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ORIGINAL CONTRIBUTION

# The effect of filler surface modification and processing conditions on distribution behaviour of silica nanofillers in polyesters

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**Abstract** Dispersion and distribution of nanosized precipitated amorphous silica particles in poly(ethylene terephthalate) PET and poly(butylene terephthalate) PBT matrices have been studied. The effect of silane coupling agent as well as processing conditions has been analysed on the basis of microscopic analysis of sample morphology. *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (A-1120) has been used as a silica surface modifier. The effect of the extrusion process performance with a single and a twin screw extruder has been tested. It has been found that the processing conditions are more important factors determining fine dispersion and homogenous distributions of filler particles in the matrix than the filler surface modification. The results obtained have revealed that single screw extrusion is preferred only for processing the composites comprising the silica modified with aminosilane, while the application of twin screw extrusion leads to homogenous dispersion and fully deagglomeration of filler particles without silane treatment. It has been established that when the concentration of silica filler increased from 3 up to 7% by weight, the secondary process of particle aggregation occurs.

**Keywords** Amorphous spherical silica · Silanes · Dispersion of fillers · Composite materials

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## Introduction

Extrusion melt compounding of dispersive nanofillers with polymeric materials is considered the most effective way for producing nanocomposites. There are many arguments for the melt processing being a preferred method for making nanocomposites for commercial use. If technologically possible, from the practical point of view, this process is more economical and more profitable than in situ polymerisation, in-situ intercalative polymerisation techniques and sol-gel methods. This procedure allows nanocomposites to be formulated using ordinary compounding devices: extruders or special mixers, without the necessity of using advanced polymer technology.

However, there are several important factors that restrict the quality of such composites and hence limit their commercial availability. The important factors influencing the end-use properties of a polymer-reinforced composite are the interfacial adhesion, filler particle size, particle shape, extent of agglomeration, distribution and dispersion in the organic matrix [1–5]. A significant improvement in the composite properties is expected for a maximum cover of the filler surface with the polymer, which is conditioned by sufficiently small filler particles and their excellent dispersion in the polymer matrix. The degree of dispersion depends on the efficiency of the aggregates breaking in the mixing process and is enhanced by application modifiers on the filler surface. Thus, when nanometric dispersion of

primary filler particles (e.g. clay platelets, silicas, fullerenes and carbon black) is obtained, the filler particle is increased and the reinforcement effect is improved [6, 7]. Therefore, knowledge of the particle size distribution and their dispersion in a polymer matrix is critical in relation to the analysis of the mechanical properties of the composites [8].

Relatively good spatial dispersion of the filler aggregates and their deagglomeration can be achieved when hydrodynamic forces acting in the process of extrusion are sufficiently high [9, 10], i.e. greater than the cohesive forces of the particles inside the agglomerates. The process of deagglomeration is strongly affected by the chemical treatment of the filler, viscosity of the matrix fluid and by the conditions of mixing.

This paper describes an approach for the examination of the effect of selected coupling agents and processing conditions on the formation of nanocomposites of thermoplastic polyesters with amorphous spherical silica. The main purpose of this research is to determine the changes in the morphology of poly(ethylene terephtahalate) (PET) and poly(butylene terephthalate) (PBT) composites, with silica as a function of two variables, that is, the silica surface modification and processing conditions. The dispersion and distribution behaviour of nanosized silica filler particles in thermoplastic polyester matrixes has been examined using scanning electron microscopy (SEM) technique. For morphology observation, the fractured surfaces of PET/$SiO_2$ and PBT/$SiO_2$ composites have been etched by air plasma.

## Experimental

*Silica filler characterisation* The silica nanofiller used in this work was synthesised in the laboratory using a novel method of precipitation from emulsion medium. This procedure is based on the preparation of two emulsions containing (1) aqueous solution of sodium metasilicate and cyclohexane and (2) hydrochloric acid and cyclohexane. In both emulsions, a non-ionic surfactant was used as an emulsifier. The reaction conducted in a reactor yielded a third emulsion containing silica. Detailed parameters of the precipitation reaction are given in [11].

