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Correlations between image-analysed morphology and mechanical properties of calcium carbonate-filled polypropylene

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Calcium carbonate-filled polypropylene composites were processed on two different high-intensity mixing devices. The resulting relationships between morphology, processing conditions and mechanical properties of these composites were studied using an electron microscope with an image-analysis system and impact and tensile testing. Only under more extreme conditions did the recently developed turbine mixer give as good a dispersion as the classical Banbury-style mixer. Relatively small additions of the filler resulted in small increases in absorbed impact energy. Semi-quantitative information about the randomness achieved in the mixing process was obtained using a dilation/counting procedure and computer-derived spatial images. Object-specific parameters such as the percentage of objects greater than 1 μm in size give good correlation with the mechanical properties of the mixture.

1. Introduction

Composites of polymers with particulate fillers have generated considerable interest, primarily due to their potential cost reduction while improving the mechanical properties [1–5]. For example, when filled with calcium carbonate ($CaCO_3$), polypropylene–elastomer blends become competitors for engineering thermoplastics with properties approaching those of acrylonitrile–butadiene–styrene (ABS) and other engineering materials. The interest in developing such composites is therefore to widen the range of application of the polymer. In highly filled polymer systems, a major problem is non-uniformity of properties due to poor dispersion of the filler in the matrix. Surface treatment of the dispersed phase by suitable coupling agents has been of some help in overcoming the dispersion problem [1, 6–8]. However, recent work [4, 9–11] also reports on the investigation of agglomeration dependency on the processing conditions and equipment. Using high-shear mixing devices, good improvements in reducing the number of the agglomerates were reported [4, 9, 10]. The mechanism of dispersion of the small particles in the mixing process has been studied by various authors for rubber–carbon-black systems. An erosion [11, 12] and an onion mechanism [13] have been proposed for the break-up of agglomerates into aggregates and unit particles. In these models the number of passages or residence time in the high-shear zone in the mixer was determined to be critical to the state of dispersion.

In this paper, we report a study on the mechanical properties of polypropylene–calcium carbonate composites prepared on two different batch processing devices. A recently developed turbine mixer (K-Mixer or Gelimat) was used to melt a polymer and simultaneously disperse and mix the filler into it. This processing device attempts only to mix and melt polymeric systems and not to pressurize as do extruders. The mixer consists of a horizontal, unheated, water-cooled cylindrical chamber within which a centred shaft rotates (Fig. 1). Staggered mixing blades are mounted on the shaft. A high-powered electric motor rotates the shaft at high r.p.m. which results in speeds of up to 45 $m\,s^{-1}$ at the blade tips. A pre-measured polymeric charge is fed through a hopper to an integrated feed screw. Once inside the chamber, the polymer charge is subjected to extremely high agitation and subsequently melts [14]. The melting/mixing times are very short and the mixing does not involve conventional shear flows. As a comparison with the turbine mixer, a more typical batch mixer, a Banbury type, was employed to prepare specimens with the same concentration of filler. It consists of two rotors and an externally heated mixing chamber (Fig. 2). The shape of the rotors induce axial mixing along the rotors towards the centre of the chamber as the material travels in a figure-of-eight pattern. This configuration results in fairly high-intensity shear mixing in the gaps and thus produces both good dispersive and distributive mixing of the components [15].

Various techniques such as optical microscopy, electron microscopy, small-angle light scattering etc. have been reported to determine the state of dispersion. However, it is often difficult to estimate the randomness or regularity of the morphology. In this study, we report the use of electron microscopy with an image analysis system to obtain qualitative and quantitative information about the effectiveness of

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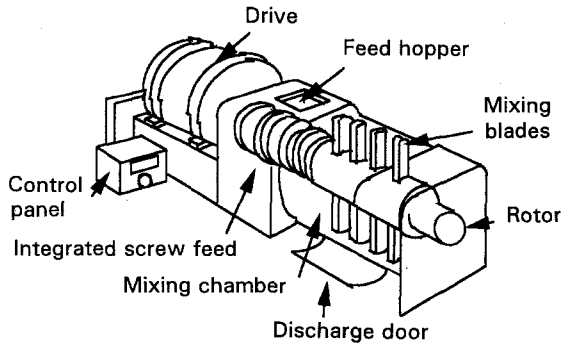

Figure 1 Schematic diagram of the turbine mixer.

dispersive and distributive mixing in the two mixers. The morphology of these composite systems was then related to their impact and tensile properties.

2. Experimental procedure

2.1. Materials

The granular polypropylene (SB-789) used in this study was provided by Himont Inc. It is a polypropylene copolymer with an MFI of 8 and an average particle size of approximately 1 mm.

The filler material was supplied by Pfizer Specialty Minerals. Two types of calcium carbonate were studied, stearic acid treated and non-stearic acid treated. The results reported in this study were obtained using particles with a unit particle size of 0.6 μm (reported by the manufacturer).

2.2. Specimen preparation

Polypropylene and calcium carbonate were dry-blended prior to processing using the turbine mixer as a low-rate blender at 100 r.p.m. for 5 min. Mixtures with 1, 3, 5, 10, 20, 40 and 60 wt% calcium carbonate were prepared and processed on the process devices described below. To all the mixtures, 0.1 wt% antioxidant (Irganox 1010, Ciba-Geigy) was added to prevent degradation of the polymer during processing.

2.3. Processes

2.3.1. Turbine mixer

A one-litre turbine mixer with temperature, torque and r.p.m. control was used to prepare samples. It has been observed for a particular charge size fed to the mixer, when the process dynamics are fixed, that the temperature of the charge rises with time in a non-linear manner. Based on a preliminary study a suitable charge size was determined to be 100 g. Process conditions such as discharge temperature were evaluated with samples containing 10 wt% filler. While an infrared probe could be used to measure the temperature inside the mixer, a thermocouple was used to read the temperature of the processed composite immediately upon discharge from the mixer. All the specimens were processed at 45 $m\,s^{-1}$ tip speed.

