Engineered Interphases in Particulate Filled Polypropylene

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The yielding behaviour of PP filled with 30 vol. % inorganic fillers has been investigated as affected by the presence of a soft engineered interphase layer (EIL) strongly adhering to the surface of individual filler particles. Strong interaction between the filler surface and EIL has been achieved *via* grafting the elastomer with maleic anhydride. A substantial increase in the yield strength, σ_{yc}, has been observed for composites containing rigid core-elastomer shell inclusions compared to composites filled with an equal volume fraction of the fillers themselves. The observed changes have been attributed to the change in local state of stress and connectivity of yielded microzones due to the presence of EIL on the particle surface. Experimental results were in a good agreement with a recently proposed theory.

There is over thirty years of research and plenty of published data on the role of interphase layer in the mechanical response of filled semicrystalline thermoplastics such as PP. Intuitively, it has been believed that this thin layer is responsible to a great extent for the variations of the mechanical properties of filled PP described in literature. However, a clear interpretation of the experimental data has not occurred till the late 80s and beginning of the 90s. In the last two decades, a significant growth in the science and technology of composite materials has been achieved. It has begun with an interest in the properties of primary components, *i.e.* fillers and polymer matrices. As the knowledge has been accumulated, it became apparent that the third entity – the region in an imminent vicinity of the surface of an reinforcement – plays a profound role in the behaviour of composites. This region was termed interface/interphase. As the importance and widespread use of particulate composites grew, interphase/interface phenomena have also been declared important for this class of materials.

Interface is commonly defined as a perfect two-dimensional (2-D) mathematical surface dividing two distinguished phases or components in a composite. Interface is characterized by an abrupt change in properties and, frequently, in chemical composition. This 2-D surface does not have any physical properties itself. For the purpose of investigation of stress transfer from the matrix to the reinforcement, one can assume that all stress transfer phenomena take place at the interface, which is then characterized by a single property – interfacial shear strength [1]. This approach is frequently used when there is an emphasis on a chemical bond between the constituents as a primary parameter controlling the mechanical response of a composite.

Interphase is a three-dimensional (3-D) layer in the immediate vicinity of filller surface, possessing physical properties different than the two main phases or components in a composite, *i.e.* matrix and filler. For the purpose of this paper, the term interphase is limited to the layers introduced on the filler surface intentionally in a controlled manner – engineered interphase layers (EIL). In these layers, gradient of chemical composition can also exist as well as a gradient of physical properties. The pivotal problem is, thus, a definition and an evaluation of an interphase thickness and its properties, namely, stiffness and fracture toughness. Interphase behaviour plays a paramount role in the ability to transfer loads from the matrix to the reinforcements, hydrolytic stability of the material, and fracture behaviour of a particulate composite.

Treating of the stress transfer phenomena as an interphase governed problem is much closer to the reality, however, the problem is substantially more complicated compared to the interface approach. Here, one can assume that the stress transfer phenomena are concentrated in the interphase. A full set of physical properties including elastic moduli, Poisson constant, and fracture toughness is then needed to character-

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ize the interphase. The complication in mathematical treatment of the interphase phenomena was the primary reason why the first close form solutions of this problem have been published only in the last decade [2—4] and the most attention was paid to the use of numerical methods.

New concepts combining micromechanical models with the macromechanics of composite bodies were able to explain experimental data and predict limits of mechanical properties. Proposed models were utilized as the link between micro- and macromechanics of the composite body. In the calculations, in addition to properties of the matrix and the filler, properties and spatial arrangement of the interphase have been included [5]. This model allows for a prediction of the structure—property relationships in PP filled with randomly distributed core-shell inclusions with EIL shell. This is of a pivotal importance in an attempt to develop and manufacture materials "tailored" to a particular end-use application.

An interphase formation, its morphogenesis and final structure are all extremely important for the resulting physical properties of the interphase and, thus, for the behaviour of any composite material. The problem of interphase formation is, however, very complex and in many aspects it is still not completely understood. The rapid advances in the technology and application of a wide range of matrices of different polarities and chemical reactivity have led to a resurgence of interest in optimizing the interfacial bonding and the performance of the interphase region in recent years. Some of the latest results have shown that the physicomechanical properties of the interphase are the primary factors controlling mechanical response of particulate composites under common conditions, especially their fracture and impact behaviour [6—9].

