

Multicomponent compounding of polypropylene

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The simultaneous compounding of polypropylene with several mineral fillers was investigated. The mineral fillers were selected on the basis of their size and shape which was spherical (glass beads), sheet-like (mica) or fibrous (wollastonite). In addition, one filler with a considerably smaller particle size (fly ash) was selected. The results of single components were as expected. In multicomponent compounding, the best mechanical properties were attained by the simultaneous use of two or more fillers. This was true for all mechanical properties. In the light of the results, it is evident that the need for a matrix polymer and other fillers can be reduced by the use of a filler with a small particle size without impairing the mechanical properties of the composite. It seems that multicomponent compounding yields somewhat better properties than single-component mineral compounding of thermoplastics. In practice, multicomponent compounding is possible using the same process as for single-component compounding.

1. Introduction

Compounding is one of the most common ways to modify the properties of thermoplastics. It has been studied with a number of materials, and the best results have been obtained with inorganic materials, mainly minerals.

Fillers are used to improve the working properties of thermoplastics, such as strength, rigidity, durability, hardness, etc. Minerals are mainly used for the filling of the so-called volume plastics (polyolefines, PVC, polyamides), and the filler contents range from 20–40 wt % [1]. Here even cut glass fibre can be included in fillers as an extreme case.

The effects of fillers depend greatly on their shape, particle size and composition [2]. Table I presents the conventional division of fillers into categories by particle shape. In mineral fillers, the particle size mainly depends on their degree of grinding; the effects of crystallinity show up only at very fine particle sizes. This is particularly evident in the case of mica, which has a tendency to cut into thinner and thinner sheets. In fibrous materials, such as wollastonite and asbestos minerals, the shortening of fibre length has a noticeable effect.

A very important problem that can usually be solved only partially is the adhesion between the minerals and the polymer. This adhesion depends on the chemical compositions both of the minerals and of the polymer. A major problem here is that the minerals and polymers are typically rather inert chemically. It is not easy to make two inert materials react. How-

ever, a number of adhesion promoters and binders have been developed to overcome this problem. They improve the adhesion at the interface, and their effect is mainly visible in the long-term properties of the composite.

2. Multicomponent compounding


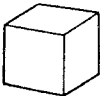
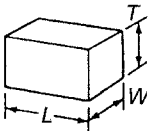
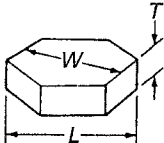
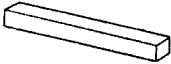
The compounding of thermoplastics is a process where the properties of the final product depend on a number of factors. Here we concentrate on the effects of multicomponent compounding on the properties of the compounded plastics. However, the properties of compounded plastics and the factors underlying them cannot be understood without a brief overview of the production process of compounded thermoplastics. A schematic presentation of the production process is shown in Fig. 1.

The properties of compounded plastics depend strongly on the following factors.

(a) The original components of the compounds. The melt flow index and molecular weight of the polymer can be used to affect blending in the melt-compounding process. The composition of the polymer can be used to affect adhesion by increasing the amount of reactive components in the polymer.

The selection of filler determines particle shape and size and their distributions. An ideal filler has a high aspect ratio and a particle-size distribution where the higher end of the distribution has been cut off. Too big particles may act as points of discontinuity in the

TABLE I Division of mineral fillers for plastics by particle shape

	Idealized shape class				
					
Particle class	Sphere	Cube	Block	Flake	Fibre
Descriptor	Spheroidal	Cubic Prismatic Rhombohedral	Tabular Prismatic Pinacoid Irregular	Platy Flaky	Acicular Elongated Fibrous
Examples	Glass spheres, microspheres	Calcite Feldspar	Calcite Feldspar Silica Barite Nephelite	Kaolin Mica Talc Graphite Hydrous Alumina	Wollastonite Tremolite Wood flour

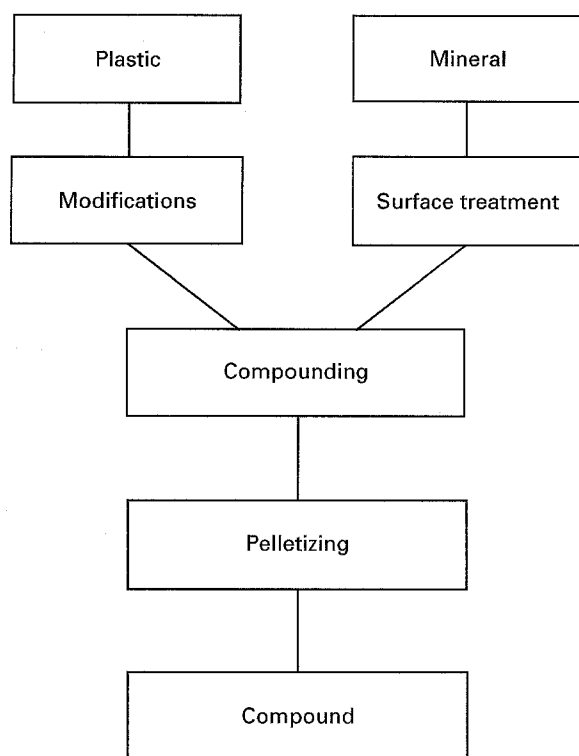


Figure 1 A schematic representation of compounding mineral-filled thermoplasts.

compound and reduce its mechanical properties. Mixing and adhesion can be affected by the surface treatment of the filler.

