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The mechanical properties of chalk-filled polypropylene: a preliminary investigation

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The results are discussed of mechanical tests on chalk-filled polypropylene. This investigation had a preliminary character and was aimed at locating points of interest for further research. The effects of a variation of the particle size of the filler, the filler content and the interfacial adhesion on the properties were examined. The observed differences were explained qualitatively on the basis of a study of the microdeformations.

1. Introduction

Polypropylene (PP) is a commercially important polymer which is of practical use in a wide variety of applications [1]. Its morphology [2, 3] means that the mechanical properties of PP are moderate, so if one wants to extend the field of application of this material, an improvement of the mechanical properties is usually necessary. A relatively easy way to improve the mechanical properties of a polymer is the addition of filler materials. In general, inorganic fillers or short glass fibres are applied to improve the stiffness [4, 5], whereas the addition of a rubbery phase is favourable to the toughness of a polymer [6, 7].

In the present study the improvement of the modulus of PP, through the addition of particulate chalk, a commercial filler, was investigated. The chalk particles are very irregularly shaped, but their average aspect ratios were close to unity. The mechanical behaviour of chalk-filled PP has been investigated, both under low speed and high speed testing conditions, as a function of the size of the chalk particles, the volume fraction of the filler and the degree of adhesion between the polymer and the filler.

The preliminary character of this study, meant that the aim was not so much to explain in great depth the observed phenomena, as to locate points of interest for further research.

2. Experimental details

As matrix material a special moulding type of PP, HM6100 (Shell), was used. As filler three different types of chalk particles, with respect to their mean particle diameter, were used: Queenfil 120 (ECC), diameter 3.5 μm, Dorcal 40 (Omya), diameter 30 μm, Durcal 130 (Omya), diameter 130 μm. Pure chalk particles were applied in order to obtain a system in which the adhesion between the filler particles and the polymer matrix was very poor. Perfect adhesion between the filler and the polymer was created by treating the chalk particles with the adhesion promotor $(CH_3O)_3$ $Si(CH_2)_3$ $NH(CH_2)_2$ $NHCH_2 - C_6H_4 - CH = CH_2 \cdot HCl$, Silane Z6032 (Dow Corning) [8]. The adhesion promotor was applied in the following pretreatment.

To a suspension of 50 g chalk in 85 ml methanol, 15 ml Z6032, 1 ml water and 1 ml acidic acid was added. This mixture was stirred for 4 h, after which it was centrifuged to obtain a sediment of chalk. The sediment was washed with 85 ml methanol, centrifuged again and dried at room temperature. In this way a very thin layer of coupling agent on the particles was obtained.

The polymer and the filler were mixed on a two roll mill at 190° C. The filler content was varied in the range of 0 to 25 vol %. Tensile bars and notched Izod bars were machined from compression moulded sheets, in accordance with ASTM D638 III and D256. The tensile tests were performed on an Instron tensile tester, which was equipped with an extensometer (l_0 = 50 mm), at a strain rate of 0.02 min^{-1}. A Zwick impact tester was used to determine the Izod notched impact strength of the samples. The tests were performed in a conditioned room at 20° C and 50% relative humidity. The degree of crystallinity of PP was determined with a DuPont DSC/DTA. The effectiveness of Z6032 as a coupling agent as well as the dispersion were checked by taking micrographs of fracture surfaces with a Cambridge scanning electron microscope (SEM). Before fracture the samples were immersed in liquid nitrogen for a few minutes.

3. Results and discussion

3.1 Degree of adhesion

The micrographs of the fracture surfaces in Fig. 1 show clearly the effect of the pre-treatment with Z6032 on the interfacial adhesion between the chalk particles and PP.

It is quite obvious that pretreatment with the coupling agent causes an excellent adhesion between PP and the particles (Fig. 1b), whereas the absence of this treatment renders a system in which the adhesion is very poor (Fig. 1a).