A part of the total amount of the filler was produced in a reactor of 5 $dm^3$, while the rest of the silica was precipitated in a reactor of 80 $dm^3$ capacity. For hydrophobicity enhancement, the silica surface was chemically treated by *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (A-1120), using 3 weight parts by 100 weight parts of silica.

The particles shape and morphology of the silica obtained was characterised by SEM technique on a Philips 515 microscope. The size of silica particles was measured in a ZetaPlus apparatus (Brookhaven Instruments) using the dynamic light scattering (DLS) method.

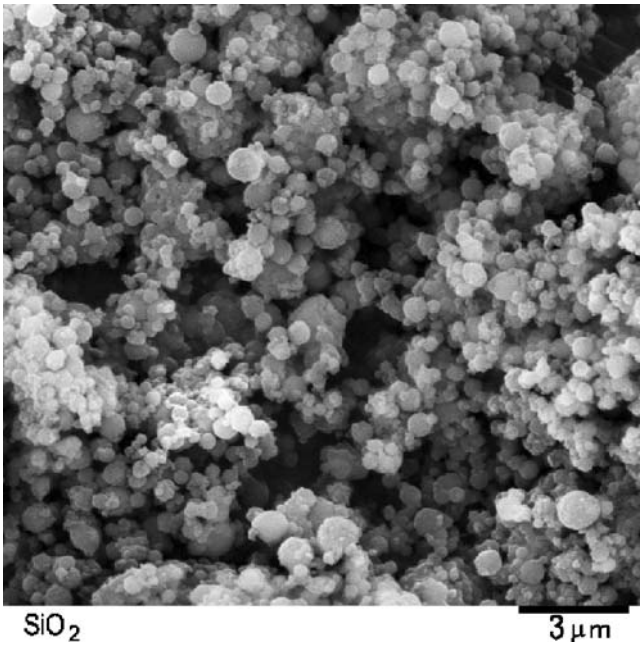



**Fig. 1** SEM micrograph of untreated silica particles, precipitated in small-scale reactor

The scanning electron micrograph presented in Fig. 1 confirmed the uniform character of the silica obtained and visualised its almost ideally spherical particles. The particle size distribution of unmodified silica precipitated in the reactor of 5 $dm^3$ capacity shows the presence of two different bands (Fig. 2). The band of a higher intensity within the particle diameter range of 392 to 685 nm is typical of primary agglomerates. The maximum intensity of 100 corresponds to particles of 490 nm in diameter. The other band with a very low intensity reflects the presence of huge agglomerates within the diameter ranging from of 3,660 to 5,900 nm. The unmodified silica sample exhibited

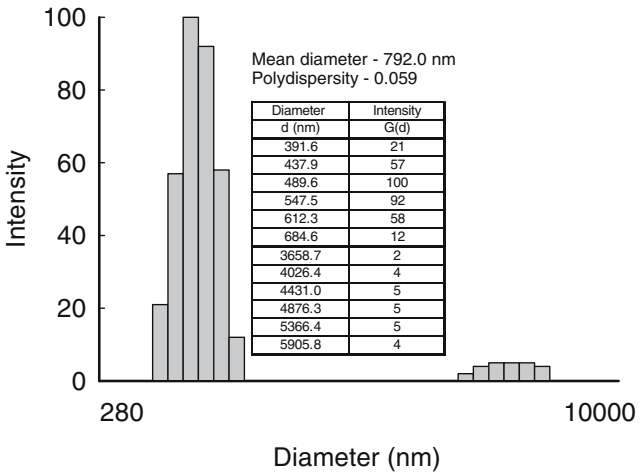



**Fig. 2** Multimodal particle size distribution of untreated silica particles, precipitated in small-scale reactor

low polydispersity (0.059) and the mean particle diameter of 792 nm.