(b) Compounding is almost always melt compounding in various batch or continuous action devices. At present the most common method is a twin-screw compounding extruder. The objective of the compounding is to disperse the filler particles completely in the matrix polymer. On the other hand, the compounding should be careful enough not to cause mechanical breaking of filler particles or thermal breaking of the polymer.

(c) Filler content is the factor that is most commonly used for controlling the effects of compounding on the properties of the composite. The filler content

should be distributed as evenly as possible in the composite. In practice, the highest filler contents are limited to 40–50 wt %.

2.1. Effects of fillers and multicomponent compounding

The effects of individual fillers on the properties of components are relatively well known. Tensile strength can usually be improved by fibrous fillers, provided that the adhesion is sufficient. Rigidity can be improved by sheet-like fillers, and the improvement depends on the aspect ratio of the filler [2]. Impact strength cannot usually be improved by mineral fillers [3]. The main exception is PVC, whose impact strength can be improved by fine-grained calcium carbonate [4].

Multicomponent compounding produces so-called hybrid structures, where the effects of two or more components are combined [5, 6]. Multicomponent reinforcing is generally used in various fibre-reinforced composites, the most well-known being the elimination of the low-impact strength of carbon fibre reinforced composites by adding glass or aramide fibres.

Multicomponent compounding is also an effective way to reduce the amount of an individual component in a composite. For example, adding a fine-grained component to a coarse filler reduces the need for a matrix polymer [7].

3. Experimental procedure

In this work the multicomponent compounding of polypropylene with three filler types was studied. The fillers were wollastonite, mica and glass beads. They are characterized in Table II. The fillers were selected on the basis of the following two criteria: they should be typical mineral fillers, and they should differ from each other as much as possible, being typical representatives of their particle shape. In addition, they should also be fillers typically used in thermoplastics.

Wollastonite is a calcium silicate with a fibrous (needle-like) particle shape; the wollastonite used

TABLE II Properties of mineral fillers

	Wollastonite	Mica	Glass spheres	Micropoz
Shape	Fibrous	Platelets	Spherical	Sphere
Size (μm)	~ 10	~ 40	$\sim 5-150$	< 0.5
Aspect ratio	~ 20	$\sim 20-100$	1	1
Density (kg m^{-3})	2500	2900	200-600	2200
Hardness (Mohs)	4-5	2-3	5-6	5-6
Colour	White	Grey	Grey	Grey

here was Finnish (Wollastonite FW10, Partek Oy, Finland). The mica was also Finnish, it was Siilinjärvi's phlogopite (Kemira Mica W40, Kemira Oy, Finland). The glass beads were commercial hollow glass beads, which can be separated directly from fly ash (Tecfil 150, Ernström Mineral Ab, Sweden).

The polypropylene used in the study was ICI's (Propathene GW 521 E), which was available in powder form. The powder form was required because the compounding took place as melt compounding in a batch-operation Haake melt-compounding machine. Using powder-like plastic in melt compounding with mineral fillers is easier than using polypropylene in the form of granulates.

The production and testing of the test materials consisted of the following stages.

(1) Surface treatment of fillers with adhesion promoters. This treatment took place as dry mixing in a mechanical Henschel mixer. The surfactant was Union Carbide silane A1100, and its amount was 2 wt % of the filler amount. Mixing time was held constant (6 min), allowing no unnecessary rise in the filler temperature.

(2) The melt compounding took place in a batch-operation Haake melt-compounding machine; compounding was continued at a temperature of 190°C until the torque curve of the compounder stabilized (at 10 r.p.m. it would be 40 min^{-1}). For all compounding runs the torque curve and temperature were recorded as a function of time. Before compounding, the materials to be compounded were weighed and blended mechanically. This method ensures very accurate filler ratios compared to continuous-operation melt-compounding methods. The compounding took place under a normal atmosphere of air, although the contact of oxygen with the melt was obstructed by the construction of the compounder.