In the field of mineral filler filled polymers, EILs formed by silane, titanate, and low-molecular fatty acid agents are essential to good performance, plausible processing or excellent appearance. Apparently, most of the understanding of the phenomena, related to the effects these substances have on the interface/interphase in filled polymers, has been acquired from technological rather than fundamental grounds [10]. Since the 1960s, there has been a substantial effort to produce thin interphases of elastomers on the surface of common reinforcements. The major thrust in these investigations was a hypothesis that the presence of a thin highly flexible layer on the surface of reinforcing fibers will contribute to an enhancement of composite toughness without jeopardizing its strength and stiffness.

In these studies, an advantage of *in situ* forming of chemically distinguished interphase was explored. Elastomers such as EPR and EPDM were chemically modified in order to introduce polar groups onto their backbone chains. Most frequently, maleic anhydride and acrylic acid were used as the grafting co-monomers [7—9]. In the process of melt mixing, carboxyl groups from the grafted co-monomer react with hydroxyls, amines or other suitable reactive groups present on the filler surface. Often, the resulting bond is a mixture of contributions from several types of interactions ranging from covalent bonds through hydrogen bonds to electrostatic interactions. Hence, a term acid-base interaction is commonly used to describe interfacial bonding in these systems. Interphases, formed in this fashion, were about 500 nm thick which was about one order of magnitude thicker than the silane or oligomer interphases commonly 20—100 nm thick.

In this paper, a procedure is presented to create an engineered interphase layer (EIL) on the surface of various particulate inorganic fillers commonly used to modify physical properties and rheology of polypropylene (PP). Maleic anhydride (MAH) grafted ethylene—propylene random copolymers (MEPR) was the material to form soft EILs. Scanning electron microscopy (SEM) and dynamic mechanical thermal analysis (DMTA) were employed to elucidate phase morphology of prepared filled polypropylenes. Effects of the EIL thickness on the yield strength of PP filled with constant filler volume fraction of 0.3 were measured and interpreted in the light of recently proposed theories.

EXPERIMENTAL

Commercial polypropylene Mosten 58.412 (Litvínov Chemical Works, Czech Republic), melt flow ratio of 4 g/10 min (230 °C, 21.6 N), was used as a matrix. Ethylene—propylene random copolymer (EPR) Dutral CO 054 (Himont, Italy), $T_g = -57\,^{\circ}\mathrm{C}$, $M_m = 180\,000\ \mathrm{g\ mol^{-1}}$, was used as an elastomer. A maleated version of Dutral CO 054 (PIB Brno, Czech Republic), containing 2 mass % of grafted MAH, was mixed with EPR to achieve the required concentration of carboxyl groups in elastomer under the same conditions as described below.

Two batches of platelet shaped $Mg(OH)_2$ filler of the same average aspect ratio of 5, and specific surface area of 7 $m^2\ g^{-1}$ and 18 $m^2\ g^{-1}$, respectively (PIB Brno, Czech Republic), were used as flame retardant fillers. Additionally, irregularly shaped $CaCO_3$ filler, Durcal 2 (Omya, Switzerland), with average particle diameter of 3.6 μm and specific surface area of 2.5 $m^2\ g^{-1}$, was used to investigate the effect of particle shape. Only untreated fillers were used to avoid the effects of commonly utilized commercial surface treatments.

PP/filler/elastomer composites were prepared by mixing all the components in a one-step procedure (PLO 651 Brabender Plasticorder, 200 °C, 50 min^{-1}, 10 min). Dog-bone shaped specimens were cut from sheets of the compounded materials which were compression-molded at 200 °C for 4 min at atmospheric pressure and 2 min under 6 MPa and cooled down under pressure at an average cooling rate of 20 °C min^{-1}. Yield strength, σ_{yc}, was measured at room temperature using an Instron 4302 Tensile Tester at a strain rate of 1.0 min^{-1}. Reported values are averaged from 5 specimens with a standard deviation less than 10 %.

Fracture surfaces for morphological observations were prepared by breaking, under flexure load in liquid nitrogen, rectangular bars of the material containing a sharp razor blade notch. The surface was then etched for 1 to 5 min in boiling n-heptane to remove the elastomer. Specimens broken during tensile tests and etched under the same conditions as above were also used. A Scanning Electron Microscope (SEM) Amray IV (Amray, USA) was used to examine the fracture surfaces.