As a result of the modification with aminosilane (A-1120), an evidently decreased tendency to form large aggregates of silica particles has been observed (Fig. 3). The particle size distribution (PSD) curve demonstrated very intense band assigned to the particles of the diameter between 300 and 430 nm and the maximum intensity corresponding to the particle diameter of 355 nm. Consequently, the mean diameter decreased from 792 nm (for unmodified $SiO_2$) to 572 nm for the sample studied. This result is somewhat different from those observed in the previous work [12] in which we reported that aminosilane promoted strong agglomeration of precipitated silica particles after modification.

According to the SEM observation carried out for the silica synthesised in the larger reactor (80 $dm^3$ capacity), the silica particles reveal almost ideally spherical shape with the mean diameter from 200 to 400 nm (see Fig. 4).

As can be seen in Fig. 5, the particle size distribution of unmodified silica shows the presence of three bands. Probably, the band with the lowest intensity indicates primary particles or small aggregates (contains a very few particles) with a diameter around 200 nm.

The second band is typical of aggregates with a maximum intensity corresponding to those of 500 nm in diameter. The third band clearly attests to a tendency of agglomerate formation. The mean diameter of silica particles has increased, and the sample reveals poor polydispersity. Moreover, the modification with aminosilane has led to a decrease in the tendency of large silica agglomerates formation (Fig. 6); this sample contains no secondary aggregates, and the mean diameter takes the lowest value.

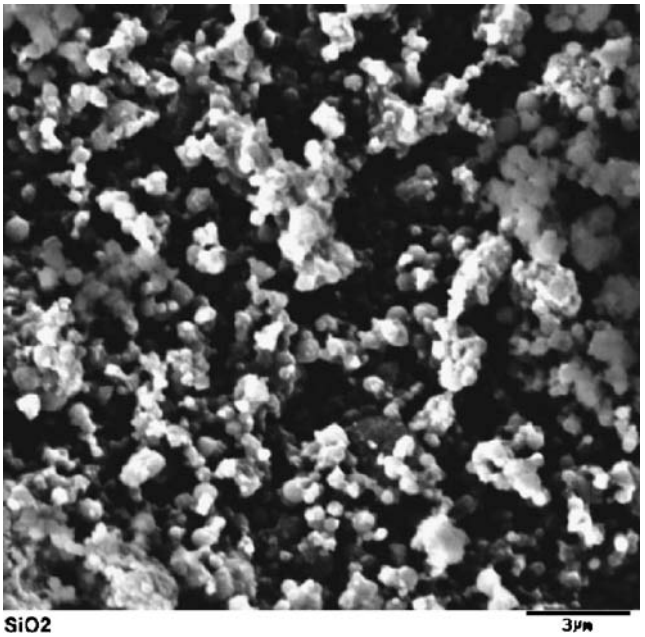



**Fig. 4** SEM micrograph of untreated silica particles, precipitated in large-scale reactor

As follows from this short characterisation, the treatment of silica surface before its use as a filler considerably determines its properties.

## Preparation of composites

The PET and PBT pellets were pulverised and pre-mixed in a rotating mixer together with 3 and 7% by weight of