(3) In the next stage, the finished compound was scraped away from the mixing chamber and blades of the extruder. After this the mass was allowed to cool to room temperature, and then it was "granulated" by cooling it to a low temperature by liquid nitrogen. The result was a mass as fragile as glass, which was crushed by pressing it mechanically. This treatment probably caused no essential changes in the components, because the granulate size was much bigger than the particle size of the fillers.

(4) The production of test materials of the "granulate" thus obtained took place in a small piston extruder. Using a piston extruder was necessary because it was the only method suitable for the small amount of test material available. Moreover, a piston extruder

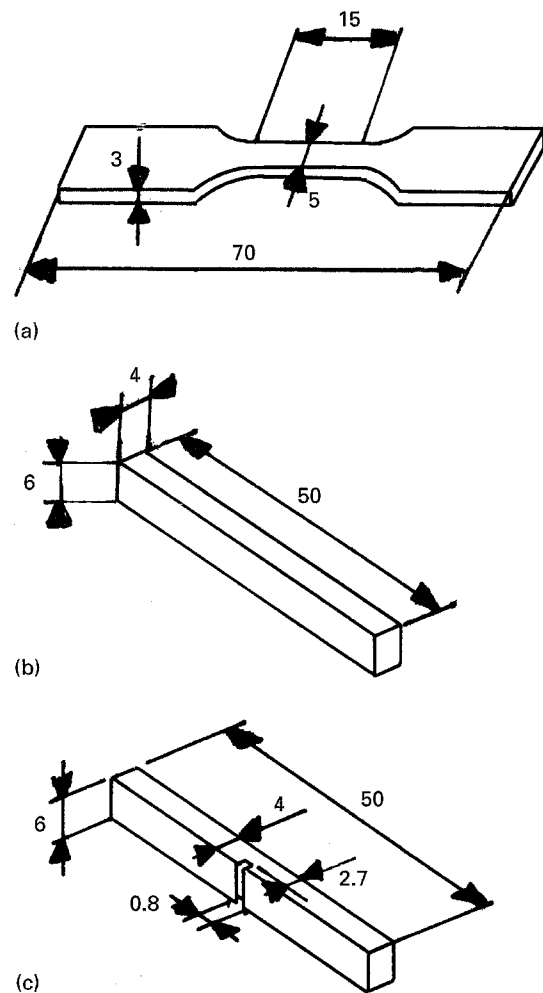


Figure 2 Shape and dimensions of the used extruded test rods. (a) Tensile strength, (b) bending strength, (c) impact strength.

does not break the mass very much. Fig. 2 shows test rods produced by this method and their dimensions (the test rods do not correspond to standards, which is also due to the scarcity of the material available).

(5) For the test materials the strengths and rigidity values were determined by tensile and flexural tests, while an impact test was used to determine their durability.

(6) The structure of the materials as characterized in two different ways. The mass structure was examined from the fracture planes of the test rods by SEM. The structure of the fillers, in turn, was analysed by SEM from the ashes of burned material.

3.1. Test compoundings

Two different sets of compounding runs were performed; one set was for characterizing the single effects

TABLE III Multicomponent compounds and their filler contents (wt %)

Wollastonite	Mica	Glass spheres	Micropoz
10	20	—	—
15	15	—	—
20	10	—	—
10	—	20	—
15	—	15	—
20	—	10	—
—	10	20	—
—	15	15	—
—	20	10	—
20	5	5	—
15	10	5	—
15	5	10	—
10	10	10	—
10	15	5	—
10	5	15	—
5	15	10	—
5	10	15	—
5	20	5	—
5	5	20	—
7.5	7.5	7.5	7.5
6	6	6	12
5	5	5	15
4.3	4.3	4.3	17.1

of the fillers. This was done because the properties of a component strongly depend on its history, and this makes it necessary to have reference material to chart the properties of multicomponent compounds. The reference single-component compounds were made in sets of different concentrations (filler contents 5, 10, 20, 30, 40, 50 wt %), because it is very enlightening to know the effects of different filler quantities on the properties of compounds.

The actual multicomponent compound set was made according to Table III with a constant filler content of 30 wt %. Here the filler contents were determined in per cent by weight, which is somewhat misleading, because using per cent by volume would always have yielded exactly the same volume fractions of components. However, this would have been extremely difficult in the case of glass beads, whose density ranged from 400–600 kg m⁻³.

4. Results and discussion

The effects of different fillers on the mechanical properties of composites are presented in Fig. 3. The results largely agree with existing sources. All results indicate the following correlations with filler contents.

(1) Small filler contents (< 10 wt %) have virtually no effect on the properties of the materials. The effects begin to show up only at larger concentrations.

(2) All fillers used here reduce impact strength. The effect of the filler on the impact strength clearly depends on the particle shape of the filler. Fibrous wollastonite reduces impact strength less than other fillers, while mica has almost the same effects as glass beads.