2.3.2. Banbury-type mixer

A Haake–Buchler Rheocord mixer (Rheomix 600)

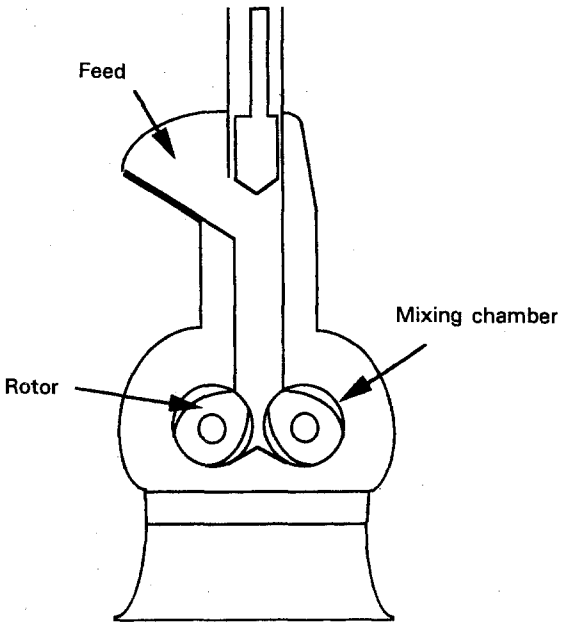

Figure 2 Schematic diagram of a Banbury mixer.

with microprocessor control of temperature, torque and r.p.m. was used to prepare samples. The charge size for mixtures prepared on this mixer was kept constant at 50 g. Samples containing 10 wt% filler were used to evaluate processing conditions such as temperature, time and r.p.m. in order to optimize the dispersion of the particles and the resulting mechanical properties. Based on this preliminary study it was decided to use 220 °C, 200 r.p.m. and 10 min blending time for this process.

2.4. Determination of dispersion

Image analysis together with various optical methods have been used to obtain quantitative and qualitative information in a wide variety of sciences [4, 9, 16, 17]. It was reported in the literature [4, 9] that detection of the largest flaws will be most important when describing the strength of the material. Such flaws or local structure differences could consist of very large particles or large agglomerates of small particles. The local structures are, however, a part of a specific texture. For example, small particles can be arranged randomly, ordered, regularly spaced, agglomerated etc. Information about the texture could therefore be important when discussing reinforcement and stress field overlap between particles [4].

The state of dispersion and texture were characterized under SEM (Jeol 840) using a backscatter detector and carbon-coated, cyrofractured test pieces. The magnification used was 1500× and acceleration voltage of 10 kV. Grey-level images representing a size 58 μm × 62 μm (480 × 512 pixels), with a pixel repetition rate of 100 times, were subsequently digitized and stored on a Bernoulli disk for further analysis (Fig. 3).

The images were analysed using a system produced by Kontron GmbH employing their Vidas software. To obtain information about particles and agglomerates as well as texture, different object- and field-specific analyses were employed. First, particle-specific features such as object diameter, shape, object area,

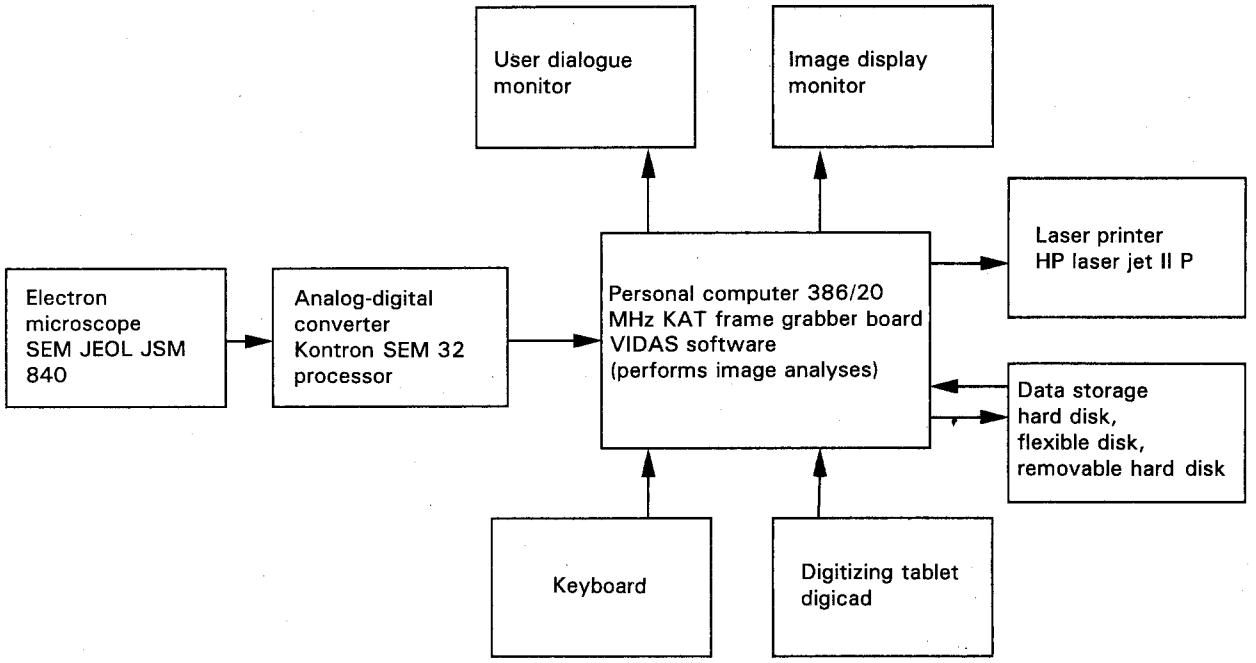

Figure 3 Flow chart with the components of the image analysis system.

orientation of the particles etc. were determined. Then field-specific parameters such as the number of objects and total area covered by the particles were measured. The latter was combined with a dilation/counting procedure [16] to obtain texture information. The use of this procedure involved growing each object in diameter by a certain amount. The growing objects would eventually merge and become one big object (Fig. 4 depicts this cycle). If all the objects are counted which have disappeared during a dilation cycle, a distribution of initial interparticle distances is obtained. Further, the distribution of the interparticle spacing can be used to classify the object distribution into random, ordered or agglomerated.

In order to characterize the field-specific analysis better, several programs were written in C program language to create random and clustered point patterns. With these programs a defined number of points could be created within the same image area as the digitized SEM images. By applying a defined structural dilation element (i.e. hexagon, square etc.) to the point pattern, compositions with well-defined particle content could be created.