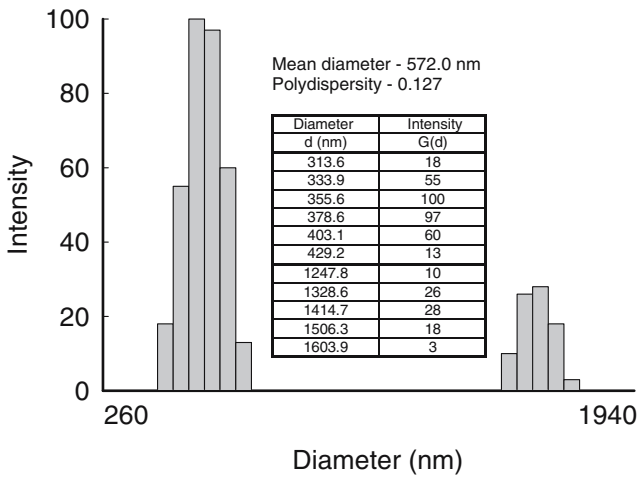



**Fig. 3** Multimodal particle size distribution of silica modified with 3 weigh parts of aminosilane

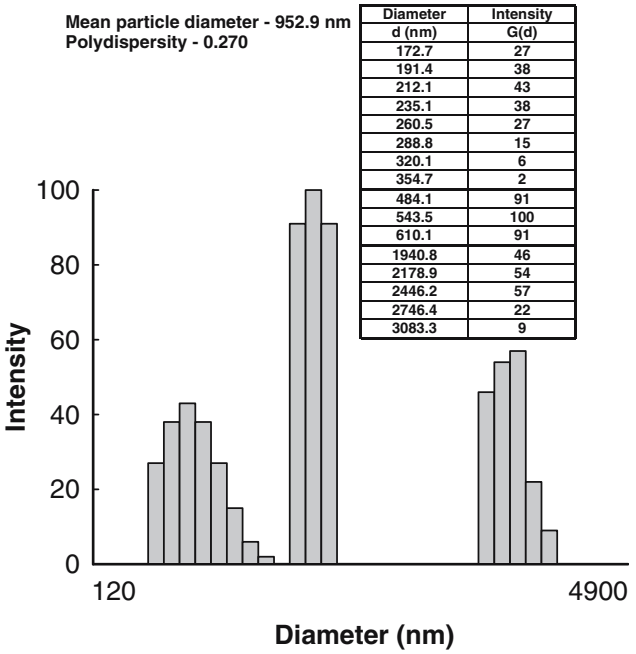



**Fig. 5** Multimodal particle size distribution of untreated silica particles, precipitated in large-scale reactor

untreated and silane-treated silica. The rotational speed of the mixer was 40 rpm to prevent component segregation. Composites were prepared using two different extruders. Pre-weighted, mixed dry components were melt-blended either in:

– Single screw extruder (32 mm screw diameter) and 30 L/D ratio, equipped with a typical shaping head, or in
– Co-rotating twin screw extruder (30 mm screws diameter) and 32 L/D ratio, equipped with kneading disc blocks and mixing elements.

The dried extrudates were palletised and injection-moulded on an Engel 80/25 machine into the dumbbell-shaped tensile test bars. The mould temperatures were set as 30 and 80 °C for PET/$SiO_2$ and PBT/$SiO_2$ composites, respectively.

The microscopic observations were performed with a Philips SEM 515 microscope.

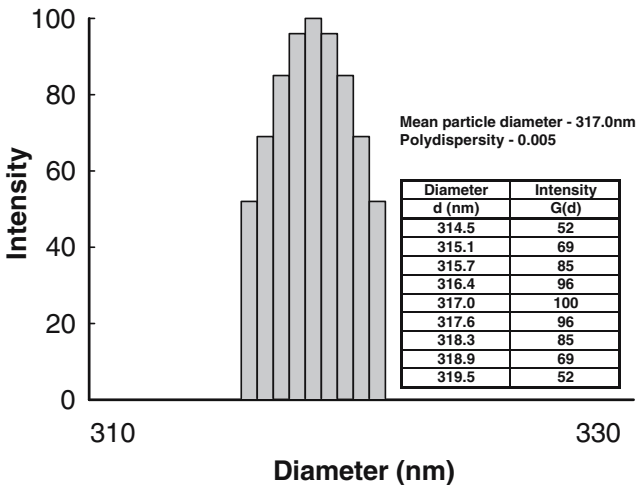
To determine the size of the filler particles at the fractured surfaces of the composites, their surfaces were treated by cold air plasma. This technique allows effective removal of the surface layer of the polymer matrix from the filler surface. Therefore, the application of plasma enables a visualisation of the inorganic particles and determination of the degree of homogeneity as well as the filler distribution [13, 14].