(3) As far as flexural and tensile strength are concerned, mica and wollastonite yield the best strengths

while glass beads reduce them. The improvement of tensile strength is rather modest with both mica and wollastonite.

(4) All fillers improve the rigidity (modulus) of composites. In the flexural test, the highest increase in modulus was measured for mica.

The results of multicomponent compounding runs are presented in Figs 4–6. In these figures, the corners of the triangle correspond to the properties of single-component compounds. The sides depict the properties of two-component compounds containing the single components of the corners. The values of three-component compounds are inside the triangle, and the filler contents can be calculated from the figure using the so-called aspect ratio principle.

The impact strengths of the composites are presented in Fig. 4. The figure reveals that the impact strengths depend greatly on the compounding used. In the figure there are two clear maximum impact strength areas, and these high impact strengths were obtained by mica/wollastonite filling. Likewise, the minimum impact strength areas are visible, and the absolute minimum was measured for a pure glass beads filling. As the value of pure plastics shown in the figure indicates, the impact strengths of all compounded plastics are clearly lower than the strength of pure plastics.

The strength and rigidity values measured in the flexural tests are presented in Fig. 5. The results indicate that flexural strengths and modulus follow a similar pattern in the case of different fillers. In all cases, flexural modulus are higher than the values for pure plastics, while glass beads reduce the flexural strength from the value of pure plastics. The effect of filler shape is particularly evident in the flexural test. The increase in rigidity caused by mica is clearly visible, and so is the decrease in rigidity caused by glass beads. The results of mica/wollastonite filling are highly interesting, because their combinations yield the best rigidity and strength values.

There is no unambiguous explanation for the high modulus and strengths obtained by mica/wollastonite compounding. In single-component compounds, the superiority of mica over wollastonite is clearly visible. The explanation probably lies in the mechanism by which the wollastonite settled between the mica particles affects the structure. Compared to wollastonite, mica has clearly bigger and sheet-like particles. Mica particles tend to orientate very strongly along the flow in extrusion. Wollastonite particles are ordered to a much lower degree than mica particles. Thus, wollastonite particles will be situated in the middle of the mica particles, and they will be less oriented. They rigidify the matrix between the mica particles more than a corresponding amount of mica would do. This phenomenon is illustrated in Fig. 7. However, we have not been able to verify this theory, because there is no method for examining the location of the wollastonite particles between the mica particles in the structure.

As a conclusion of this combined effect of mica and wollastonite, it can be noted that in the case of flexural strength, multicomponent compounding yields better results than expected.