These programs used a random number generator available on personal computers to create x and y coordinates. For the random point pattern a minimum interparticle distance could be defined in order to determine the sensitivity of the dilation/counting technique. In the case of the clustered point pattern the random number generator was used again to create a starting point (seed) within the defined image area. The next x and y pair is created using the old x and y pair as seed number for the random number generator. Furthermore, by applying an "agglomeration" factor the range in which the new point could be placed was limited.* By changing the "agglomeration" factor, the degree of agglomeration could be changed. Images obtained from this simulation and the resulting histograms could then be compared with the results obtained from the particle-filled composites.

2.5. Mechanical testing

Tensile test and falling-weight impact test specimens were injection-moulded at 220 °C using a Mining and Chemical Products Ltd MCP 100 SA injection-moulding machine. Tests were carried out at 23 °C. The dimensions of the falling-weight impact test specimens were 37.0 mm diameter, 3.1 mm thickness. The instrumented falling-weight impact tester (Rheometrics RDT-5000) was interfaced with a PC to record the force–displacement data at a rate of 500 kHz. The impact speed used for the test was 5.08 m s^{-1}. The total absorbed energy was the basis for comparing all the materials. Tensile testing was done using an Instron (type TT-B). The tensile test specimens (type M-I) followed ASTM D638 and were tested with a crosshead speed of 10 cm min^{-1}. The yield stress data were used as the basis for comparing the composites.

3. Results and discussion

3.1. Dispersion

3.1.1. Turbine mixer

The turbine mixer involves a relatively short batch processing time. During the first stage of about 3 s the solid particulates are slowly heated to the polymer fusion temperature of 162 °C by an intense thermokinetic energy transfer which has been modelled by a drag-flow heat dissipation model [14]. During the second stage the fused mass rises in temperature very quickly from the fusion temperature to a preset discharge temperature. Fig. 5 shows the decrease in average object size with the increase in total processing time and hence discharge temperature.

* This type of clustering is also referred to as the Levy Flight model [18].

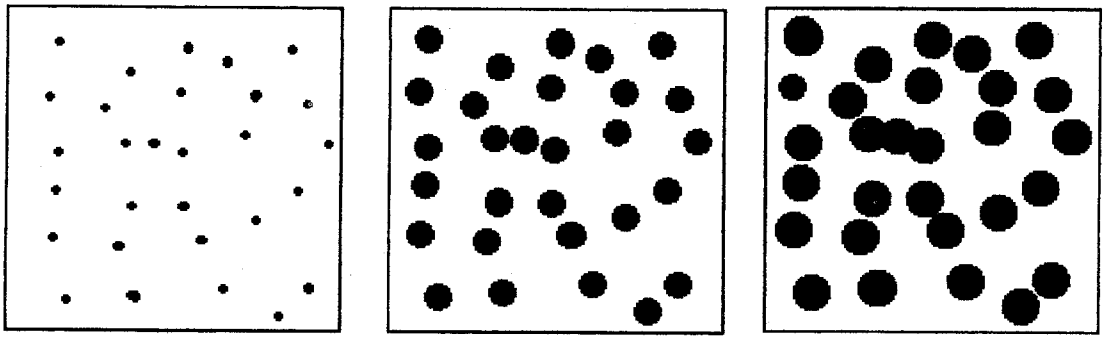

Figure 4 Dilation–counting cycle.

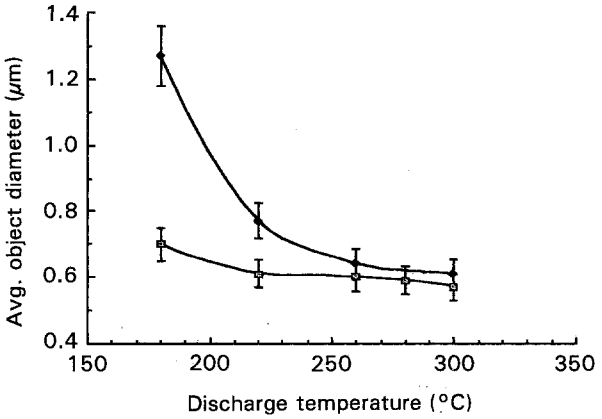

Figure 5 Turbine mixer: average object diameter versus discharge temperature for composite with 10% $CaCO_3$: (⊡) with and (◆) without stearic acid.

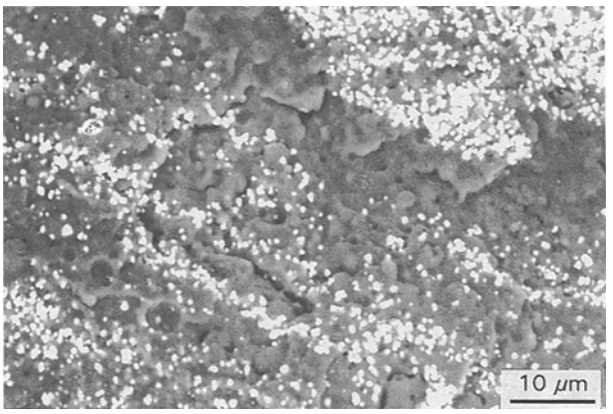

Figure 6 SEM Image of a composite processed at 180 °C.

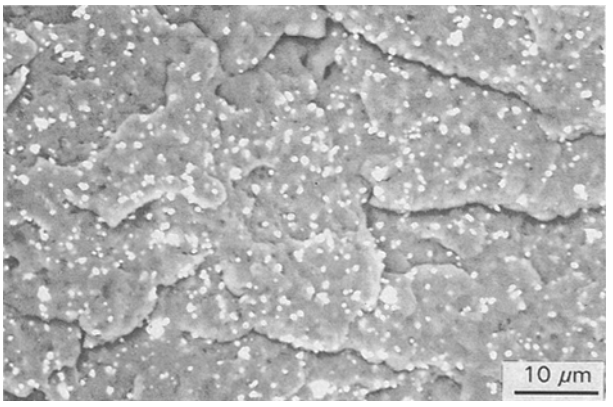

Figure 7 SEM Image of a composite processed at 220 °C.

