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

P. H. TH. VOLLENBERG, D. HEIKENS
Laboratory of Polymer Technology, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

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: Queenfill 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 promoter (CH₃O)₃ Si(CH₂)₃ NH(CH₂)₂ NHCH₂ – C₂H₂ – CH = CH₂ · HCl, Silane Z6032 (Dow Corning) [8]. The adhesion promoter 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 (l₀ = 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).
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

\[
\sigma_{\text{dewetting}} = A r^{-1/2}
\]

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 3.5\( \mu \)m 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