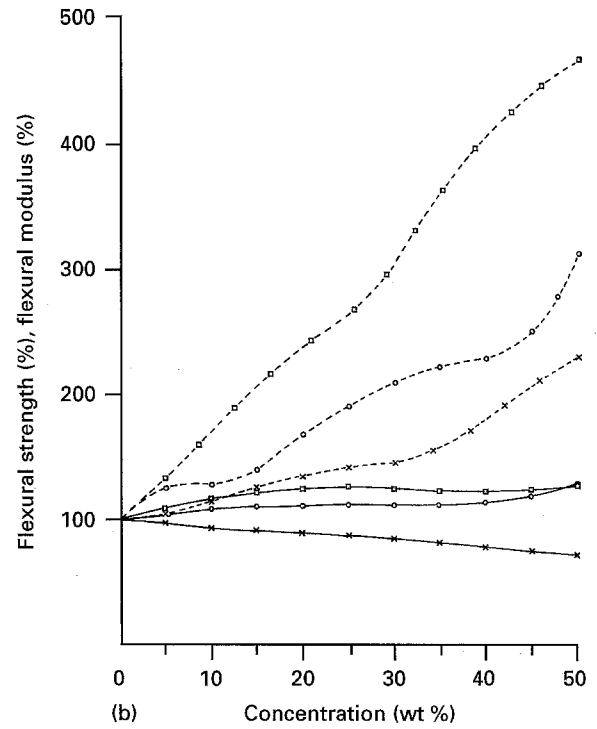
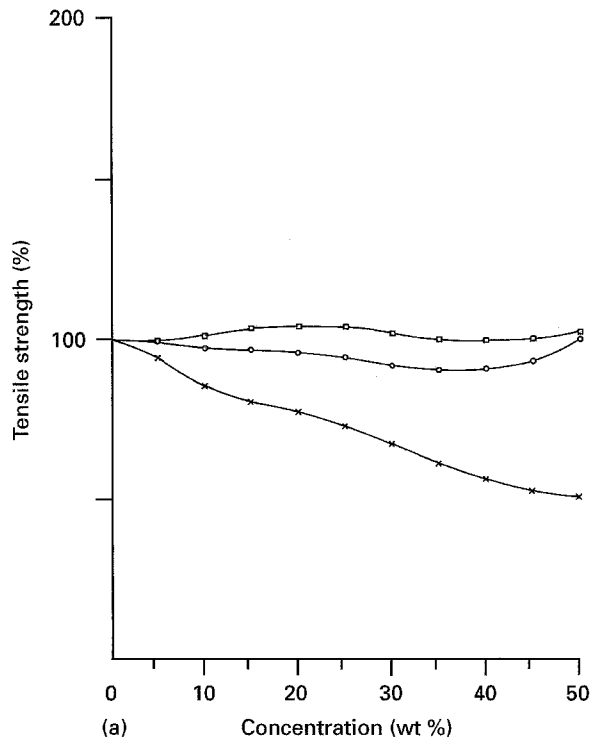
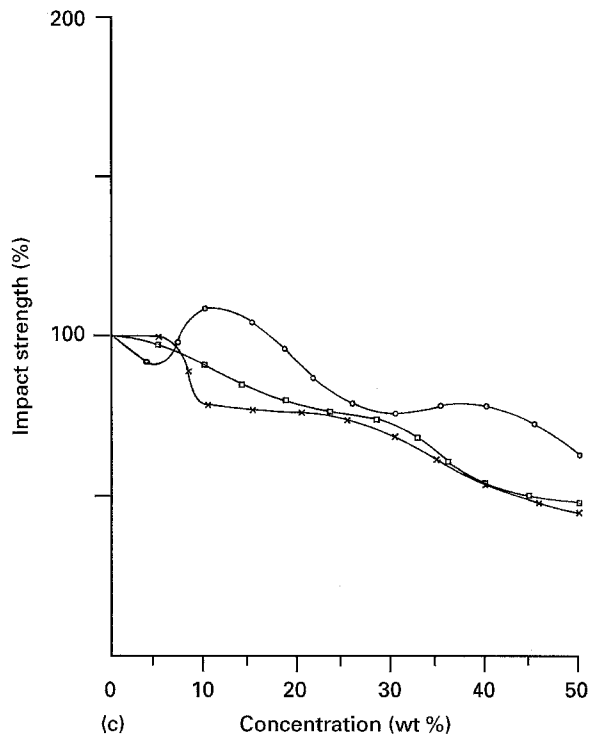


Figure 3 Effect of filler content on the mechanical properties of polypropylene: (a) tensile strength, (b) (—) flexural strength and (---) modulus, (c) impact strength. (O) Wollastonite, (□) mica, (×) glass spheres.



Tensile strengths and fracture elongations for different filler combinations are presented in Fig. 6. As can be seen in the figure, for mica/wollastonite compounds, tensile strengths remain rather constant at all filling ratios. Glass-bead filling, in turn, reduces tensile strength in all cases. A most interesting result is that mica has a stronger effect on tensile strength than wollastonite, although the particle shapes would suggest just the opposite. It is also rather odd that adding glass balls reduces the properties of wollastonite-filled compounds more than those of mica-filled compounds. One explanation would be that in this case the surface treatment used for the mineral is more effective for mica than wollastonite and glass beads.

This assumption is also supported by the fact that both wollastonite and glass beads are silicates, and the used surface treatment is not very effective for silicates.

For the deformation capacity, the results of the tensile test indicate that by far the highest fracture elongation values are reached with wollastonite-filled compounds. This value is even higher than the value for pure plastic.

The fracture elongation of a compound is affected both by the filler and by the thermal decomposition of the matrix during the compounding. In practice, the

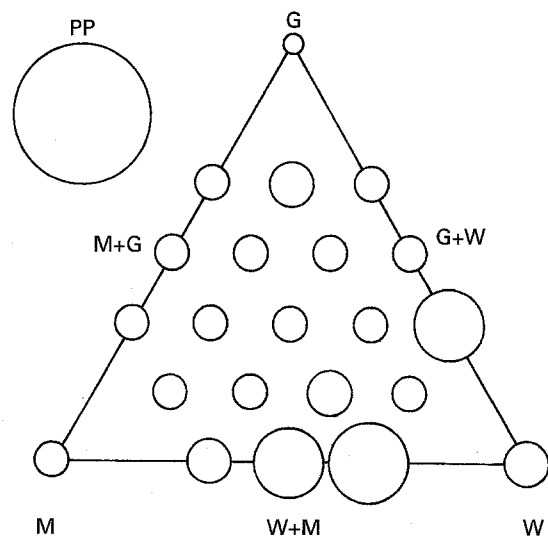


Figure 4 Impact strength of multicomponent compounded polypropylene (PP) pure (unfilled) polypropylene (mica, M; wollastonite, W; glass beads, G) at a total filler content of 30 wt %.