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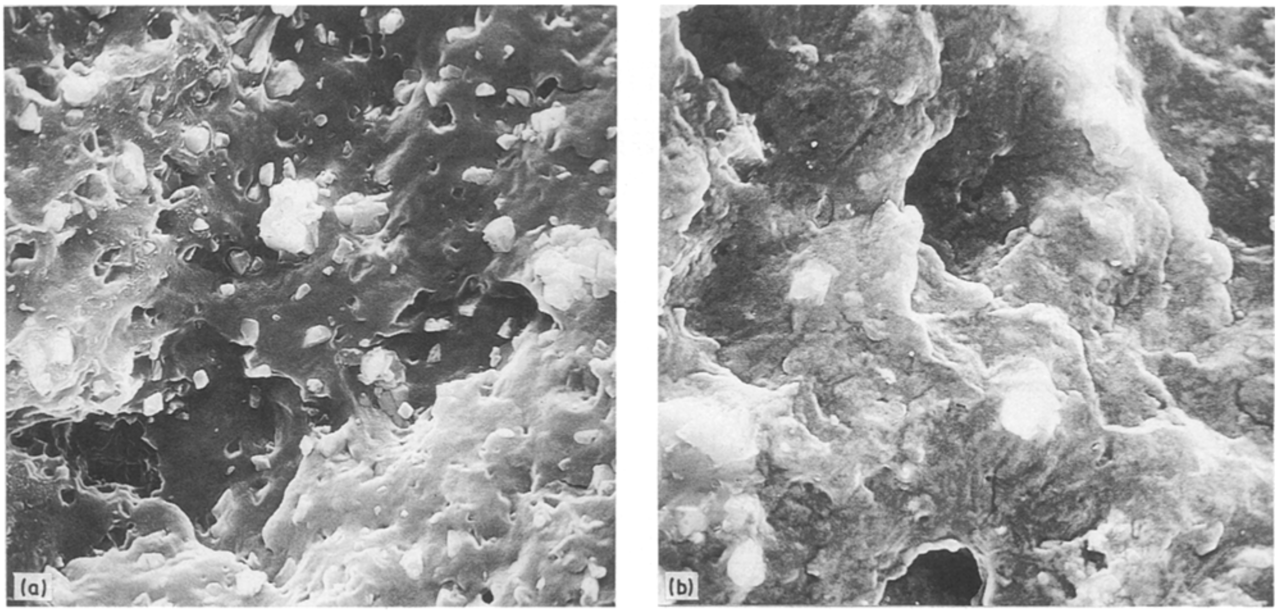


Figure 1 The fracture surfaces of PP filled with (a) pure chalk and (b) chalk treated with Z6032.

3.2. Stress–strain behaviour

There was a clear distinction between the results of the tensile tests of the composites which contain poorly adhering and excellently adhering chalk particles. Therefore these two systems are discussed separately.

3.3. Poorly adhering chalk

The stress–strain diagrams in Fig. 2 of PP filled with poorly adhering chalk reveal that the behaviour is a function of the particle size of the filler.

In the case of a poorly adhering filler, three successive stages occur during a tensile test [9–11]: linear elastic behaviour, dewetting of the filler particles and plastic deformation. It is to be expected that the second stage, dewetting, occurs as soon as the stress–strain curve deviates from the elastic line.

It is possible to apply the Griffith theory [12] to the phenomenon of dewetting. If we assume that the size of the dewetting cavity at the filler particle is proportional to the radius r of the particle, the Griffith theory predicts that the cavity is formed at a stress which obeys a formula of the form

$$\sigma_{\text{dewetting}} = Ar^{-1/2} \tag{1}$$

where A is a constant that depends on the system. Therefore this theory predicts that in the case of large particles dewetting will take place at a lower stress than in the case of small filler particles. This is in agreement with the observed stress–strain behaviour (Fig. 2).

It is noteworthy that the process of dewetting in the material filled with 3.5μm particles is initiated at about the same stress level at which it is seen that the reference PP deviates from the elastic line. From this the preliminary conclusion could be drawn that in case of still smaller filler particles dewetting does not occur, as in that case the plastic deformation processes are

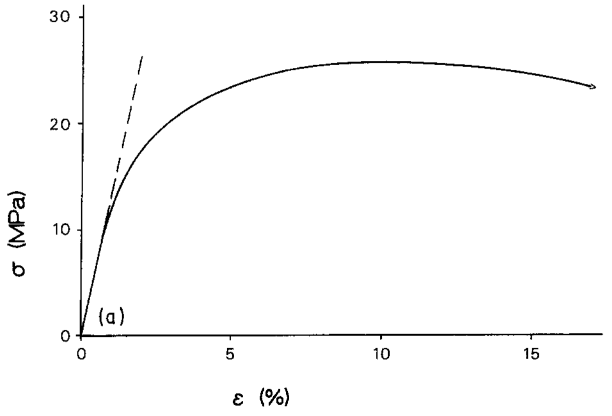
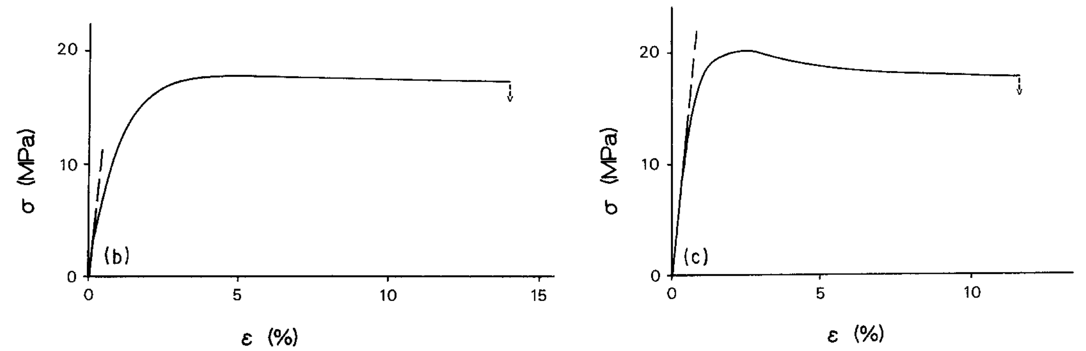