The stearic acid-treated $CaCO_3$ shows less agglomeration, as indicated by the smaller average object size. This decay of agglomerate fraction with longer residence time during the higher-shear second stage in the mixer agrees with the dispersion model proposed in the literature [11, 13]. Also, the average object size as observed in image analysis of the SEM images (Figs 6 and 7) is being reduced between 180 and 220 °C discharge temperature. At shorter processing times and lower discharge temperature the mixture is fluxed less homogeneously, which leads to visible agglomeration (Fig. 6). Supporting observations were made with the dilation/counting technique (Figs 8 and 9). At 180 °C considerable agglomeration is evident from the large spike at an interparticle spacing of less than 0.5 μm, as well as the longer-range collapsing of particles at the larger interparticle spacing, 4.4 to 11.2 μm.

3.1.2. Banbury-type mixer

Paralleling the turbine mixer studies, the average object size was studied for treated and untreated calcium carbonate as a function of process conditions. Fig. 10 shows the decrease of object size versus r.p.m. using a mixture with 10 wt% filler and a unit particle size of 0.6 μm.

Similar to the mixtures in the turbine mixer, the composites made of the stearic acid treated $CaCO_3$ show smaller average object sizes at corresponding rotor speeds. Only minor changes were observed in the spatial arrangement of objects between the shortest processing time at low temperature and r.p.m. when compared with the longest processing time, high temperature and r.p.m. (Figs 11 and 12). Also the dilation/counting results in Figs 11 and 12 do not pick up any agglomerates and the mean interparticle distance for both conditions is 1.5 μm.

Fig. 13 compares the turbine and the Banbury-type mixer for effectiveness of breaking up agglomerates at higher concentrations under the best processing conditions for each processing device (turbine mixer, discharge temperature 220 °C, total processing time 5 s; Banbury mixer, 220 °C, 200 r.p.m., 10 min). While at higher concentration more particles merge or cannot be resolved at a constant magnification, it is clearly visible that the Banbury mixer is more effective

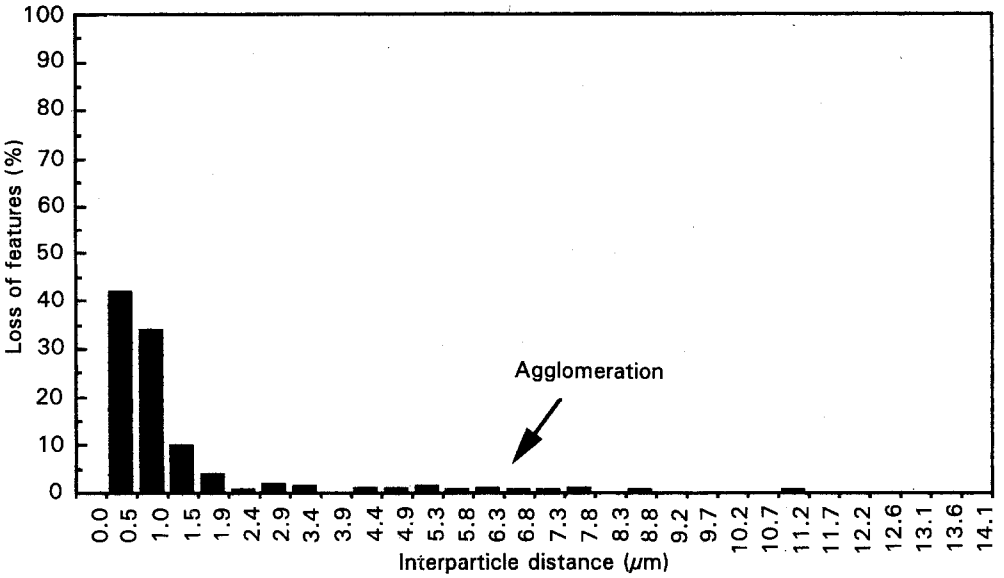

Figure 8 Turbine mixer: dilation counting profile, discharged at 180 °C. 10% $CaCO_3$ with stearic acid.

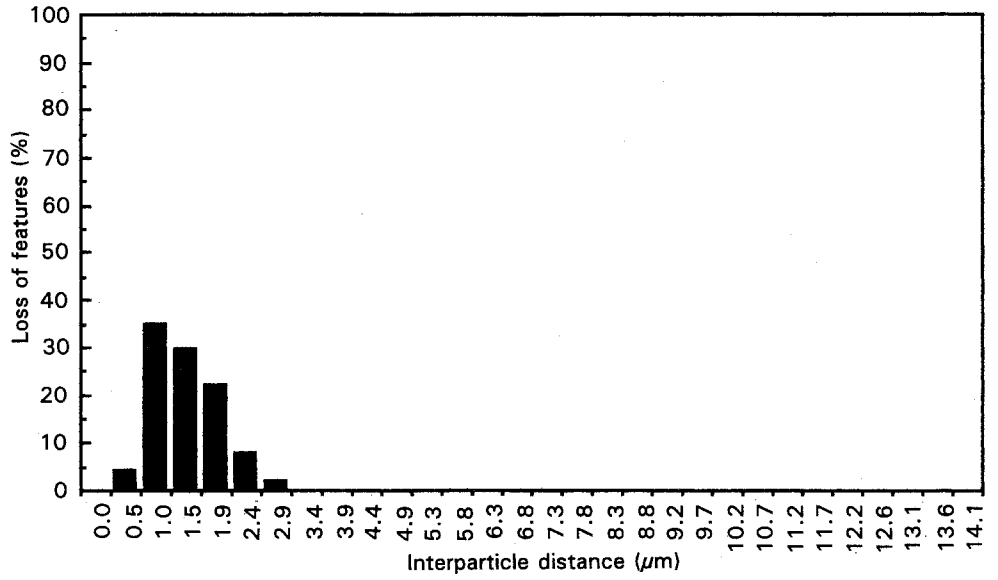

Figure 9 Turbine mixer: dilation counting profile, discharged at 220 °C. 10% $CaCO_3$ with stearic acid.

at higher loadings in breaking up agglomerates, leading to a smaller average particle size.