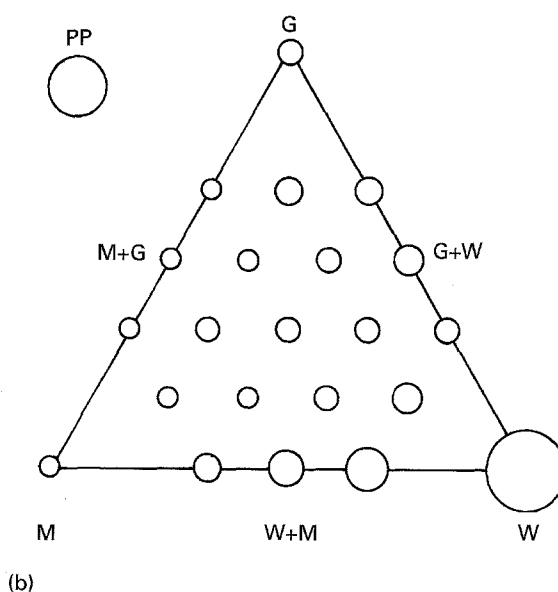
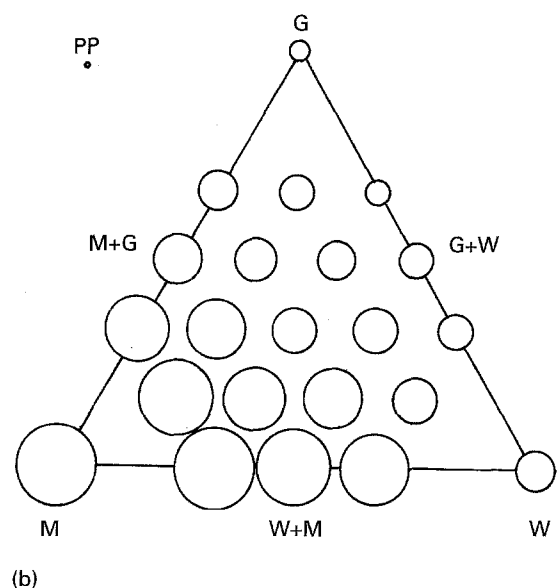
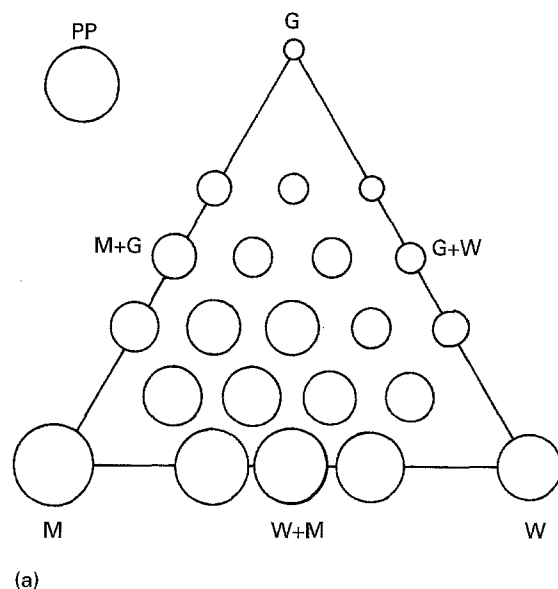
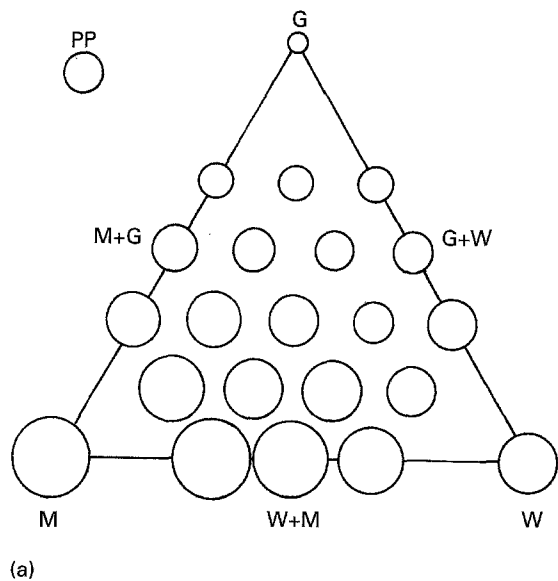


Figure 5 (a) Flexural strength and (b) flexural modulus of multi-component compounded polypropylene at a total filler content of 30 wt %. (See Fig. 4 for key.)

Figure 6 (a) Tensile strength and (b) fracture elongation of multi-component compounded polypropylene at a total filler content of 30 wt %. (See Fig. 4 for key.)

filling and the thermal decomposition of the matrix compensate the effects of each other, and separating the effects is practically impossible.