## Results and discussion

### Microscopic observation of the composite microstructure obtained with the single screw extruder

Valuable information on the dispersion and distribution of silica in PBT was provided by the scanning electron micrographs. It should be pointed out that only the samples etched by air plasma were subjected to microscopic investigation, as this procedure permitted a precise localisation of $SiO_2$ on the polymer surface. Otherwise, the polymer layers could cover the inorganic particles.

Figure 7 displays the SEM micrograph of the PBT composite with 3% of pristine $SiO_2$, after etching by air




| Diameter d (nm) | Intensity G(d) |
|---|---|
| 314.5 | 52 |
| 315.1 | 69 |
| 315.7 | 85 |
| 316.4 | 96 |
| 317.0 | 100 |
| 317.6 | 96 |
| 318.3 | 85 |
| 318.9 | 69 |
| 319.5 | 52 |

**Fig. 6** Multimodal particle size distribution of silica modified with 3 weigh parts of aminosilane

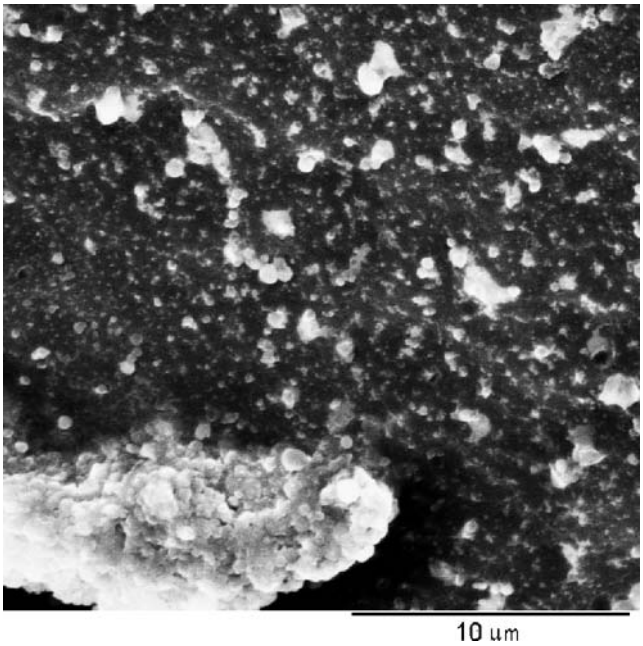



**Fig. 7** SEM micrograph of PBT/3% $SiO_2$ composite, processed with single screw extruder

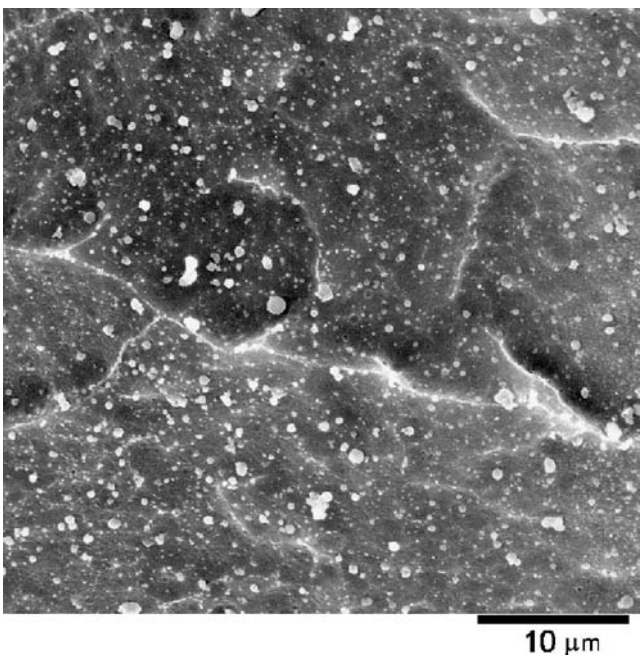



**Fig. 8** SEM micrograph of PBT/3% $SiO_2$ composite, (silica modified with aminosilane) processed with single screw extruder

plasma. The figure presents a strongly bonded agglomerate with its specific shape built of a large number of almost ideally spherical particles of silica. This behaviour of silica could be associated with its specific surface character. Large numbers of silanol groups (≡Si–OH) on the surface of precipitated silica promote formation of stable clustered agglomerates [15]. As a consequence, when the unmodified silica is subjected to simply polymer-filler melt mixing processes, the decomposition of filler agglomerates is very poor (see Fig. 7).

