composite of 20 vol% filler content. The distribution agrees well with experience and shows

strong parallel orientation of the particles to flow direction at the wall of the mold and their random orientation in the core of the specimen. The strength and stiffness of the composites increase considerably, parallel to the orientation of anisotropic particles, and decrease perpendicular to that[42].

Structure-property Correlations

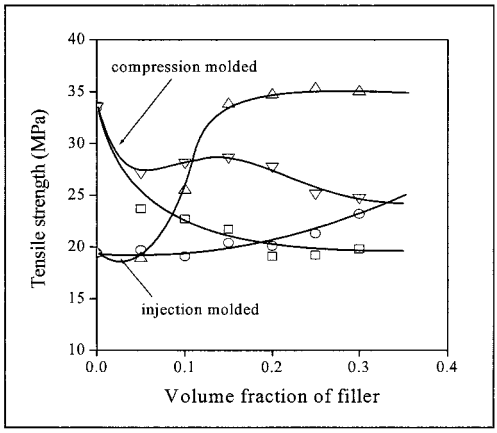

Figure 6. The effect of various parameters on the tensile strength of PP composites; (□, ○) $CaCO_3$, (▽, △) talc.

The effects of filler contents on the tensile strength of particulate filled PP composites are plotted in Figure 6. The composites were injection or compression moulded, and contained $CaCO_3$ or talc particles, i.e. three factors were changed in this series of experiments: filler type, composition and processing technology. The strengths of the various composites differ significantly from each other; that of the PP/talc composites of 30 vol% filler content exceeds by far the strength of the material containing $CaCO_3$ in the same amount. As discussed before, several structure related factors may influence the properties of these composites, some are associated with the filler and some with the matrix polymer. The crystal modification of the polymer, the size of the

morphological units, crystallinity, as well as the orientation of the crystalline and amorphous phases, all affect the properties of the product. Moreover, all are influenced by processing technology and modified by the strong nucleating effect of talc. The distribution of the filler, homogeneity, aggregation, the anisotropy of filler particles and their orientation, as well as orientation distribution, may also play an important role in the determination of composite properties. Naturally more than one factor acts simultaneously and the determination of the dominating one is difficult. The possible effects of the various factors are analyzed quantitatively in the following sections and an attempt is made to determine the most important ones.

Experimental

Stamylan P16M10 (DSM, The Netherlands) polypropylene homopolymer was used as matrix polymer. Hydrocarb 95 T $CaCO_3$ (Omya, Switzerland – A_f = 11.0 m^2/g, d = 1.0 μm) and Luzenac 10M00S talc (Luzenac, France – A_f = 8.0 m^2/g, d = 3.4 μm) were added to PP to produce the composites processed by injection molding.

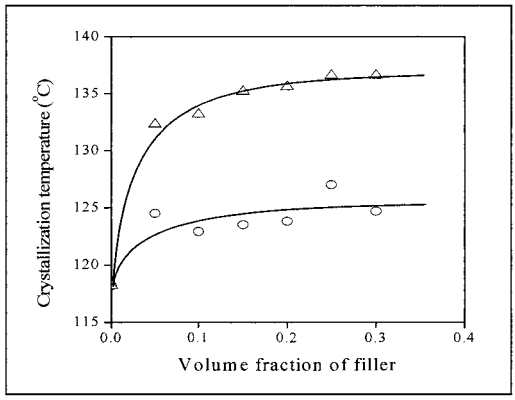

Figure 7. Effect of filler type and content on the crystallization temperature (lamella thickness[43,44]) of the PP matrix; (○) $CaCO_3$, (△) talc.

Different grades of filler were introduced into the composites prepared by compression molding:

Durcal 2 (Omya, Switzerland – A_f = 3.3 m^2/g, d = 3.6 μm) and Finntalc M05 (Finnminerals, Finland – A_f = 8.4 m^2/g, d = 2.8 μm). The composition changed between 0 and 0.3 volume fraction in 0.05 volume-fraction steps. Homogenization was carried out using a Brabender DSK 42/7 twin-screw compounder; the blends and composites were cooled in a water bath and pelletized. Specimens were prepared by compression or injection molding, respectively. Tensile testing was carried out at 50 mm/min cross-head speed. Young's modulus (E), yield (σ_y, ε) and ultimate (σ, ε) properties were determined from recorded force vs. elongation traces. The nucleation effect of the fillers and the crystallinity of the composites were studied in the DSC 30 cell of a Mettler TA 3000 Thermal Analysis System. 10 mg samples were measured in two heating and cooling cycles, at a rate of 10 °C/min. Relative changes in filler orientation were followed by ESR spectroscopy[21,40,41]. The dispersed structure and orientation of the talc particles were studied by scanning electron microscopy (SEM) on fracture surfaces prepared at liquid nitrogen temperature.