Figure 2 Stress–strain diagrams of (a) pure PP, (b) PP filled with 20 vol % of poorly adhering 130 μm chalk particles and (c) PP filled with 20 vol % of poorly adhering 3.5 μm chalk particles. Fracture is indicated by a vertical arrow.



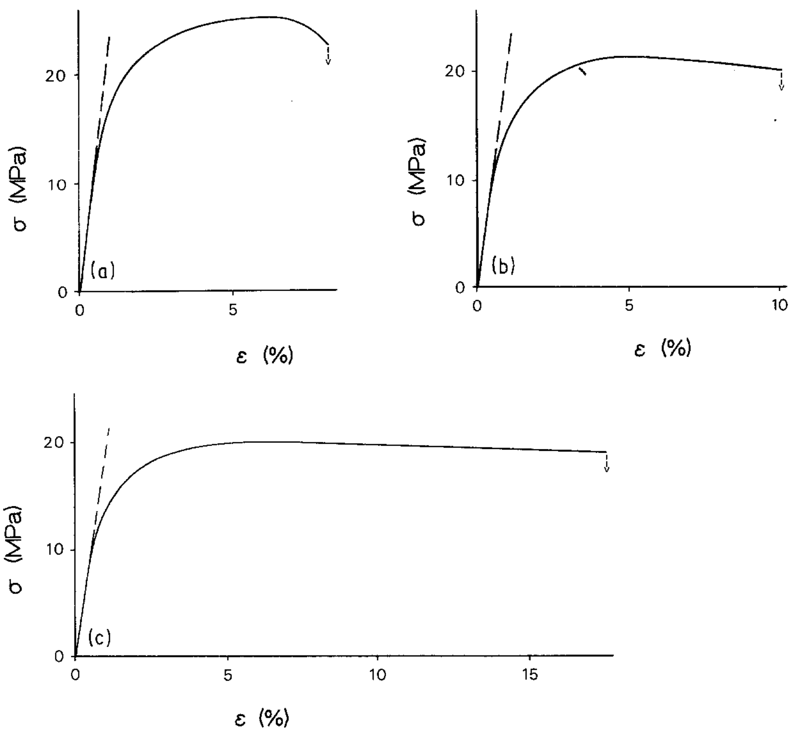


Figure 3 Stress–strain diagrams of PP filled with 15 vol % of excellently adhering (a) 3.5 μm, (b) 30 μm and (c) 130 μm chalk particles. Fracture is indicated by a vertical arrow.

initiated at a lower stress than dewetting and become responsible for the bending off of the curves.

As the used chalk particles have a very broad particle size distribution, it is not justified to apply Equation 1 quantitatively. For this reason further research is necessary with filler materials that have a narrow particle size distribution (e.g. glass spheres), so that final conclusions can be drawn on the applicability of a Griffith-like theory.

At the applied strain rate, a material like PP usually displays necking from a strain of about 20%. As can be seen from Fig. 2, in the case of the filled polymer the materials break before a strain of 20% is reached and therefore necking does not occur. This will be discussed in more detail in a following section.

3.4. Excellently adhering chalk

In Fig. 3 the stress–strain diagrams of PP filled with excellently adhering chalk are shown as a function of the particle size of the filler. It can be seen that the deviation from the elastic line for all three stress–strain curves takes place at about the same stress level. At this point the local plastic deformation processes and the diffuse shearing as in pure PP are initiated. As a result of the stress concentration at the chalk particles, the local processes will start at the particle–matrix interface.