4.1. Four filler compounds

In addition to the above-mentioned compounds, some experiments were made with four filler compounds. The fourth filler was a mineral filler with a much smaller particle size and a particle shape as neutral as possible. The selected filler was a very fine-grained fraction of fly ash: a commercial filler named Mikropoz.

Fig. 8 shows the effect of the fine-grained filler on the tensile strength, fracture elongation, flexural strength, modulus and impact strength of a compound. In making the compounds the total filler content was kept constant, and the Mikropoz was used to replace part of the other fillers.

As Fig. 8 clearly shows, using the fine-grained filler has no noticeable effect on the properties of the com-

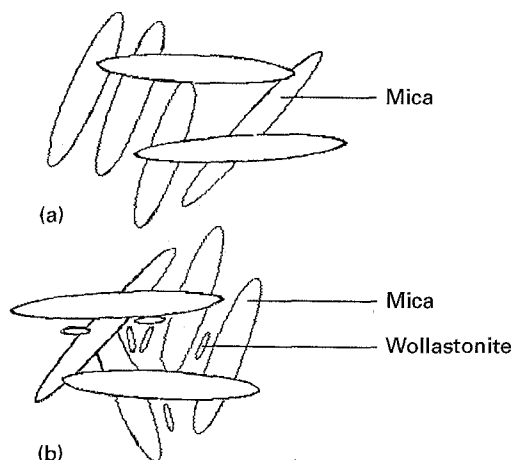


Figure 7 A diagram of the filler structures of compounds filled with (a) mica and (b) mica/wollastonite.

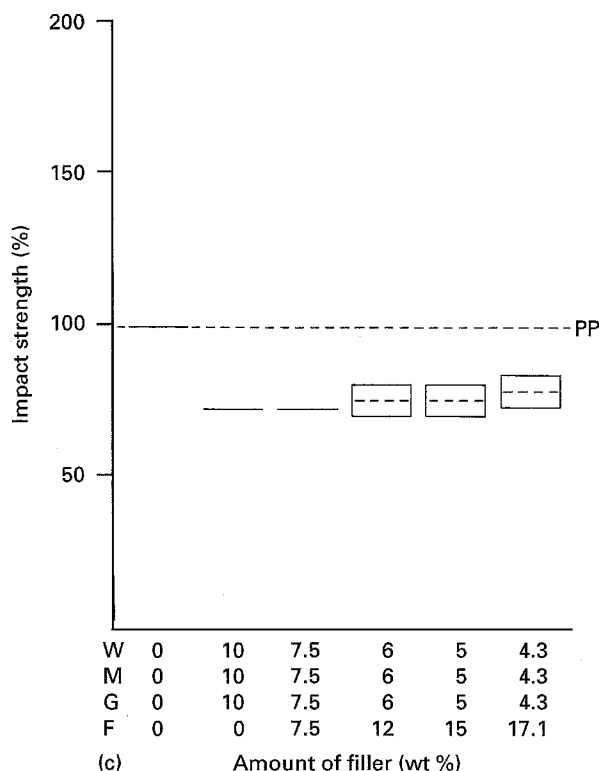
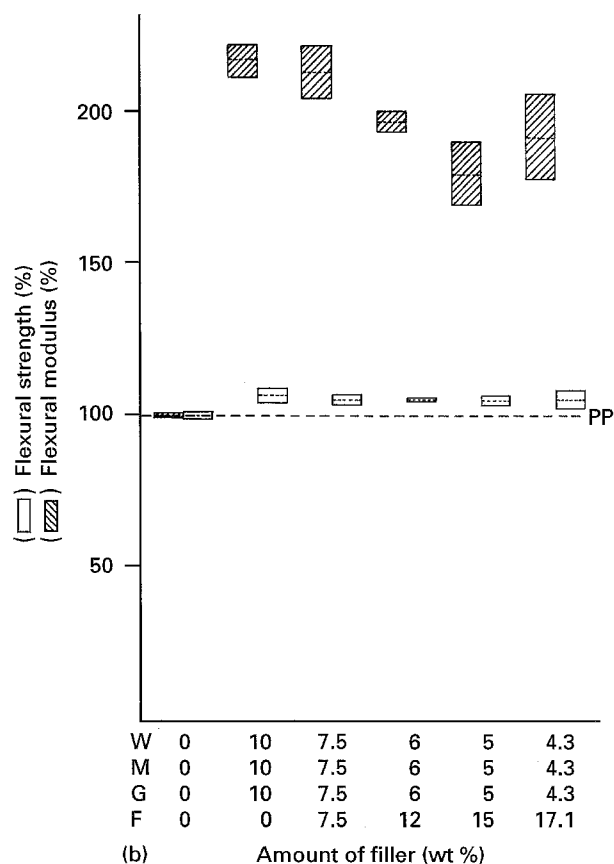
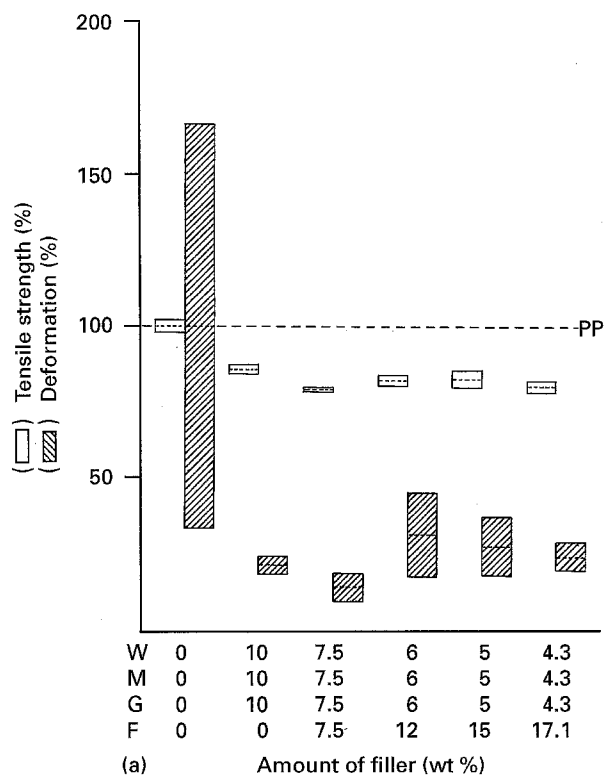


