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Electron spin resonance investigation of filler orientation in compression and injection molded polypropylene based composites

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Summary

Electron Spin Resonance (ESR) spectroscopy was applied for monitoring the orientation and distribution of filler particles in polymer composites by measuring the magnetic anisotropy of naturally occuring Mn(II) centers in $CaCO_3$ and in talc. The amplitude ratio of characteristic ESR bands gives the order parameter. The orientation of the particles changes as a function of composition, depends on processing technology, the type of molding (injection *vs* compression molding) and has a specific spatial distribution in the cross-section of the injection molded specimen. Correlation is found between average orientation of anisotropic particles and the mechanical properties of various composites.

Introduction

The filler content of polymer composites strongly influences mechanical properties, such as deformation or failure of tensile specimens (1-3). This effect can be explained either by the nucleation when the particulate filler modifies the crystallinity of polymer matrix (4-6), or the orientation of anisotropic particles that can be rather substantial if the aspect ratio, that is the ratio of maximum and minimum dimension of crystallites, is large (7-9). In order to clarify the importance of these factors, the properties of talc- and $CaCO_3$- containing composites were compared. The former particle has a large aspect ratio, the ratio of maximum and minimum dimension of platelets is around 20-30, while the same parameter is not larger than 2 for the calcite particles. In polypropylene (PP)- based composites a rather poor correlation was found for the deformation and failure data with the amount of polymer crystallinity measured by DSC, suggesting only a minor role of nucleation (10). In other words, it is the orientation of particulate fillers that should play a decisive role. The particle orientation can also be investigated by scanning electron microscopy. The electron spin resonance (ESR) technique, however, can offer a more straightforward way to obtain quantitative data for orientation (11). Since ESR can detect only paramagnetic materials, the polymer matrix and the pure filler cannot produce signals. However, some impurity centers in the crystalites, *e.g.* the Mn(II) ions substituting Mg(II) in talc or Ca(II) in $CaCO_3$, can be easily studied irrespective of the complexity of heterogeneous composite structure. By making use of the ESR-determined orientation data, we established that the interaction between the polymer chain and the filler is strongly different in different matrices, like polystyrene (PSt), PP, polyethylene (PE) and polyvinylchloride (PVC) (11).

The next important factor to be considered is the shape of filler particles. We compare the properties of composite filled with calcite or talc, where the former has a small and the latter a very large aspect ratio, respectively. The interaction of polymer and filler producing the particle orientation can also influence the deformation and failure properties. This phenomenon can be studied by analysing the correlation between mechanical properties and filler orientation as a function of composition (the proportion of filler in the composite). In order to understand the reason why the stress and tensile strengths are so different for specimens produced by compression molding and injection molding, we compare the orientational effect on flow patterns emerging in the composites processed by the above techniques.

ESR spectroscopy can also be used to derive spatial distribution of orientations. We determine the particulate orientation within the cross-section of tensile specimen that gives an imprint of flow pattern in the process of injection molding.

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Results and discussion

The main concept of orientation analysis of ESR spectra was formulated in our earlier papers (11,12). Here we define only the main features. The paramagnetic ions, such as Mn^{2+} in crystals produce anisotropic signals. This means that the resonance position of a single crystal depends on the orientation of crystallographic axis with respect to the magnetic field. The Mn^{2+} ions have an S=5/2 ground state; resonance can be detected between the magnetic states with the selection rule $\Delta M=1$. In non- or weakly- oriented powders, the highly orientation-dependent transitions could not be detected and only the central (1/2,-1/2) resonance line can be seen, where the zero-field term gives no contribution up to the second order approximation. Since the ^{55}Mn nucleus has I=5/2, this central transition splits into a six-line hyperfine pattern. Each line in this pattern shows some orientation dependence due to the high order terms of the zero-field interaction. This angular dependence gives an extra structure of the hyperfine line in powder samples, where typically three main features can be distinguished: the parallel, the perpendicular and the 45^0 bands. Here we speak about a parallel resonance if the magnetic field is aligned parallel with the symmetry axis of magnetic interactions. This is not necessarily identical with the crystallographic axis, but in our case the magnetic symmetry axis agrees with the *c*-direction. The separation of above mentioned bands is different in each line of the hyperfine multiplet. In our previous work (11) we have found the best separation in $CaCO_3$ for the fourth line, while in talc the first hyperfine line presents the best separation, Thus, in the forthcoming analysis the orientation dependence of this band will be investigated (Figure 1).