According to Goodier [13] the stress concentration at a spherical filler particle is independent of the radius of that particle. As a first approximation the chalk particles can be considered to be spherical. Therefore the stress at which the plastic deformation is initiated should be independent of the size of the chalk particles. This is in agreement with the experimental results.

From Figs 3 and 4 it can be concluded that the yield stress depends on the chalk concentration and on the particle size. The yield stress is defined here as the maximum in the σ–ε diagram. From Fig. 4 it appears that the yield stress of PP filled with adhering particles is always lower than for pure PP.

This can be explained as follows. The strain e of a material during a tensile test can be divided into the strains caused by the different microdeformation processes: elastic deformation (e_{el}), local microdeformation (e_{loc}) and diffuse microdeformation (e_{diff}). Crazes and shear bands are considered as local microdeformations, whereas the process of diffuse shearing in PP, which occurs in the bulk of the matrix in relatively large volume elements, is a typical example of a diffuse microdeformation process. As a first approximation the total strain e can be assumed to consist of a series connection of the three strains [14]

$$e = e_{\mathrm{el}} + e_{\mathrm{loc}} + e_{\mathrm{diff}} \qquad (2)$$

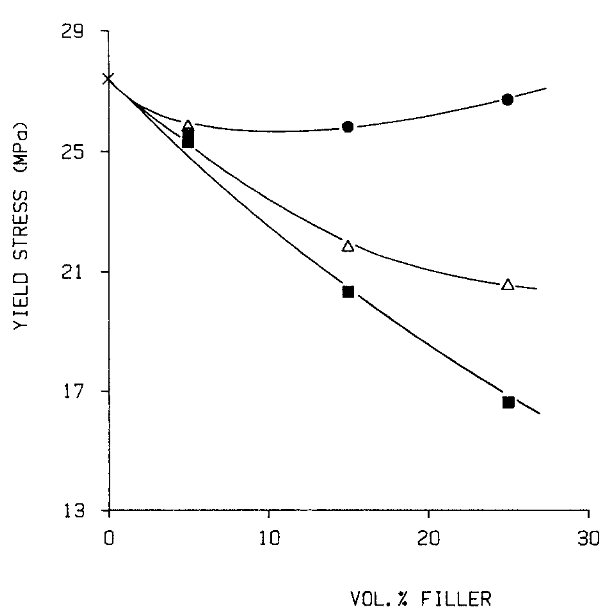


Figure 4 The yield stress as a function of the volume fraction of the filler for 3.5 μm (●), 30 μm (△) and 130 μm (■) chalk particles.

The amount of strain caused by the microdeformation processes is of course a function of the applied stress and the deformation time. Moreover, the presence of local microdeformations has an effect on the propagation of the diffuse microdeformation process. Therefore, Equation 2 can be rewritten as

$$e = \sigma/E + e_{\text{loc}}(\sigma, t) + e_{\text{diff}}(\sigma, t, e_{\text{loc}}) \quad (3)$$

$$\sigma = E[e - e_{\text{loc}}(\sigma, t) - e_{\text{diff}}(\sigma, t, e_{\text{loc}})] \quad (4)$$

In Fig. 4 it can be observed that for 130 μm particles the yield stress decreases with the particle concentration. This must be due to the large increase of local microdeformation around the particles, the effect of which is represented by the second term in brackets in Equation 4. The third term, representing the affect of diffuse shear will decrease somewhat at increasing concentration as the amount of polymer decreases in that direction. So the increase of the local deformation term surpasses the decrease of the diffuse shear term.

The decrease of the yield stress with concentration, however, is much less for 30 μm particles and zero for 3.5 μm particles. As still local deformation takes place around the particles, the effect of which can be taken as proportional to the volume concentration, this result must be due to a strong decrease of diffuse shear. The explanation must be that the diffuse shear is progressively hampered by the local microdeformations at decreasing particle diameters.

The hampering can be understood as shear bands or crazes formed in an earlier stage of the stress strain tests at lower applied stress, as they will be initiated at sites of stress concentrations at the particle surfaces. The hampering effect will be proportional to the surface area of the crazes or shear bands. Assuming that the area of a craze or shear band is proportional to the area of the filler particle, a "blocking area" (BA) can be introduced

$$\text{BA} = C_1 n r^2 \quad (5)$$

where C_1 is a constant and n the number of filler particles with a radius r. Combination of Equation 5 with Equation 6

$$n = C_2 \phi / r^3 \quad (6)$$

where ϕ is the volume fraction of the filler and C_2 is a constant, gives

$$\text{BA} = C_3 / r \quad (7)$$

C_3 is a constant.