3.2. Spatial point patterns from computer models

The results obtained by the dilation/counting technique were now compared with results from synthesized images. The images were classified as follows: (a) randomly dispersed points in a field with defined point density and (b) agglomerated point pattern in a field of defined point density. Figs 14 and 15 depict the computer image of the random point pattern and the resulting analysis using the dilation/counting technique, respectively. A small minimum interparticle distance results in a sharp increase of particles lost over the first two dilation cycles, followed by a gradual decay of the class sizes in the histogram. A computer image with the same volume percentage of filler, but a larger minimum interparticle distance (Fig. 15), results

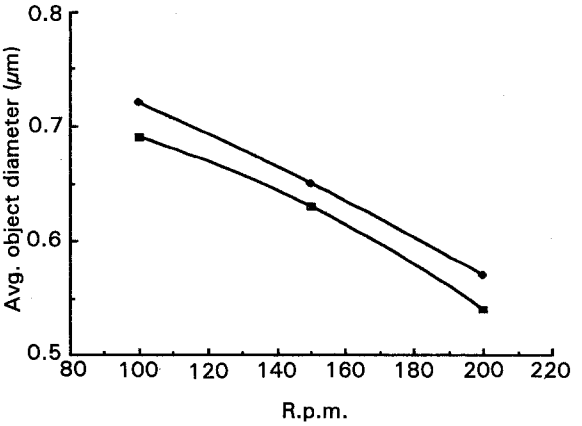

Figure 10 Banbury mixer: average object diameter versus r.p.m.; 10% filler, processed at 220 °C/10 min. (■) with stearic acid and (◆) without stearic acid.

in a more gradual decrease in merging particles after the interparticle distance peak. Both histograms show a Poisson distribution of the interparticle spacing.

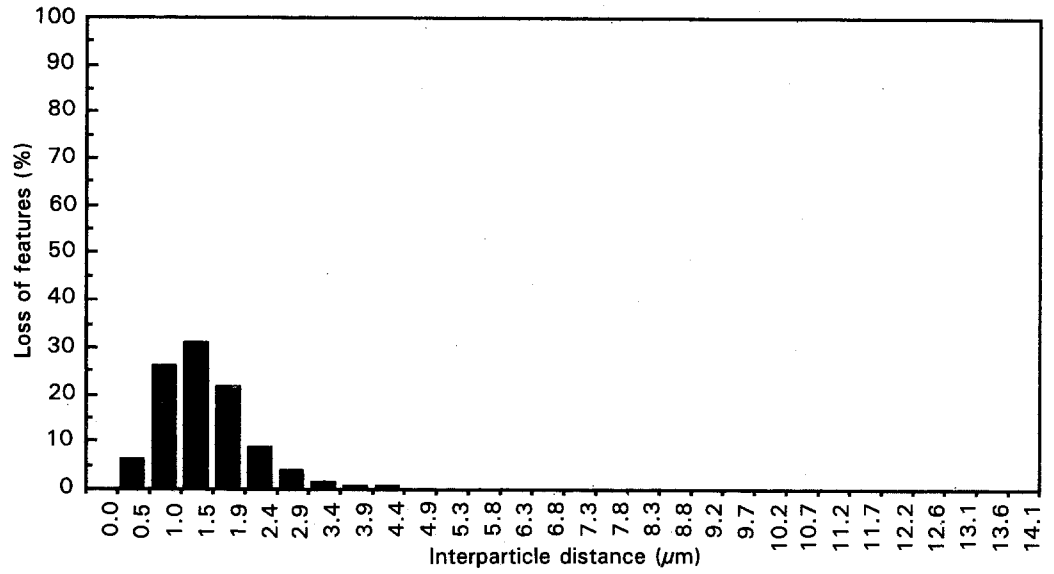

Figure 11 Banbury mixer: dilation counting profile processed at 180 °C/5 min, 100 r.p.m.; 10% $CaCO_3$ with stearic acid.

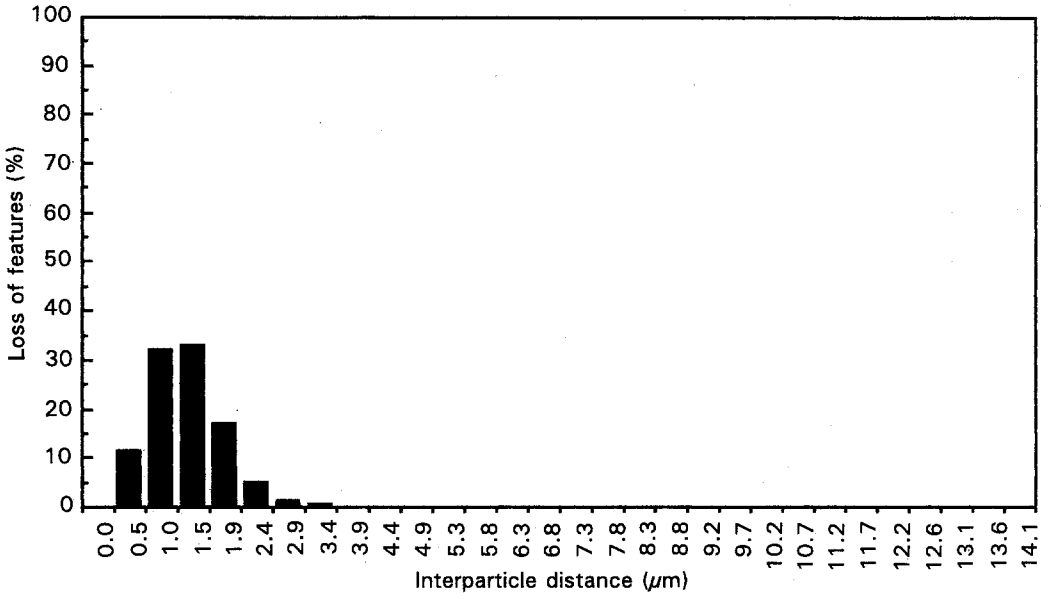

Figure 12 Banbury mixer: dilation counting profile processed at 220 °C/10 min, 200 r.p.m.; 10% $CaCO_3$ with stearic acid.