Let us introduce a partial orientation, *e.g.* increase the amount of crystallites having the *c*-axis parallel with the field. In this case the amplitude of the parallel band increases, while that of the perpendicular band decreases. Thus, the intensity ratio of parallel and perpendicular bands can characterize the orientation: if it is large compared to the value measured in a non-oriented sample, the particles are oriented along a direction where the *c*-axis is parallel with the magnetic field; if it is diminished, a perpendicular orientation occurs. We will denote by parameter R the amplitude ratio of parallel and perpendicular band measured in the oriented sample, divided by the same ratio in a non-oriented sample . A computer simulation of ESR spectra gives the correlation between the P_2 order parameter and R : if the extent of orientation is small, these parameters are proportional each other, but for large orientation a more complex relation exists (12).

As for the mechanical properties, one of the most important questions is the orientation of anisotropic filler particles. In case of $CaCO_3$ there are orthorhombic fracture surfaces normal to the *c* axis, making possible orientation by mechanical stress. The milling of filler, however, is also important. When we compared the orientational properties of $CaCO_3$ obtained from different sources (Durcal 2, marble and Millicarb, chalk) only the first one gave substatial orientation, where the electron microscopic picture revealed clear surfaces (11). In the case of talc, the platelets have a large aspect ratio and the *c* axis is normal to the large surface. Similarly for both fillers the parallel orientation represents a preferential alignment, where the normal to the platelets points to the direction of the magnetic field. In the ESR experiments, the tensile specimen was oriented in different ways with respect to the magnetic field. Two directions can be distinguished in the sample: the *z* axis which is normal to the plate formed by compression molding or rolling, and the *x* axis of injection or stretching. Spectra were recorded in three different specimen orientations: when the field was parallel either to the *z* or *x* axes, or it was aligned perpendicularly to these directions (*y* axis setting). The respective R_z, R_x and R_y parameters give a complete description of filler orientation.

In case of compression molding, R_z was found to be always larger, while R_x and R_y smaller than one, respectively. Apparently, the flow of the polymer in the *xy* plane orients the platelets preferentially normal to the *z* direction. It is remarkable that a rather mild shear can produce substantial orientation in talc-filled composites. In the case of stretching, the R_x parameter has the largest value. In the tensile specimen produced by injection molding a more complex picture arises: in the vicinity of walls, shear stress aligns platelets parallel with the wall; *i.e.* R_z or R_y is large close to the *xy* or *xz* walls, respectively. In the core of the specimen, the small value of R_x is the most evident consequence of the orienting effect of shear stress.

The contact of polymer matrix with the surface of particulate filler can impart a substantial reinforcement strength to the composites. This interaction can be studied if we compare the degree of orientation in samples where the volume percent of filler is changing from 5 to 30 in PP based composites prepared either by compression or injection molding. In case of compression molding the

orientation of $CaCO_3$ is strongly reduced for high filler content, while the orientation of talc was only slightly reduced (Figure 2). We see that the oriented layer structure is much less disturbed by the direct interaction of particles of high aspect ratio, as compared to the case where the anisotropy is small. We think this is the reason why the mechanical properties, such as Young' modulus, tensile strength or shear stress , are so different in composites filled by talc and $CaCO_3$. We observe remarkably good correlation between the mechanical properties and orientation as a function of composition: while for $CaCO_3$ the tensile strength and yield stress are much smaller for large filler content, in the case of talc the reduction is small (Figures 3 and 4).