According to Equation 7 the blocking area is inversely proportional to the filler particle size, which supports the above mentioned explanation.

3.5. Necking in chalk-filled PP

From experiments it appears that the strain at which necking is initiated in chalk-filled PP, depends on the volume fraction chalk. As larger volume fractions of chalk are applied, the strain at which necking occurs increases, until at about 10 to 20 vol % filler necking even no longer takes place at all (see Table I).

This can be explained as follows. Necking is a process of shearing (bulk flow) that spans the whole cross-section of a tensile bar. As said before, in the case of a filled polymer, the filler particles act as stress concentrators and therefore the local microdeformation processes shear band formation and/or crazing take place at these filler particles at rather low applied stresses.

TABLE I Strain at which necking is initiated or fracture occurs (indicated as fr.) in chalk-filled PP.

Vol % filler	Poor adhesion		Excellent adhesion	
	Filler particle size		Filler particle size	
	3.5 μm	130 μm	3.5 μm	130 μm
0	20%		20%	
5	23%	21%	23%	22%
15	fr. 16%	fr. 23%	fr. 9%	fr. 18%

These microdeformation processes are initiated throughout the whole tensile bar and disturb the diffuse process of necking in the way discussed before. This makes necking impossible in more highly filled polymers.

3.6. Young's modulus

The Young's modulus of a composite, consisting of a matrix material and a dispersed phase that are both structureless (continuous), is independent of the dimension of the dispersed phase. The local stresses in the composite under load are only dependent on the ratio of the distance between particles of the dispersed phase to the dimension of these particles. At a certain volume fraction of dispersed phase, this ratio is constant and therefore independent of the dimension of the dispersed phase.

Kerner [17] has derived an equation, which has been modified for the maximum packing density of spheres by Nielsen and Lewis [18], that describes the Young's modulus of particulate filled polymers quite accurately. In this equation the Young's modulus is of course independent of the particle size of the filler.

In Fig. 5 the experimental Young's moduli of PP filled with excellently adhering chalk and poorly adhering chalk are plotted as a function of the volume fraction filler.

The Young's moduli of PP filled with excellently adhering chalk particles fit the modified Kerner equation very satisfactorily. The data needed for the calculations are listed in Table II.

Surprisingly, the Young's moduli of PP filled with poorly adhering chalk particles appeared to be dependent on the particle size of the filler. In the case of the 30 μm chalk particles the modulus is in accordance with the predictions according to the Kerner equation, but the 3.5 μm chalk particles cause higher and the 130 μm chalk particles lower Young's moduli. Because

TABLE II Data used for the calculations according to the modified Kerner equation