Quite different are the SEM results obtained for composites of PBT with treated silica. Figure 8 shows the morphology of the PBT/3% $SiO_2$ composite surface with aminosilane-coupled silica. The spatial dispersion of the filler particles is relatively good; however, a few aggregates are still visible. This microphotograph proves that silica surface treatment affects the powder morphology reducing the agglomerate size. Such modifications are responsible for the observed changes in the dispersion behaviour (Fig. 8), influenced by particle–particle interactions and by the fluid media infiltration into interparticle spaces.

## Microscopic observation of the composite microstructure obtained with the twin screw extruder

The dispersion behaviour of unmodified silica particles introduced into the PET matrix is illustrated in Figs. 9 and 10. Morphology observation of PET/3%$SiO_2$ (by weight) composites documented relatively good spatial dispersion of the inorganic filler.

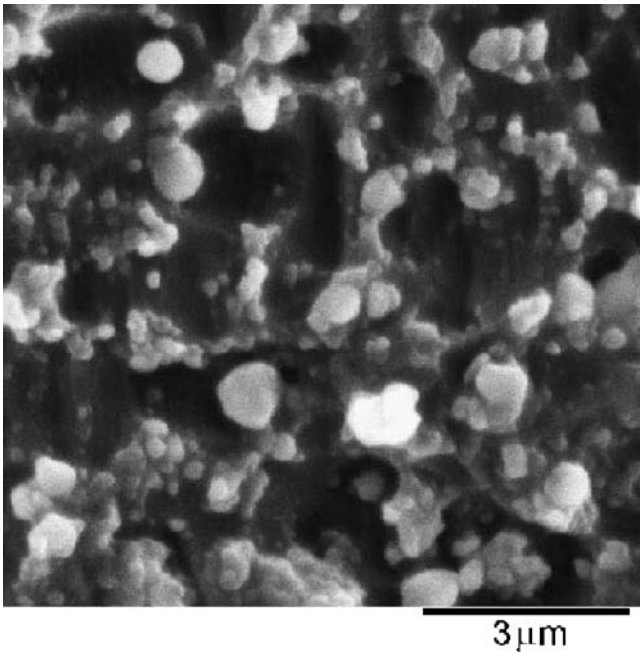



**Fig. 10** SEM micrograph of PET/3% $SiO_2$ composite, processed with twin screw extruder (sample at higher magnification)

Figure 9 presents a homogeneous dispersion of the spherical silica particles with no evidence of huge agglomerates. This means that the hydrodynamic forces applied in the process of extrusion broke the agglomerated structure of unmodified silica. The presence of primary and secondary agglomerates in the bulk of silica was confirmed in the particle size distribution tests (see Fig. 5).