Crystalline Structure

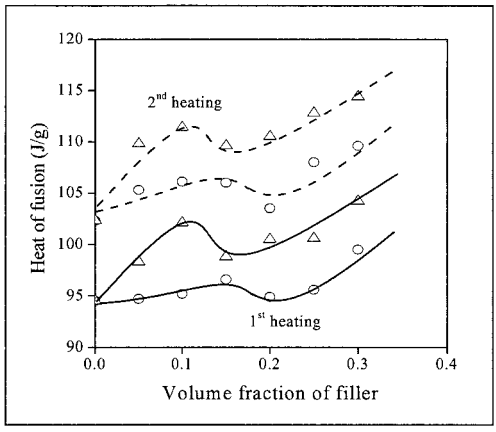

Figure 8. Influence of processing technology and filler type as well as content on the crystallinity of the matrix polymer. Symbols are the same as in Fig. 7.

The nucleation effect of a filler can be deduced from non-isothermal crystallization experiments;

the onset of crystallization as well as the crystallization peak temperature are related to nucleation and thus to the size of the crystalline units[43,44]. In Fig. 7 the crystallization peak temperatures of the composites are plotted as a function of composition for injection moulded composites

According to this figure, talc has a strong nucleating effect while $CaCO_3$ a much weaker one. The different effects on nucleation and the resulting dissimilarities in crystalline morphology may be the cause of the differences in the properties of talc and $CaCO_3$ filled PP composites. The crystallinity of the composites prepared with the two fillers shows characteristic differences too (Figure 8). Crystallinities measured in the first and the second heating cycles, respectively, differ considerably from each other. The first cycle reflects the effect of processing technology, i.e. injection molding in this case, on crystallinity. During the first heating cycle this is completely erased and only the effect of the filler influences crystallinity in the second run. According to the figure the effect of processing technology and the introduction of the filler are completely independent from each other. The orientation of the amorphous and crystalline phases has not been measured, although these might also influence properties.

Particle Related Structure

The presence of aggregates was not detected in the composites. The shape of $CaCO_3$ and talc particles differ significantly from each other. Although $CaCO_3$ particles are not spherical, their aspect ratio is close to 1. The anisotropy of talc particles is more significant; their aspect ratio is around 20-30. Although contradictory information is reported on the effect of anisotropy, it certainly influences composite properties. During sample preparation, i.e. processing, orientation of the particles takes place even under the apparently mild shearing conditions of compression moulding[21,40]. Both $CaCO_3$ and talc orientates, but the final result is evidently different because of the different aspect ratio of the two fillers.

Average values of orientation were measured both in injection moulded specimens and compression moulded plates by ESR spectroscopy. Relative values related to the sample with the smallest orientation are plotted in Figure 9 as a function of composition. Composition dependence differs, it decreases continuously in the compression moulded specimens and exhibits

a maximum in the injection moulded specimens. The tendency in the composition dependence of orientation indicates that with increasing filler content filler particles hinder each other in movement, and the probability of particle interaction increases. Not only is the average orientation different, but also its distribution in the specimens prepared by the two techniques. Most of the talc particles are oriented normal to the direction of pressure in the compression moulded plate, while the complicated flow pattern of injection molding leads to a different distribution. Particles are oriented parallel to the wall near to it and almost vertically to that in the core of the specimen. It is obvious from these results that the orientation of anisotropic filler particles changes significantly strongly with composition and that these changes may have a pronounced effect on properties.