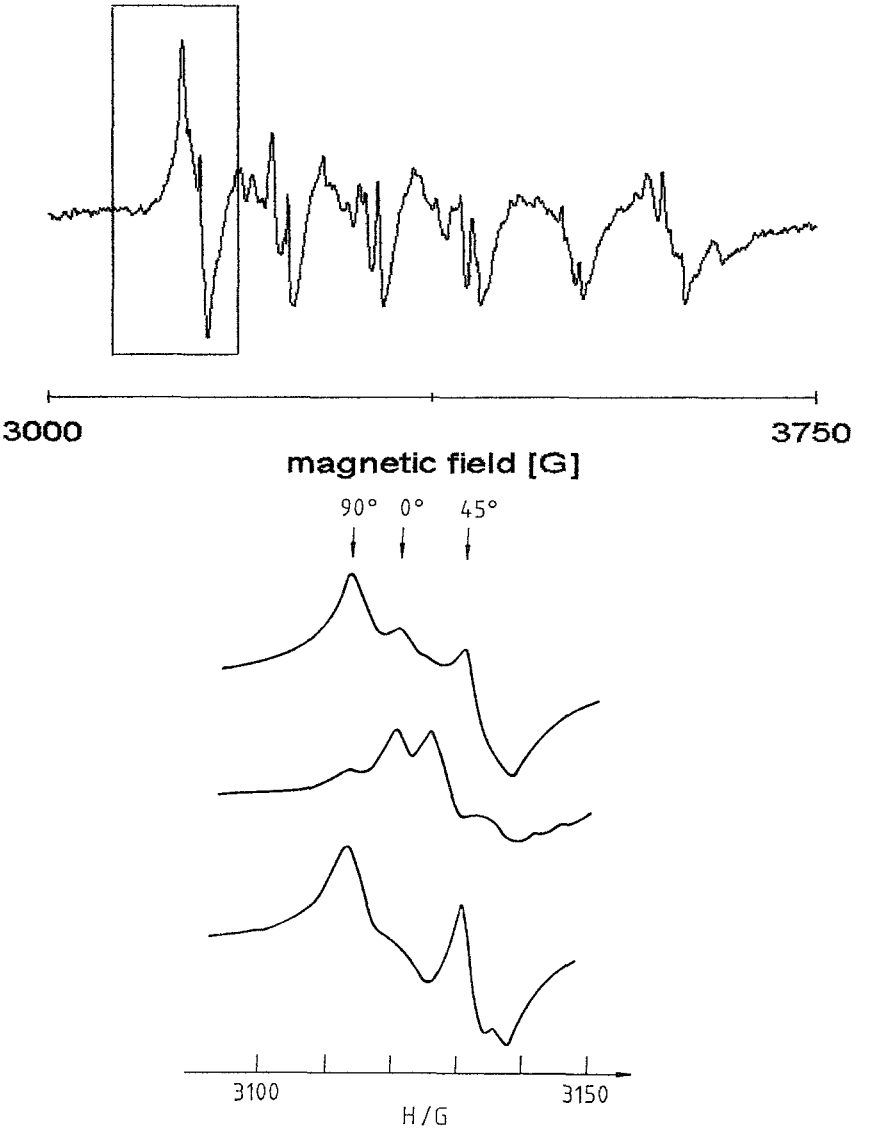

Figure 1 The Mn(II) ESR spectrum of talc filled PP, upper: complete one, down: the first line is shown for the unoriented (top) and oriented samples if the magnetic field is parallel with the normal of plate, (middle) or perpendicular to it (bottom).

In the injection molded specimen the orientation of talc particles reveals a maximum behavior: the strongest overall orientation was found for 15% filler content. This fact shows that the formation of an oriented layer in the composite can even reinforce its strength with respect to the pure polymer blend.

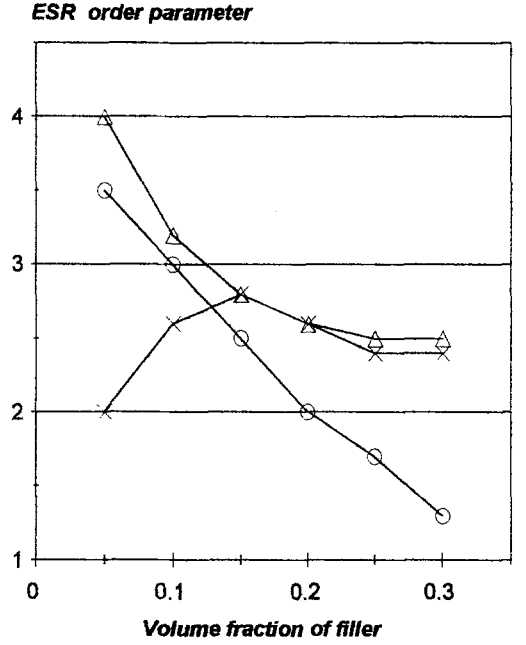

Figure 2.
Composition dependence of orientation parameter in PP matrices, Δ compression molded composite (CMC) with talc, O: CMC with $CaCO_3$, X: injection molded composite (IMC) with talc