	Young's modulus (MPa)	Poisson's ratio
PP	1560	0.42
Chalk	35000	0.20

Maximum packing density $\phi_m = 0.64$

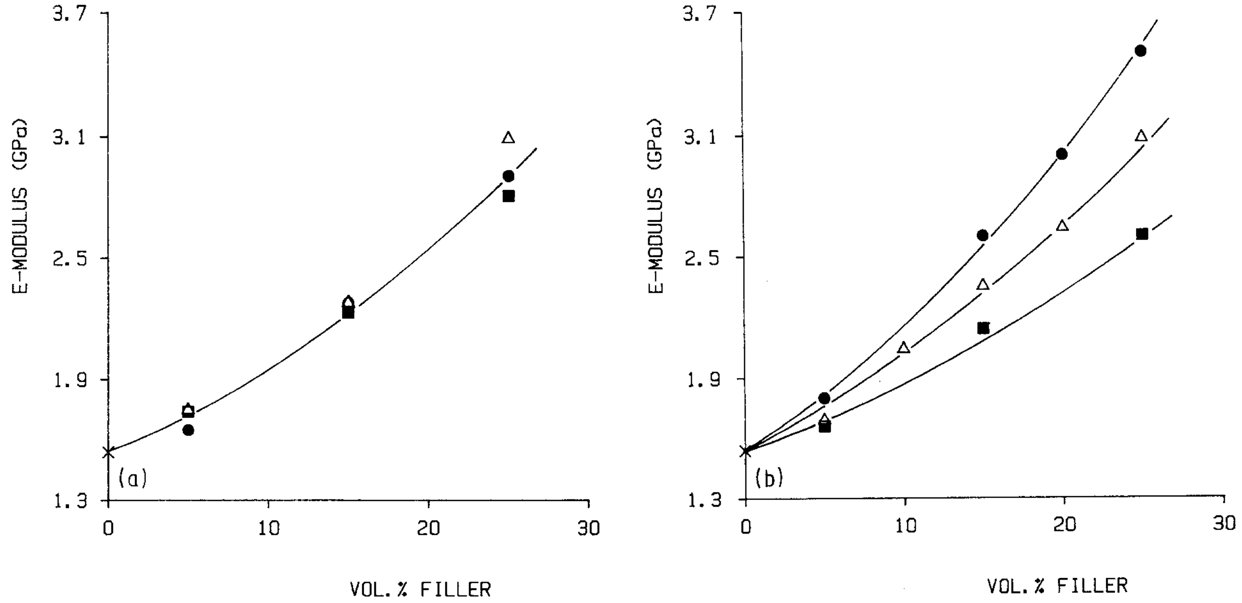


Figure 5 The Young's modulus of PP filled with (a) excellently and (b) poorly adhering chalk particles as a function of the volume fraction of the filler for 3.5 μm (●), 30 μm (△) and 130 μm (■) chalk particles. In (a) the curve is calculated with the Kerner equation.

of the semi-crystalline character of PP it was investigated whether the morphology and/or the crystallinity of the PP-matrix was affected by the presence of the chalk particles. With DSC the degree of crystallinity was determined of filled PP as a function of the volume fraction of 3.5 μm and 130 μm chalk particles. In Fig. 6 the results are shown.

Within the range of experimental error, the degree of crystallinity appeared to be independent of particle size and volume fraction of the filler, and equal to that of pure PP. So the particle size dependence of the Young's modulus is obviously not caused by differences in the degree of crystallinity as such.

Another explanation is that a certain layer of PP at a filler particle, e.g. the first row of spherulites, acts as an interphase. If the size of this interphase is small enough, say about 1 μm, its Young's modulus can be assumed to have a value between those of PP and chalk. If the thickness of the interphase is assumed to hardly depend on the size of the filler particles, the amount of interphase along with the Young's modulus of the material in its entirety, would increase with decreasing particle size.

The application of an oxygen–plasma etching technique made it possible to study the size of the spherulites of PP filled with 3.5 μm chalk particles with the SEM. The introduction of chalk particles in PP causes a considerable drop in the size of the spherulites (Fig. 6), but the particles always appeared to be much smaller than the spherulites, which is in contradiction with the assumption of an interphase.

It is therefore not clear whether, and how, the size of the spherulites plays a part in the explanation of the particle size dependence of the Young's modulus. Further research is necessary, e.g. with an amorphous polymer as a matrix material, to answer the question if the particle size dependence is caused by the semi-crystalline character of PP.