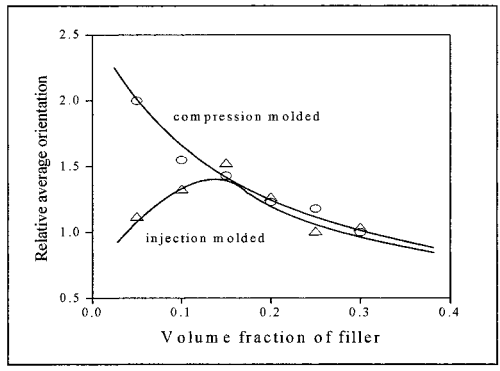

Figure 9. Effect of processing technology on the orientation of talc particles in PP composites. Symbols are the same as in Fig. 7.

Quantitative Evaluation

According to Figure 6 the strength of the composites changes both with processing technology and filler type. Talc reinforces PP relative to $CaCO_3$ and causes even absolute reinforcement in injection moulded samples. A decrease in strength is observed as a function of filler content for the compression moulded specimens. The composition dependence of strength can be predicted

by a simple model, which takes into account the effective load-bearing cross-section of the matrix, the strain hardening of the polymer due to elongation and matrix/filler interaction[45]:

$$\sigma_T = \sigma_{T0}\,\lambda^n \frac{1-\varphi}{1+2.5\varphi}\exp(B\varphi) \tag{4}$$

where σ_T and σ_{T0} are the true tensile strengths ($\sigma_T = \sigma\lambda$, $\lambda = L/L_0$) of the composite and the matrix, respectively, n is a parameter expressing the strain hardening tendency of the matrix and B is proportional to stress transfer from the matrix to the dispersed phase, i.e. to interaction. When strength is expressed in reduced form, $\sigma_{Tred} = \sigma_T\,(1 + 2.5\varphi)/(1 - \varphi)$, or relative form, $\sigma_{Trel} = \sigma_{Tred}/\sigma_{T0}$, linear correlation of the variables should be obtained as a function of composition in a semi-logarithmic plot.

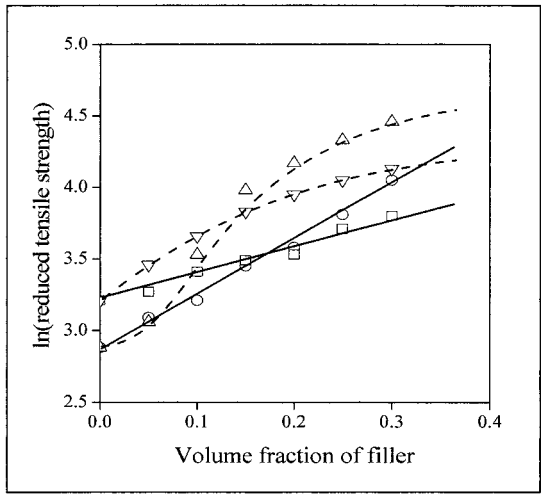

Figure 10. Reduced strength of particulate filled PP composites plotted against filler content in linear form. Symbols are the same as in Figure 6.

Figure 10 shows reduced strength in linear representation. $CaCO_3$ filled composites correspond to the prediction; they give straight lines with different slopes and intersections. Intersections

represent matrix properties, which reflect the dissimilarities in structure resulting from the two processing technologies. It has been shown earlier that B depends on the size of the interface and the thickness of the interphase[46], i.e.

$$B = (1 + A_f \rho_f \ell) \ln \frac{\sigma_{Ti}}{\sigma_{T0}} \tag{5}$$

where A_f and ρ_f are the specific surface area and the density of the filler, while ℓ and σ_{Ti} are the thickness and strength of the interphase, respectively. The investigated $CaCO_3$ fillers differ both in specific surface area and interaction, since Hydrocarb 95 T was surface treated with stearic acid. It has been shown, however, that specific surface area has a more pronounced effect on the value of B than on surface treatment[47,48]. Indeed, composites containing the filler with the larger specific surface area exhibit a steeper slope, in spite of the weaker interfacial interaction in this system.