RESULTS AND DISCUSSION

Two sets of experiments were carried out. In the first series, rigid filler and elastomer volume fractions were kept constant at $\varphi_f = 0.3$ and $\varphi_e = 0.1$, respectively, resulting in a constant total inclusion volume fraction of $\varphi_{tot} = 0.4$. MAH content per rigid filler mass was varying from 0 to 2 mass %. SEM micrographs have revealed that an increasing MAH content in the MEPR resulted in a change of the phase morphology from a random spatial arrangement of the rigid and soft inclusions at 0.0 mass % MAH to a complete encapsulation of the rigid filler by the MEPR above about 1.0 mass % MAH (Fig. 1). The effect of MAH content in the MEPR phase on the yield strength for the PP filled with either $CaCO_3$ or $Mg(OH)_2$ is depicted in Fig. 2. For comparison, solid lines plotted in Fig. 2 represent yield strength of PP filled with randomly distributed rigid fillers of the same total filler volume fraction of 0.4, the same particle size and size distribution and with no adhesion to the matrix.

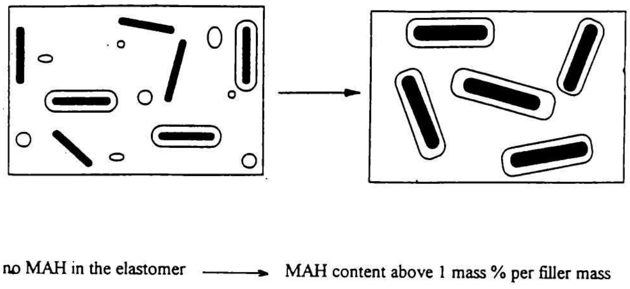

Fig. 1. Schematic representation of the encapsulation process visualizing the transition between "random" and "complete encapsulation" phase morphologies in the $PP/Mg(OH)_2/EPR$ ternary composite induced by an addition of MAH grafted EPR (MEPR).

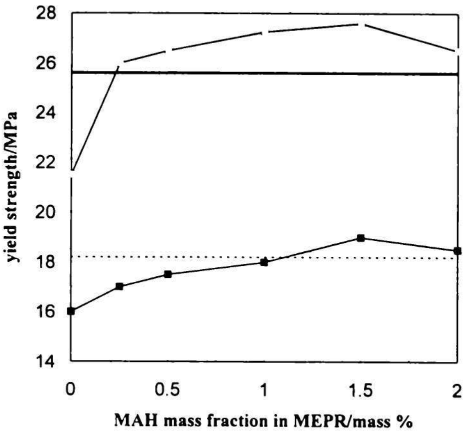

Fig. 2. Dependence of the composite yield strength on the content of MAH in the elastomer phase at constant material composition $\varphi(PP) : \varphi(\text{filler}) : \varphi(MEPR) = 6 : 3 : 1$. Open squares represent systems containing $Mg(OH)_2$ as the filler and filled squares represent the system filled with $CaCO_3$. Full and dashed lines represent the yield strength of binary $PP/Mg(OH)_2$ and $PP/CaCO_3$ composites, respectively, with no filler—matrix adhesion. Total content of the filler particles in these binary composites equals the sum of filler and elastomer inclusions in the ternary composites, *i.e.* 40 vol. %.

The yield strength, σ_{yc}, increases with an increase in MAH content in MEPR. The absolute values of σ_{yc} are, however, significantly lower than those obtained for the case of rigid interphase since the effect of even a small amount of encapsulating elastomer reduces the effective stiffness of the reinforcing filler to close to that of a void in the matrix. The process of encapsulation reduces the triaxial stresses at the rigid filler surface, thereby changing the failure mechanism from crazing to shear yielding [11—14]. As a result, a change in the macroscopic deformation response of the composite from brittle to ductile has been observed. The addition of MAH into the elastomer phase (MEPR) results in a loss of stiffness of the composite [7], however, it promotes a ductile failure and leads to an increase in the yield strength at constant composition. The overall material ductility increases despite the slight reduction in the binary matrix yield strain caused by the removal of the dispersed elastomer from the PP bulk to the filler surface. For MAH content above 1.0 mass %, where a morphology characterized by a complete encapsulation of the filler by the elastomer is approached, the ternary composite may be visualized as a binary composite of PP with embedded complex $\varphi(MEPR):\varphi(\text{filler}) = 1:3$ core-shell inclusions. Since there is no adhesion between the PP matrix and the elastomer shell of these complex inclusions, the analysis of the composite yield strength can be described using the concepts proposed among others by *Nicolais* and*Narkis* [15]. A lower limit of σ_{yc} can be predicted meaningfully only in the ideal case of complete encapsulation. SEM micrographs revealed