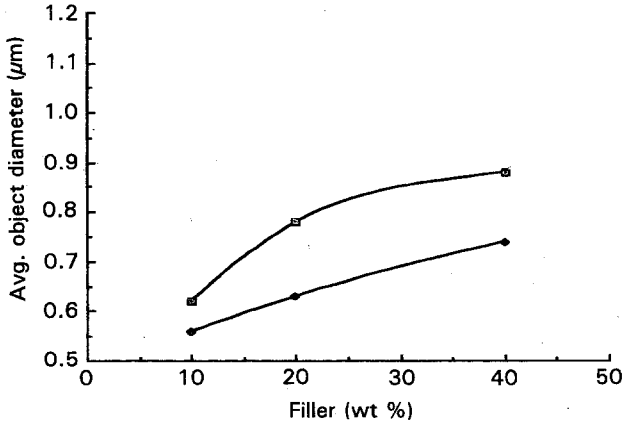

Figure 13 Comparison turbine/Banbury mixer: average object diameter versus filler wt%. $CaCO_3$ with stearic acid; (⊡) turbine mixer (5s), (◆) Banbury mixer (10 min).

Actual results from the Banbury mixer (Figs 11 and 12) indicate similarity to these simulated textures.

In contrast to these random point patterns, two examples of clustered point patterns are shown with the same amount of filler (Figs 16 and 17). Both histograms indicate that a large number of objects merged during the first few dilation cycles. Neither of these histograms showed a Poisson-like distribution of interparticle distances. The simulations are both more closely related to the results obtained on the turbine mixer. The latter example with a larger number of small clusters shows a slower decay in lost objects past the maximum, with some merging occurring after 28 dilations (Fig. 17). Similar observations were made for the SEM image of the actual systems produced on the turbine mixer at low discharge temperature (Fig. 8).

3.3. Mechanical properties

Using different mechanical testing procedures, such as a low strain-rate tensile and a high strain-rate falling-weight impact, an attempt was made to determine the sensitivity of these tests to the state of dispersion.

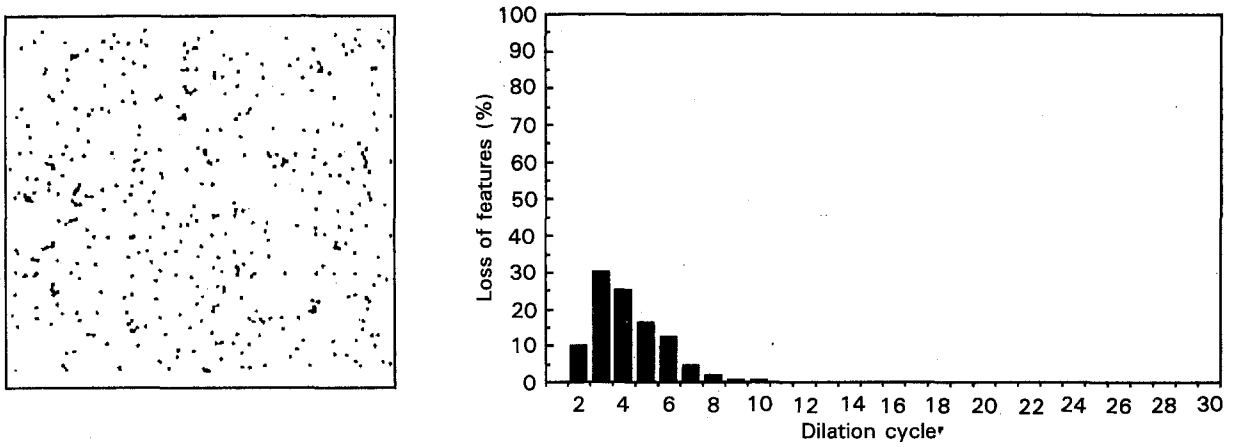

Figure 14 Computer image: random point pattern (4 pixel minimum distance).

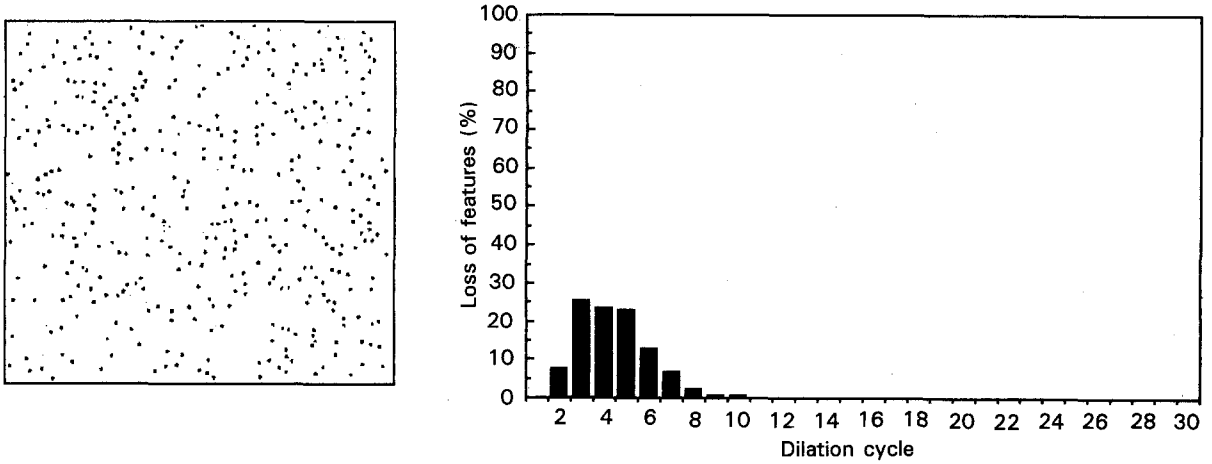

Figure 15 Computer image: random point pattern (16 pixel minimum distance).