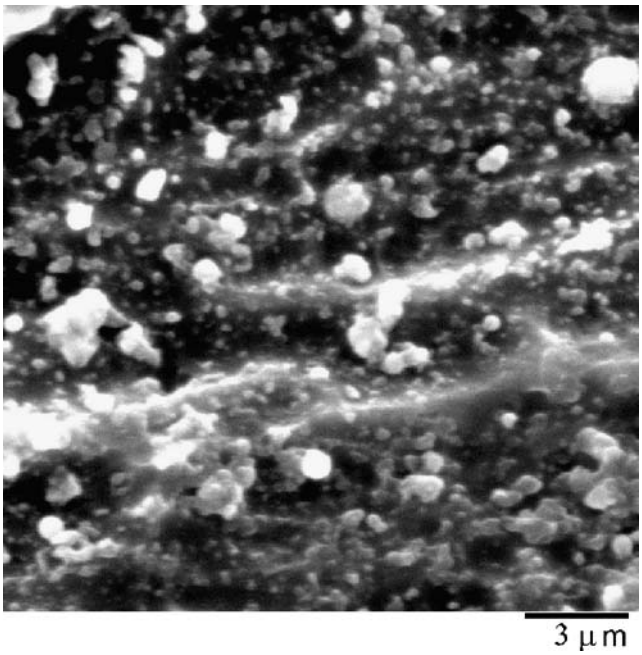



**Fig. 9** SEM micrograph of PET/3% $SiO_2$ composite, processed with twin screw extruder

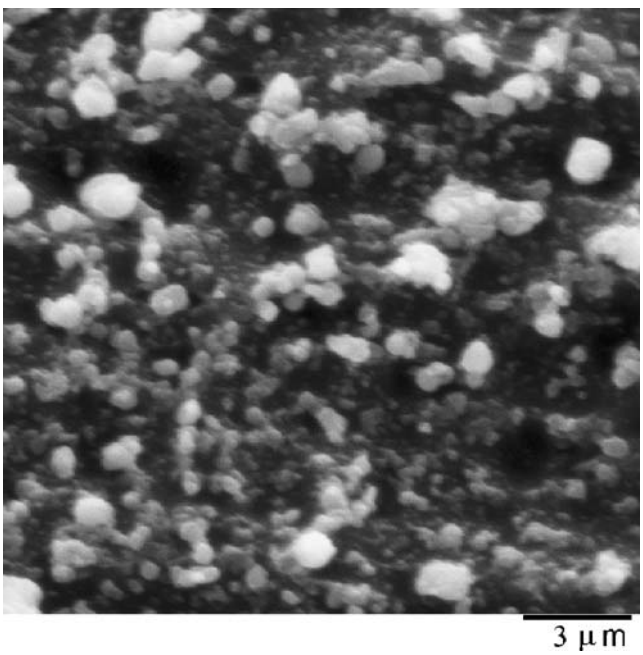



**Fig. 11** SEM micrograph of PET/7% $SiO_2$ composite, processed with twin screw extruder

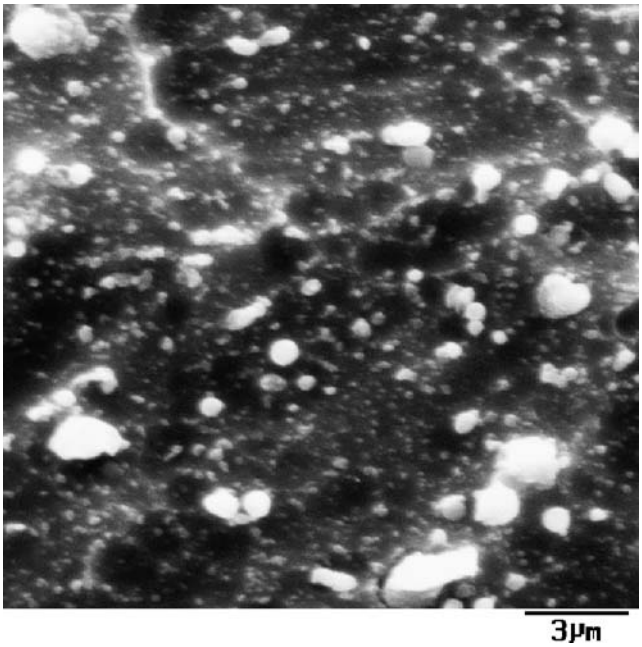



**Fig. 12** SEM micrograph of PET/3% $SiO_2$ composite, processed with twin screw extruder (silica modified with aminosilane)

As expected, the micrographs of the samples obtained from the twin screw extruder evidence no or small concentration of $SiO_2$ aggregates (Fig. 9). This finding indicates that processing of unmodified fillers with PET leads to a homogeneous dispersion of the filler particles. This figure shows no evidence of huge agglomerates and only a few aggregates. As follows from the SEM observations under greater magnifications, in the composites from the twin screw extruder (see Fig. 10), the particles smaller than 400 nm are uniformly dispersed throughout the polymer matrix.