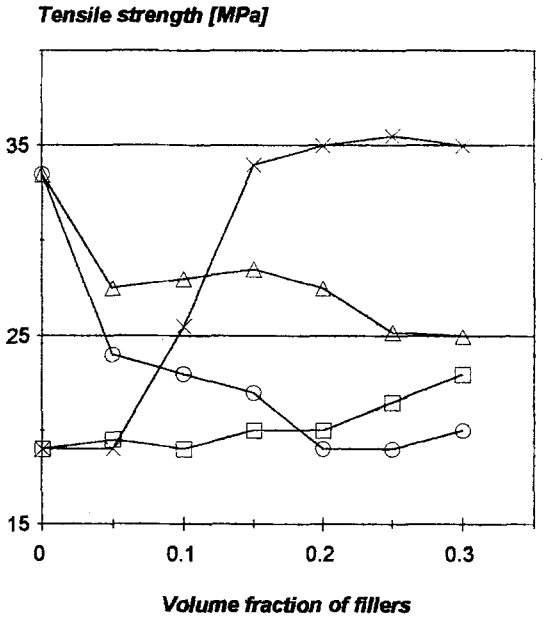

Figure 3.
Composition dependence of the tensile strength in PP matrices, Δ: CMC with talc, O: CMC with $CaCO_3$, X: IMC with talc, □: IMC with $CaCO_3$

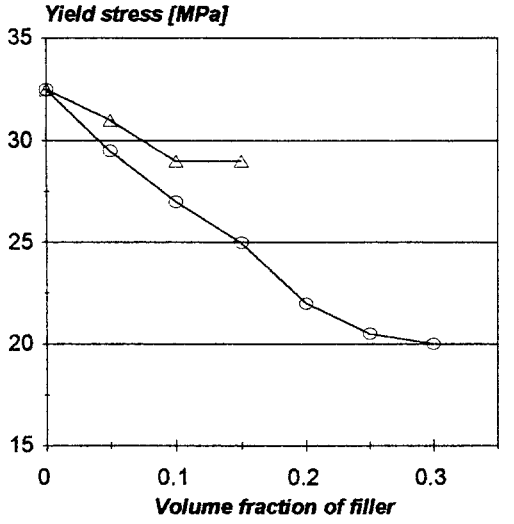

Figure 4.
Composition dependence of the tensile yield stress, PP matrix, Δ: CMC with talc, O: CMC with $CaCO_3$

Experimental

Polymer composites: The matrix was polypropylene (ethylene-propylene copolymer with an ethylene content less than 5%, TVK, Hungary; Typolen K 501), filler additives: Durcal 2, (milled $CaCO_3$ with average particle diameter 3μm, produced by Omya, Switzerland), millicarb (milled $CaCO_3$ with average particle diameter 3μm, Omya), talc (Luzenac 10M00S, Luzenac, France).

The composition ratio of fillers changed between 0. and 0.3 volume fraction in 0.05 steps. The ingredients of the composites were mixed in a Rheomix 600 mixing chamber of a Haake Rheocord EU 10V plastograph at 50 min-1 speed for 10 min. The mixing temperature was 185 ^{0}C for PP composites of injection molded and compression molded, as well.

From the plates tensile specimens were cut and stretched at 100 mm/min deformation rate. Rectangular plates were cut from the compressed and stretched samples. The plates were mounted on a goniometer in which the rotation axis was perpendicular to the direction of magnetic field. The ESR spectra were recorded by a JEOL type JES-FE-3X spectrometer in X-band with 100 kHz field modulation. The measurements of mechanical properties are described elsewhere (10).

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