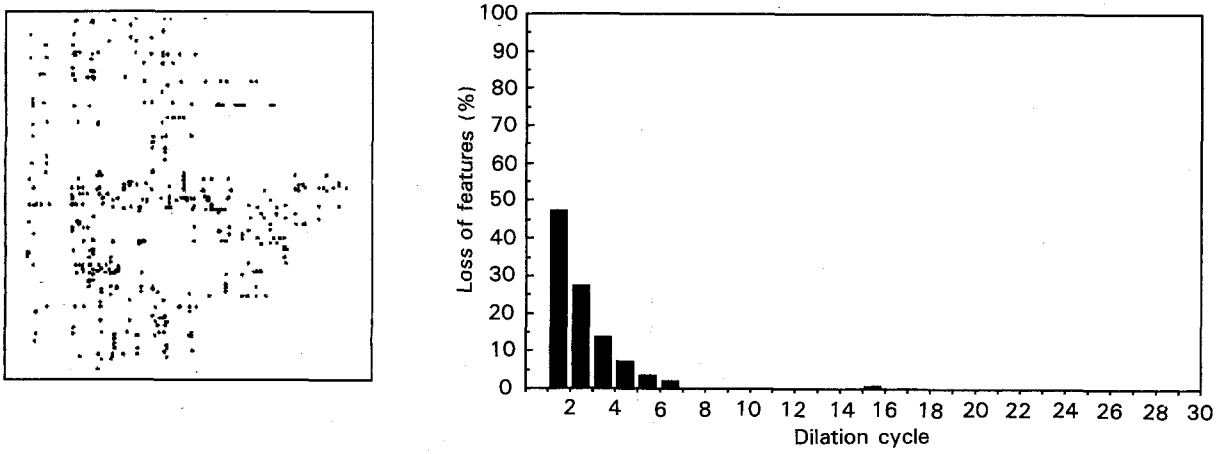

Figure 16 Computer image: clustered point pattern (Levy flight model, $D = 0.45$).

Fig. 18 compares the absorbed impact energy versus filler weight percentage for the two mixers under optimum processing conditions. The turbine mixer is effective only at very low filler concentration in dispersing the particles well. When average interparticle spacings, evaluated from the texture analysis, were used to correlate the impact results it was found that they were not very sensitive to a loss in impact energy (Fig. 19). However, if the percentage of particles larger than 1 μm for each concentration was plotted versus the impact energy good agreement was found (Fig. 20). Fig. 20 shows that the decrease in impact energy corresponds closely to the increase in the percentage of objects greater than 1 μm. Furthermore, the percentage of the objects larger than 1 μm is found to be the lowest between 10 and 20% filler for the Banbury-type mixer. These findings are in agreement with data from the literature [5].

Yield stress data (Fig. 21) indicate a modest increase in yield stress for samples prepared on the Banbury mixer, while samples prepared on the turbine mixer showed little change. It is of interest to note that the

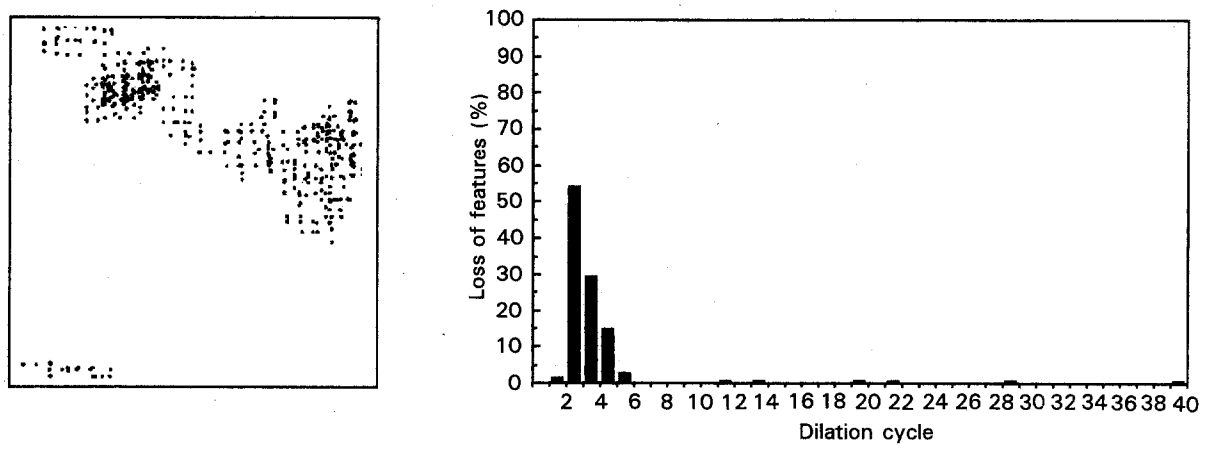

Figure 17 Computer image: clustered point pattern (Levy flight model, $D = 1.85$).

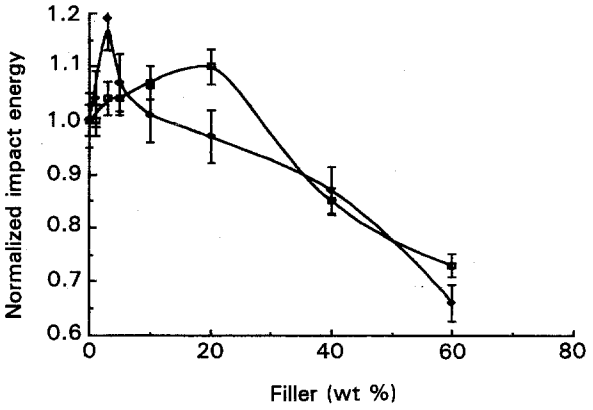

Figure 18 Comparison of turbine and Banbury mixer: normalized impact energy versus filler wt%. $CaCO_3$ with stearic acid, processing at 220 °C; (⊡) Banbury mixer, (◆) turbine mixer.

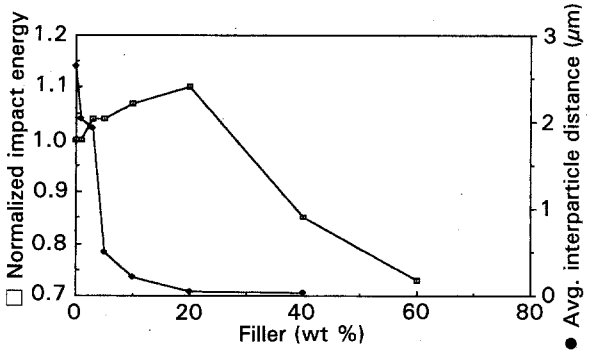

Figure 19 Banbury mixer: (⊡) normalized impact energy and (●) average interparticle distance versus filler wt%.