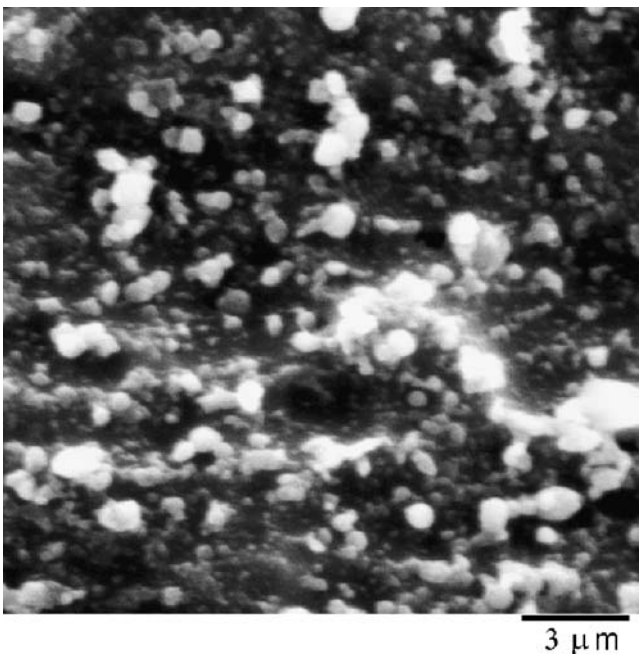



**Fig. 13** SEM micrograph of PET/7% $SiO_2$ composite, processed with twin screw extruder (silica modified with aminosilane)

In contrast to the above, in the samples with the silica content of 7% weight, the particles of this filler are closely surrounded by other particles, and agglomerates are formed (see Fig. 11).

The morphology observed for PET composites with aminosilane-modified silica is very similar to that described above. Figures 12 and 13 present the microstructures of PET filled with 3 and 7% of modified silica, respectively. As expected, the aggregate shapes and agglomerate formation are determined by the filler weight concentration. Consequently, the spherical silica particle aggregation is observed only for the higher filling rate.

The SEM studies of PET/$SiO_2$ composites obtained with the single or the twin screw extrusion have confirmed the behaviour of the inorganic filler, reported for PBT composites with amorphous silica.

## Conclusions

The results of our study have shown that the degree of the filler dispersion in the polymer matrix is determined by the filler particle surface modification and by the mixing process conditions. If the filler is silica, the dispersion of its particles is mostly affected by the conditions of mixing. The results have also suggested that particle deagglomeration process occurs mainly by the erosion mechanism depending on detachments of small aggregates from the outer surface of the agglomerates. It means that degree of silica dispersion is determined mainly by breaking the $SiO_2$ aggregates via intensive shear during extrusion, as follows from a comparison of the SEM observations carried out for samples prepared with single and twin screw extruder. In all cases, silica surface modification with aminosilane has been found to promote good dispersion and homogenous distribution of silica filler particles in the polymer matrix. At the low filler loading rate (3% by weight), the silica particles are well separated and homogeneously dispersed in the polymer matrix, when the concentration of silica filler reaches 7% by weight, aggregation of particles occurs and a complete failure of the mechanical properties of the material is expected. In our previous study, we have found that the exceeding of 5% by weight concentration of $SiO_2$ in PET matrix leads to a change in the polymer behavior from ductile to completely brittle [16].

We have to add that these findings refer mainly to the composites made of thermoplastic polyesters. Some changes should be expected with different polymers used

as a matrix, in particular, if they are characterised with a different viscosity in the molten state.

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