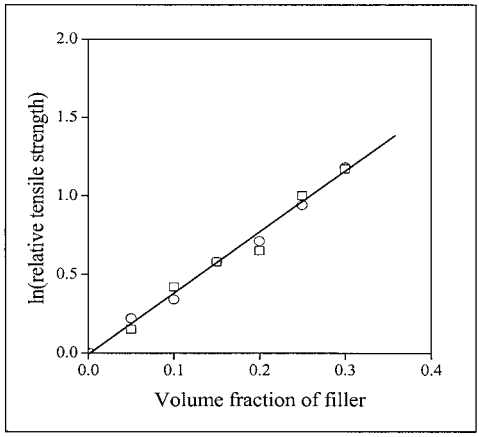

Figure 11. Relative strength of PP/$CaCO_3$ composites normalized by taking into account the differences in filler characteristics (B). (○) injection moulded, (□) compression moulded.

After taking into account the effect of different specific surface areas and interaction of the fillers by normalizing B, the relative strengths of the $CaCO_3$ filled composites were plotted in the linear form (Figure 11). The two sets of data fall onto the same line, proving that the effect of processing technique influences matrix properties independently of the characteristics of the fillers, a factor which was eliminated by calculating relative quantities. The result also show that the dissimilarity in the properties of the two series of composites filled with the different $CaCO_3$ fillers is caused mainly by the different specific surface area of the fillers and, to a lesser extent, by different interaction (surface treatment). The independent effect of processing technology and filler characteristics is in agreement with the results of Figure 8, which showed similar composition dependence of crystallinity in the two heating runs. Injection moulding changed the absolute amount of crystallinity, but not the tendency implemented by the presence of the filler.

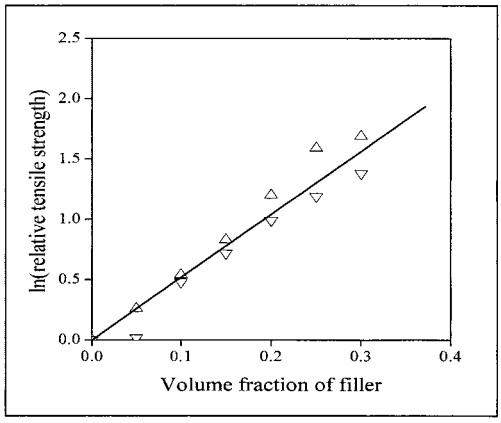

Figure 12. Linear plot of the relative tensile strength of PP/talc composites after correction for crystallinity and orientation. (△) injection moulded, (▽) compression moulded.

However, the non-linear character of the composition dependence of the talc filled composites still remains to be explained. In order to take the nucleation effect of the talc particles and their orientation into account, the strengths of the composites filled with talc were corrected by a simple approach. Relative crystallinity and orientation were calculated by relating strength

measured at each composition to the smallest value determined in each series. Subsequently, composite strength was divided by this relative parameter characterizing structure. Reduced and relative strength values were calculated and plotted in the linear from; the latter correlation is shown in Figure 12. Correction according to crystallinity does not have any effect on strength; it does not change the shape of the correlations presented in Figure 10, it modifies their position only slightly. However, taking into account average particle orientation results in straight lines. If we plot the natural logarithm of reduced values against composition, the slope and interception of the lines obtained for two sets of composites are different again, due to the differences in processing conditions as well as in the orientation distribution of the particles. The effect of talc type can be neglected here, because the particle characteristics (specific surface area, particle size) of the two grades used are very similar to each other. These results emphasize again the major role of particle anisotropy, particle orientation and orientation distribution in the determination of composite properties.

Conclusions

The structure of particulate filled polymers is often more complicated than expected; particles are rarely distributed homogeneously in the matrix. Segregation is usually negligible under practical conditions, but aggregation must always be expected and checked for. The presence of aggregates deteriorates overall polymer properties, especially impact resistance. Anisotropic particles are always orientated, and the extent and direction of orientation determines properties. A case study on the structure and properties of particulate filled PP has shown that composites prepared with $CaCO_3$ and talc has significantly different properties. Tensile strengths were very different, both as a function of particle properties and processing condition. The application of a simple model proved that it is not the nucleating effect, but the anisometric particle geometry of talc that results in its strong reinforcing effect. Processing technology determines the structure of the matrix and the orientation of anisotropic particles; both influence properties significantly. The results obtained prove that the relation between the structure and properties of particulate filled polymers is usually quite complex, practically, always several factors influence properties simultaneously.

Acknowledgements

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