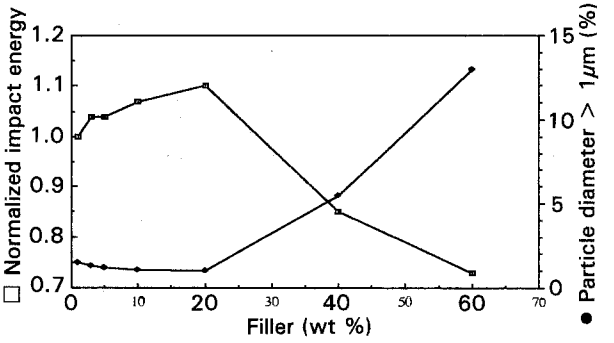

Figure 20 Banbury mixer: (⊡) normalized impact energy and (●) percentage of particles > 1 μm versus filler wt %.

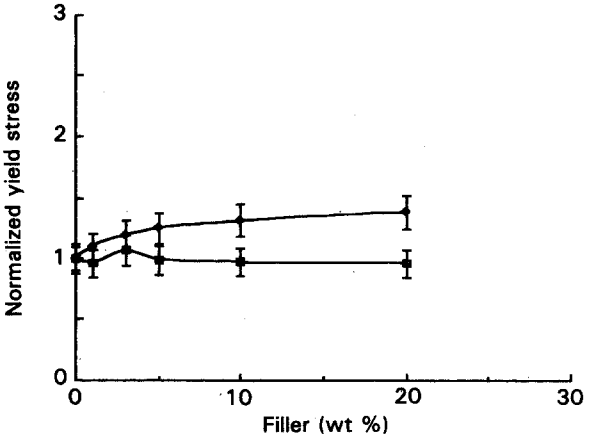

Figure 21 Comparison of (⊡) turbine and (◆) Banbury mixer: normalized yield stress versus filler wt%. Untreated $CaCO_3$.

highest yield stress was observed at a filler content up to 20%, the same as for the impact results. A model has been proposed [19–20] to predict yield stress data of particulate-filled composites which makes allowance for the packing density and the interfacial adhesion. The value of the yield stress of the composite is given by

$$\sigma_{yc} = \sigma_{ym}(1 + V_f)(1 + AV_f)^{-1} \exp(BV_f) \quad (1)$$

where A is the particle density factor (2.5 for hexagonal close packing); B is an empirical factor that includes interface interactions and anisotropy of the filler and has to be evaluated from experimental data. σ_{yc} is the yield stress of the composite while σ_{ym} is the yield stress value for the unfilled matrix. When the data obtained in the experiment were fitted to Equation 1 it was found that the results up to 5 wt% filler were in close agreement with the model (Fig. 22). Increasing the filler concentration led to a reduction in the parameter B, indicating a loss in effective surface area that would withstand the applied load. Data from the image analysis (Fig. 13) support this result, indicating an increase in object size with filler weight percentage. Agglomerates not only have a smaller specific area in contact with the polymer matrix, but also act as stress concentrators [2, 4] which in both cases leads to reduced mechanical properties.

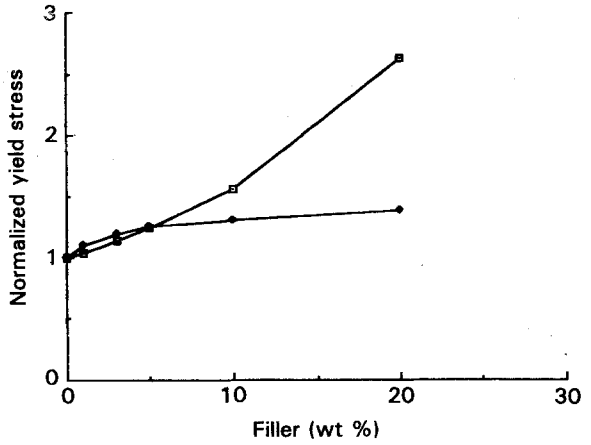

Figure 22 Comparison of (◆) experimental yield data from Banbury mixer versus (⊡) values calculated from Equation 7 with $A = 2.5$, $B = 10.0$.

4. Summary and conclusions

This study investigated the influence of various processing conditions on the morphology of a particulate-filled thermoplastic and the resulting mechanical properties. A turbine mixer and a Banbury-type mixer were used to prepare specimens with a wide range of filler content as well as different unit particles sizes.

The turbine mixer provides good dispersion at higher temperatures considering the short processing time, but generally is inferior to the slower Banbury-type mixer. To achieve good dispersion on the turbine mixer longer fluxing times and higher discharge temperatures had to be used. The stearic acid treatment provided some improvement in dispersing the calcium carbonate particles in the polymer matrix, in particular at higher filler concentrations. The composites prepared on the turbine mixer with lower discharge temperature were highly agglomerated. It is evident that the process parameters contribute significantly to the overall texture of the mixture.

At low filler concentrations small increases in impact energy can be achieved with the addition of calcium carbonate filler, but this is not commercially attractive because the filler content corresponding to the best improvement is relatively small and the maximum impact energy increase is low. For highly filled systems where it is desirable to maintain mechanical properties, the coated filler and the Banbury process run at higher temperature and r.p.m. are preferred.

The results of this study suggest that all the mechanical properties measured were affected by the presence of agglomerates. In particular the falling-weight impact and tensile measurements showed good agreement with the morphological data.

Image analysis coupled with the electron microscopy was found to be a powerful tool in characterizing the morphology of polymer composites. The texture of the morphology was analysed using a dilation/counting technique on the image analyser to obtain qualitative information about the spatial arrangement of the particles. Further, the presence and extent of agglomeration could be determined.

Some correlation between the spatial arrangement in simulated cluster patterns and actual images of composites could be established, in particular for mixtures processed on the turbine mixer. Mixtures from the Banbury-type mixer showed close agreement with a randomly arranged point pattern. However, information from object-specific rather than field-specific analysis, such as unit object (particle/agglomerate) sizes, had to be used to quantify the impact of agglomerates on the mechanical properties. In particular the number fraction of object sizes greater than a certain size was shown to be useful for correlation with the mechanical properties of the composites. Specifically, the fraction of objects larger than 1 μm was used for the particles with a unit size of 0.6 μm. Changes in average object sizes were generally found to be sensitive only to big changes in the agglomeration content. In contrast to some literature findings [2], no bimodal distribution of particles was observed.

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