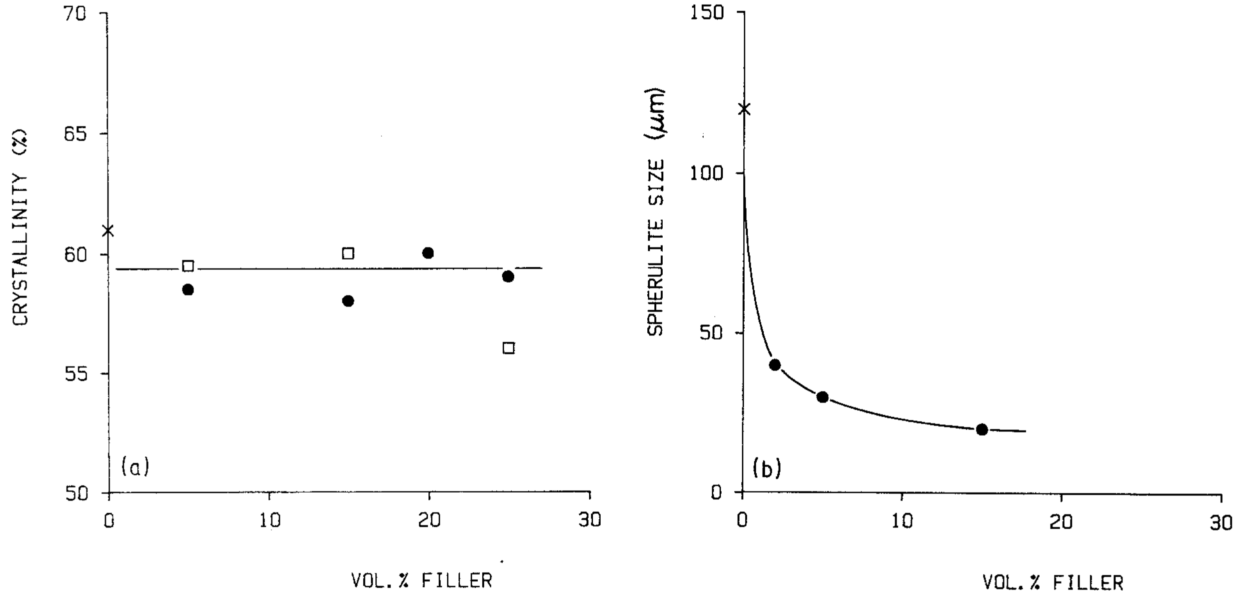


Figure 6 (a) The crystallinity and (b) the size of the spherulites of PP as a function of the volume fraction of the filler for 3.5 μm (●) and 130 μm (□) chalk particles.

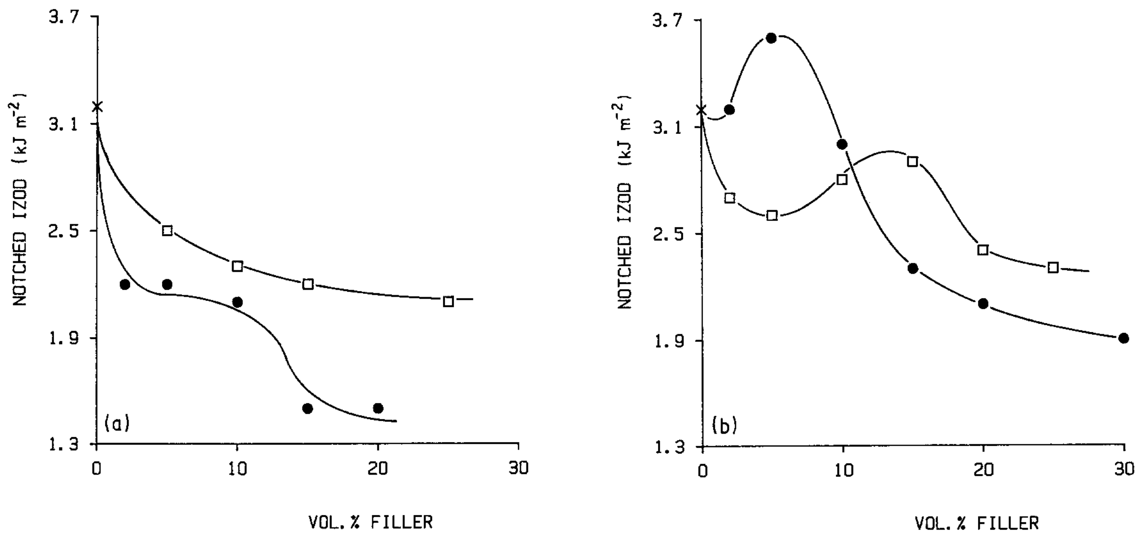


Figure 7 The notched Izod impact strength of PP filled with (a) excellently and (b) poorly adhering chalk particles as a function of the volume fraction of the filler for 3.5 μm (●) and 130 μm (□) chalk particles.

3.7. Notched Izod impact strength

The results of the impact tests of PP filled with poorly adhering and excellently adhering chalk particles are presented in Fig. 7. In the case of perfect adhesion an increasing amount of filler results in a decreasing impact strength, whereas in the case of poor adhesion a maximum in the impact strength is observed at a certain volume fraction of the filler. The location of this maximum depends on the particle size of the filler.

The difference in behaviour of PP filled with excellently and poorly adhering chalk has to be explained with a fundamental difference in deformation behaviour. Very special equipment is needed to observe the deformation mechanisms during an Izod impact test. Unfortunately those facilities were not available. Instead, the deformation mechanisms were studied under a light microscope during a (slow) tensile test.

At this point it should be admitted that it is possible that the deformation behaviour depends on the speed of testing. Therefore, the explanations based on this study have to be considered as preliminary, and a study of the deformation mechanisms at high speed should eventually lead to final conclusions.

The microscopic study showed that at perfectly adhering chalk particles exclusively crazes are created. This could explain its decreasing affect on the impact strength.

By increasing the amount of perfect adhering chalk the "tough" deformation mechanism shearing of PP is increasingly replaced by the "brittle" mechanism crazing (see Fig. 8a), in the same way as discussed in Section 3.2.