Figure 8 The effect of replacing fillers (M, mica, W, wollastonite and G, glass beads) with a fine-grained filler, F (solid glass spheres) in multicomponent compounded polypropylene, on (a) tensile strength and fracture elongation, (b) flexural strength and modulus, and (c) impact strength (PP) pure (unfilled) polypropylene.

pound. Only flexural modulus shows a clear decrease. A particularly interesting observation here is that in the light of these results, a fine-grained filler can be used to replace over half of the actual fillers without impairing the properties of the compound.

4.2. Filling empty space and the free distance of the matrix

The properties of multicomponent compounds can no longer be explained by the conventional theory of compounded plastics. The results clearly prove that combining two or more fillers yields properties that

cannot be reached by single-component compounds.

In the light of the results of this work, the following theory could be postulated. In the flow of the melt, different fillers tend to move and orientate in different ways. It is clearly evident that sheet-like and fibrous particles have the strongest orientation tendency. The effect of particle size appears in the fact that fine-grained particles are able to locate between the big particles and may even facilitate the melt flow.

Mineral filler particles form a sort of three-dimensional reinforcing skeleton in the structure, if the filler content is sufficiently high. In such compounds, one structural parameter can be the free distance of the plastic matrix. The free distance here means the diameter of the largest ball that could be placed between the mineral particles.

The effect of the free distance could be examined, for instance, as a function of the reinforcing effect as follows. The longer the free distance, the lower are the strength, modulus and durability of the compound. This phenomenon can be explained by the number of contact points: the fewer the contact points, the higher the tension in a contact point. This assumption would also explain the effect of fine-grained fillers, which greatly reduces the free distance of the matrix.

5. Conclusions

The results for single-component compounds were fully in line with existing sources. The absolute

strength properties were not directly comparable with those measured in earlier works, because the properties of mineral-filled composites depend directly on the particle size and shape of the filler (as well as their distributions), the surface treatment of minerals, the compounding and extrusion processes. In practice, sufficient evidence of the similarity of results is given by the similarities in the effects of different factors.

As regards multicomponent compounding, it can be noted that combining fillers with suitable particle shapes yields better results in the case of two- or three-component compounds than what could be obtained with single-component compounds. This was particularly evident in flexural strength, where combining a sheet-like and a fibrous filler (mica/wollastonite) yielded some astonishing results. A result of particular interest was also the effect of wollastonite in the fracture elongation of a compound: the fracture elongation of a wollastonite-filled compound was higher than that of pure plastic. It should be borne in mind that wollastonite is an exceptional filler in thermoplastics: in polyamide, for instance, it has been noted to improve strength, rigidity and impact strength at the same time.

Also worth noting is the result of adding a fine-grained filler among other fillers in a three-component compound without increasing the total filler content.

The results prove that using a fine-grained filler may considerably reduce the need of other fillers.

In the light of the results of this work, using two or more fillers in mineral-filled thermoplastics is feasible, because selecting suitable fillers and filler ratios improves the mechanical properties of the compound. In practice, this improvement can be achieved in one process, which also reduces the overall costs of the compound.

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