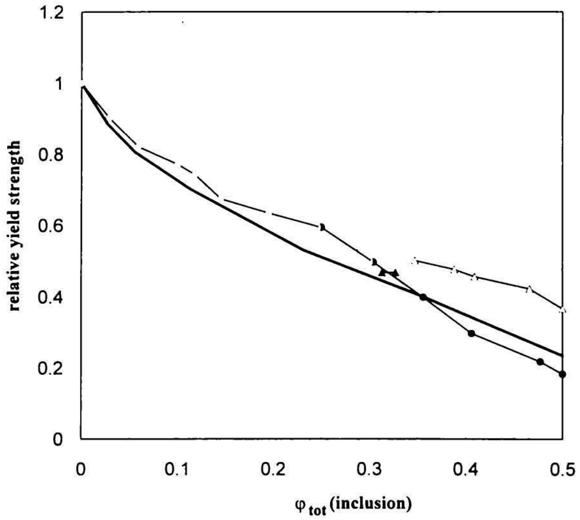

Fig. 3. A comparison of the dependence of the composite yield strength relative to that of the neat PP on the total inclusion volume fraction φ_{tot}(inclusion) for binary PP/$CaCO_3$ composites (circles) with that for the ternary PP/MEPR/$CaCO_3$ composites (triangles). Filled circles and triangles represent brittle failure, half-filled are for a "mixed" mode of failure (some specimens failed in a brittle manner, some exhibited yielding). Solid line is the predicted lower limit (eqn (*1a*)).

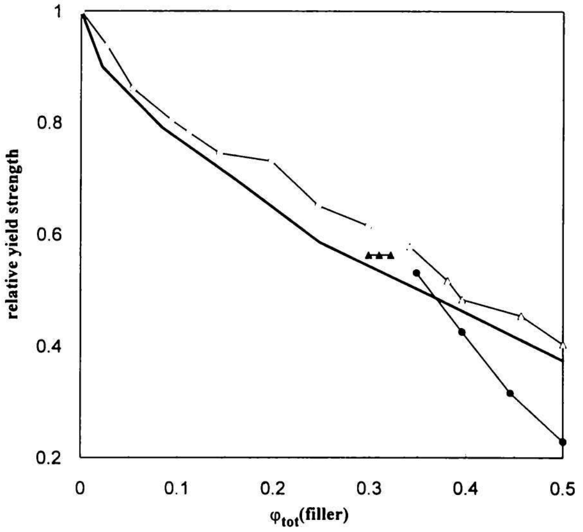

Fig. 4. Symbols as in Fig. 3 for $Mg(OH)_2$ type A filled systems. Solid line, eqn (*1b*).

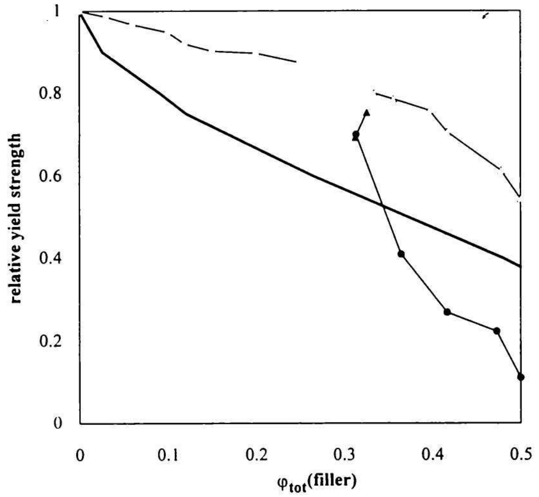

Fig. 5. Symbols as in Fig. 3 for $Mg(OH)_2$ type B filled systems. Solid line, eqn (*1b*).

that under the mixing conditions used, a complete encapsulation was achieved for contents above 1.0 mass % MAH.

In the second series, rigid filler volume fraction and MAH content per filler mass were kept constant at 0.3 mass % and 1.5 mass %, respectively, based on the results from the series discussed above. The morphology characterized by a complete encapsulation was achieved for all the composites from this series. It was idealized that the increasing MEPR content could be visualized as a thickenning of a uniform elastomer layer firmly adhering to the filler surface and with no adhesion to the surrounding PP. It has been shown previously that the enhancement of filler—elastomer adhesion by maleating the elastomer phase causes preferential chemical bonding of the elastomer on the filler surface during a melt mixing of the components.

The effect of elastomer volume fraction, φ_e, on the tensile yield strength, σ_{yc}, of ternary composites with filler volume fraction of $\varphi_f = 0.3$ and 1.5 mass % MAH (based on mass of rigid filler) in the elastomer phase is shown in Figs. 3—5. At the MEPR volume fractions below 0.02, all three sets of composites investigated were brittle and ductile at $\varphi_e > 0.02$. Above $\varphi_e = 0.02$, the yield strength of the ductile composites decreased monotonically over the whole interval of elastomer concentrations studied ($0.0 < \varphi_e < 0.2$).

