Influence of the filler particle shape on the elastic moduli of PP/CaCO₃ and PP/Mg(OH)₂ composites

Part 2 Enhanced interfacial adhesion

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The effects of enhancing the interfacial adhesion between fillers and PP matrix on the Young's and shear moduli were observed within wide concentration intervals of both filler and adhesive agent. Calcium carbonate and magnesium hydroxide were used as-received and/or with the surface hydrophobized by the long-chain fatty acids. A copolymer of polypropylene and maleic anhydride containing about 1 wt/wt% of grafted maleic anhydride was used for the interface modification. The analysis, based on the classical models, showed the necessity of their simple modification considering the increase in the amount of immobilized matrix with enhancing interfacial adhesion. Maleated polypropylene influenced both the matrix-filler interface and matrix bulk due to the interactions of carboxyl groups with basic centres on the filler surface or on the impurities in the matrix bulk. The greater extent of the immobilized matrix on the filler surface caused the creation of the particles hyperstructure at a lower Mg(OH)₂ content than in systems with "zero" adhesion.

1. Introduction

One possible means of long-term improvement of strength and creep of particulate composites is the enhancement of the filler-matrix adhesion, particularly at higher temperatures. The internal thermally induced stresses existing in composites with rigid particulate fillers are the consequence of the different coefficients of the thermal expansion of the filler and matrix [1]. As the simply calculated values of these stresses on the particular surface are about 10 MPa in PP/CaCO₃ composites, the commonly used assumption about perfect adhesion in the low deformation region is valid [2]. No published information exists dealing with the determination of the concentration region within which this presumption is valid. Very probably, the presumption of perfect interfacial adhesion looses its validity with increasing filler volume fraction due to the formation of voids and other interfacial defects [3].

Some papers dealing with the effects of adhesion on the elastic moduli of PP/CaCO₃ composites have been published, but no structural explanation of these effects has been proposed, if the adhesive agent has the same chemical nature as the matrix [4].

Considering the arguments put forward above, the objective of our study was: (i) to establish the influence of the interfacial adhesion on the viscoelastic response of the PP/CaCO₃ and PP/Mg(OH)₂ composites with different particle shapes, and (ii) to investigate the applicability of existing classical models for the blends studied.

2. Experimental details

Commercial polypropylene (PP) Mosten 58.412 (Chemopetrol, Czechoslovakia), melt index 4 g/10 min (230°C, 21.6 N), was used as a matrix. Maleated PP containing 1 wt/wt% grafted MA was used as an adhesive agent. PP and maleated PP (MPP) were mixed in various ratios to achieve the required concentrations of carboxyl groups in the matrix.

Calcium carbonate Durcal 2 (Omya, Switzerland), magnesiu hydroxide Kisuma 5B, Kisuma 7B (Kyowa, Japan) and Reachim (USSR) were used as fillers. Their characteristics are listed in Table I. CaCO₃ was used as-received and also surface treated with 0.3 wt/wt % stearic acid and 0.5 wt/wt % calcium stearate. Mg(OH)₂ was also used both as-received and surface treated with 2 wt/wt % oleic acid by the producers. Particles of Kisuma 5B and Reachim had the form of hexagonal plates and Kisuma 7B had needle-shaped particles.

The components were compounded in the Brabender PLE 651 plastocorder at 200°C, 50 r.p.m. for 10 min. The plaques, 1 mm thick, were compression moulded out of compounded materials at 210°C. The specimens cut from the plaques were annealed at 114°C for 1.5 h and then cooled at the rate of 5°C min⁻¹. Measurements were carried out on the PL.
DMTA and free oscillating torsion pendulum at 23°C, 1 Hz.

3. Results and discussion

3.1. Composites with the constant filler content

3.1.1. Introductory notes

Only the Sato–Furukawa model [5] exists for the analysis of the dependence of elastic moduli on the strength of interfacial adhesion. Unfortunately, this model was derived for the case of reinforced rubbers and therefore derivation conditions do not allow use of this model for PP/CaCO₃ composites. For this reason the modified Kerner–Nielsen equation [6] must be used

\[
\frac{M_e}{M_m} = \frac{1 + AB\psi v_f}{1 - B\psi v_f}
\]

(1)

considering the modifying function \(\psi\) in the form

\[
\psi = 1 + \frac{1 - \frac{v_f^{max}}{(\psi v_f)^2}}{v_f^{max}}
\]