During a tensile test excessive cavitation takes place at poorly adhering chalk particles (Fig. 8b), which involves shearing processes in the PP at these spots. Therefore, when PP is filled with poorly adhering chalk particles the "tough" deformation process of diffuse shearing is partially replaced by another "tough" mechanism, the formation of local shear bands. It is possible that these two "tough"

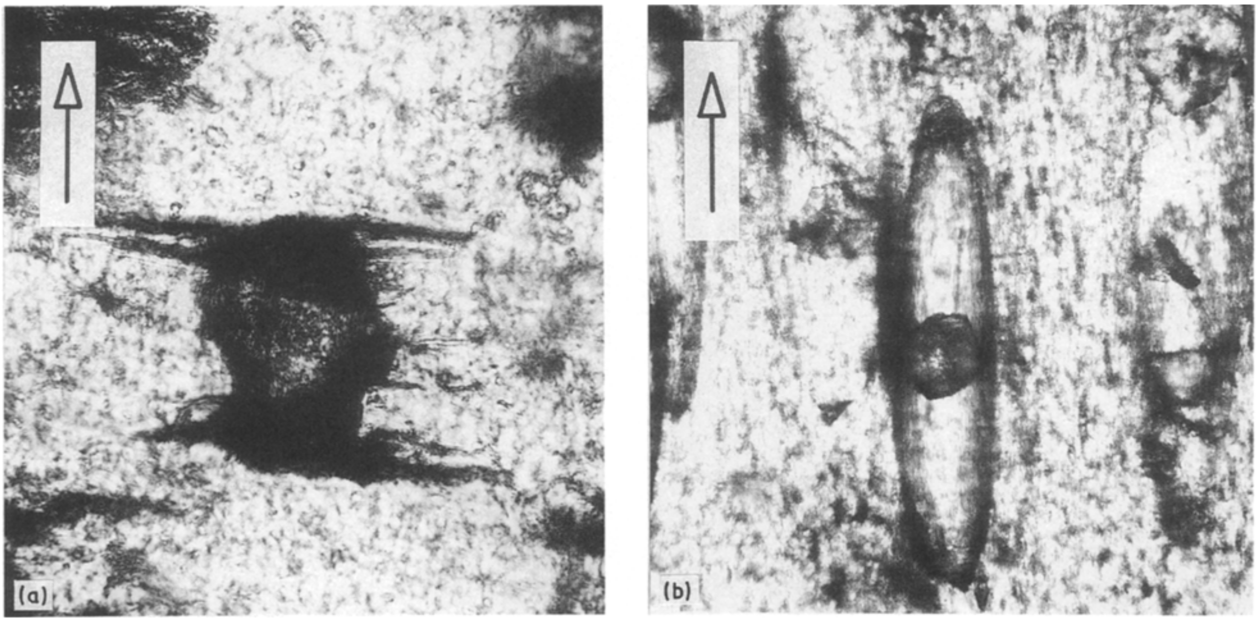


Figure 8 Crazes formed at (a) an excellently adhering chalk particle and (b) cavitation at a poorly adhering chalk particle, both in a PP-matrix. The arrow indicates the direction of the applied stress.

deformation mechanisms create a maximum in the impact strength at a certain combination.

In Fig. 7 it can be seen that the location of this maximum depends on the particle size of the filler. In the same way as discussed in the explanation of the particle size dependence of the yield stress, this may be due to an increasing hampering of the diffuse processes in the case of smaller filler particles.

Again we should make it very clear that a study of the deformation mechanisms at high speed, or at low temperature testing is necessary to confirm the above explanation.

4. Conclusions

The stress at which dewetting takes place in PP filled with poorly adhering chalk particles can probably be described by a Griffith-like theory. Further research, applying fillers with a narrow particle size distribution, is necessary to confirm this conclusion.

The increase of the yield stress with decreasing particle size can be explained by the hampering of the diffuse shear processes by the presence of a large amount of shear bands and crazes at the filler particles. The fact that necking no longer occurs in PP filled with more than 10 to 20 vol % of chalk can be accounted for in a similar way.

The modified Kerner equation provides a satisfactory description of the Young's modulus of PP filled with excellently adhering chalk particles. However, the Young's modulus of PP filled with poorly adhering chalk particles appears to exhibit a particle size dependence. The explanation for this behaviour is still unknown.

The notched Izod impact strength of PP filled with poorly adhering chalk is higher than that of PP filled with excellently adhering chalk. In the former case there even appears to be a maximum in the impact strength that depends on the particle size of the filler. This maximum may be due to a favourable combination of two shearing processes: diffuse shearing and the formation of shear bands. Therefore it also appears useful to investigate the deformation behaviour, which eventually may lead to the optimal properties of filled polymers as a function of the particle size of the filler.

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