A lower limit of the tensile yield strength, σ_{yc}, can be predicted in the case of complete encapsulation by a uniformly thick elastomer layer and no adhesion between the core-shell inclusions and the PP matrix using one of the following two equations [7, 15]

$$\frac{\sigma_{yc}}{\sigma_{yo}} = (1 - 1.21\varphi_f^{2/3}) \qquad (1a)$$

$$\frac{\sigma_{yc}}{\sigma_{yo}} = (1 - \varphi_f^{2/3}) \qquad (1b)$$

where σ_{yc} is the composite yield strength, σ_{yo} is the yield strength of the neat PP, φ_f is the core-shell inclusions volume fraction, *i.e.* $\varphi_f = \varphi_e + 0.3$. As it was shown previously [5], eqn (*1a*) can be utilized for the $CaCO_3$ filled composites, which contain irregular, approximately spherical particles, while eqn (*1b*) appears to provide a better fit of the data for the composites reinforced with the randomly arrayed, platelet shaped particles of $Mg(OH)_2$.

In Fig. 3, experimental data are shown for binary PP/$CaCO_3$ and ternary PP/MEPR/$CaCO_3$ blends. In both cases, PP was filled with untreated $CaCO_3$ particles. In the binary composites (circles in Fig. 3), the change of yield strength with filler concentration was well described by eqn (*1a*) in the range of $0.0 < \varphi_f < 0.25$. Beyond the $CaCO_3$ volume fraction of 0.25, the composite shows brittle rather than ductile behaviour (filled circles in Fig. 3). For the PP filled with complex core-shell inclusions consisting of rigid core and EIL elastomer shell, no change of the brittle tensile strength was observed below MEPR volume fraction of $\varphi_e = 0.02$. For the MEPR volume fractions above 0.02, the ductile character of the failure has been restored, with the yield strengths (open triangles) blending in smoothly with the data on the binary composites. It was shown previously [8] that the treatment of the $CaCO_3$ with calcium stearate for the purpose of creating a nonbonding surface had principally the same effect.

The behaviour of PP filled with the two $Mg(OH)_2$ fillers is similar to that described above for $CaCO_3$ filled PP. The changes of yield strength of the binary composite filled with the 7 m^2 g^{-1} $Mg(OH)_2$ particles are described well by eqn (*1b*) up to $\varphi_f = 0.3$ (Fig. 4). Beyond this concentration the material becomes brittle and its strength is less than expected from a ductile material of the same composition. Addition of more than a few percent MEPR elastomer to the composite with $\varphi_f = 0.3$ restored the ductile character of its failure, and the yield strength data blended well into the data obtained on the binary composites. The same results were obtained for the PP filled with 18 m^2 g^{-1} $Mg(OH)_2$, although the yield strength values were somewhat higher than those predicted by the lower bound equation (Fig. 5). One could speculate on the reasons for the observed discrepancy, however, no conclusive experimental evidences have been obtained to propose a plausible interpretation. There is, however, a project in progress to provide such an evidence.

CONCLUSION

The increasing MAH concentration in the elastomer phase at a constant rigid filler and elastomer phase generated a phase morphology that was close to the ideal case of a complete encapsulation of the rigid filler by the elastomer at contents above 1.0 mass % MAH. The state with no adhesion at the [core-shell inclusion]/[matrix] boundary and the sharp reduction of triaxial stress at the rigid filler surface because of the soft coating of maleated elastomer contributed to a mechanical response of the composites that was similar to that of a ductile matrix filled with voids, thereby minimizing both yield strength and stiffness.

In the case of complete encapsulation, the increasing thickness of the soft elastomer EIL with increasing MEPR concentration resulted in a restoration of a ductile mode of failure by changing the localized state of stress and the connectivity of the plastically deformed microzones. In the filler volume fraction range of commercial interest, *i.e.* from $\varphi_f = 0.30$ to 0.50, the placement of the elastomer EIL can cause a two- to three-fold change in the yield strength of the materials compared to the case with rigid EIL and strong matrix—filler adhesion [7].

Our experimental data showed that one can generate commercially viable materials exhibiting upper bound and lower bound behaviour. By an appropriate choice of processing conditions, rigid filler size, shape and concentration, elastomer content, and the distribution of an adhesion promoter between the phases, one should be able to tailor stiffness and strength properties over a wide range with the distance between the lower and upper limiting properties being for filled PP of the order of 300 %.

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