(2)

where \(A\) and \(B\) are constants, \(M_e\) and \(M_m\) are, respectively, the composite or matrix moduli, \(v_f\) is an apparent filler volume fraction taking into account interfacial interactions, and \(v_f^{max}\) is the maximum apparent filler volume fraction [7]. For the PP/CaCO₃ composites, \(A = 1.17\), \(B = 0.956\) for the Youngs modulus and 0.961 for the shear modulus. The apparent filler volume fraction can be defined in the form [8]

\[
v_f = (1 + b) v_t
\]

(3)

where \(b\) is the “degree” of matrix immobilization. This means the product \((bv_t)\) is \(v_t\) is the immobilized matrix volume fraction. Two simplifying conditions were proposed: (i) the equality between the filler and immobilized matrix moduli, and (ii) the possibility of reaching the value \(v_f^{max} = 1\) at which all remaining matrix is immobilized. Hence

\[
v_f^{max} = v_f^{max} + v_t = 1
\]

(4)

where \(v_f^{max}\) is the maximum volume fraction of the filler depending only on the filler shape and its space packing [6]. As no evidence exists for the dependence of the interlayer thickness (on the filler surface) on the filler volume fraction, the increasing of the composite moduli with the strength of adhesion can be attributed to the “effective thickness” of the interlayer increasing. In the simplest manner (no agglomerates), the effect of the enhancement of the interfacial adhesion is comprised of the change of the interlayer effective thickness, \(t_{eff}\) [9]

\[
t_{eff} = \frac{b}{S_f \psi t}
\]

(5)

where \(S_f\) is the specific surface area of the filler, and \(\psi t\) is its density.

By analogy, we modified the Halpin–Tsai equation introducing the apparent filler volume fraction \(v_{fa}\) [6]

\[
\frac{M_{1,T}}{M_m} = \frac{1 + A_{L,T} B_{L,T} v_{fa}}{1 - B_{L,T} v_{fa}}
\]

(6)

and considering real values of Mg(OH)₂ particle average aspect ratio, \(p^*\). In Equation 6, \(A\) and \(B\) are constants depending on the modulus measurement pattern, shape of the particles, their orientation and inherent properties of the composite components. We supposed that the mechanical destruction of the filler particles did not depend on the amount of maleated PP (MPP) and that the average aspect ratio did not change significantly with increasing interlayer thickness. Considering the simplifications put forward above, the effects of the interfacial adhesion can be considered in the same way as in the PP/CaCO₃ composites. The simple Tsai approximation [6] was used for calculation of the modulus, \(M_e\) of composites with randomly oriented particles from transversal, \(M_t\), and longitudinal, \(M_l\), values of composites with unidirectionally aligned filler particles

\[
M = \frac{1}{3} M_t + \frac{5}{6} M_l
\]

(7)

3.1.2. Unfilled polypropylene modified with maleated PP

The increase in \(E'\) and \(G'\) moduli of unfilled PP with the MPP volume fraction, \(v_{MP}\) = 0.4 (Fig. 1) can be explained from the composite point of view. PP can be considered as a composite with an amorphous “matrix” and crystalline “filler” in this model [10]. In

<table>
<thead>
<tr>
<th>Chemical nature</th>
<th>Grade</th>
<th>Specific area (m²/g)</th>
<th>Density (g/cm³)</th>
<th>Young's modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>Average aspect ratio, (\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>Durcal 2</td>
<td>3.3</td>
<td>2.71</td>
<td>72</td>
<td>28</td>
<td>irregular approximately spherical (\beta \approx 1)</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>Kisuma 5B</td>
<td>7</td>
<td>2.36</td>
<td>64*</td>
<td>25*</td>
<td>hexagonal lamellae (\beta \approx 5)</td>
</tr>
<tr>
<td></td>
<td>Reachim</td>
<td>6.8</td>
<td>2.36</td>
<td>64</td>
<td>25</td>
<td>hexagonal lamellae (\beta \approx 5)</td>
</tr>
<tr>
<td></td>
<td>Kisuma 7B</td>
<td>37</td>
<td>2.36</td>
<td>64</td>
<td>25</td>
<td>needles (\beta \approx 25)</td>
</tr>
</tbody>
</table>

*The values \(E\) and \(G\) moduli of Mg(OH)₂ were estimated from the relation between elastic moduli and hardness of materials.