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Influence of the filler particle shape on the elastic moduli of PP/$CaCO_3$ 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 Youngs 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/$CaCO_3$ 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/$CaCO_3$ 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].

Low molecular adhesive agents (titanate, silane, zircoaluminate, etc.) cannot form a strong adhesive bond between PP and fillers. Short molecules of these substances, although they can create a relatively strong bond with the filler surface, do not form either a chemical bond with the PP molecules or physical entanglements causing an improvement in PP cohesive strength. For these reasons, high molecular adhesive agents are preferred which create strong bonds with the filler surface and form physical entanglements with the formal matrix in the bulk.

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/$CaCO_3$ 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), magnesium hydroxide Kisuma 5B, Kisuma 7B (Kyowa, Japan) and Reachin (USSR) were used as fillers. Their characteristics are listed in Table I. $CaCO_3$ 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 plasticorder 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 $5^\circ C\,min^{-1}$. Measurements were carried out on the PL

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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/$CaCO_3$ composites. For this reason the modified Kerner–Nielsen equation [6] must be used

$$\frac{M_c}{M_m} = \frac{1 + ABv_{fa}}{1 - B\psi v_{fa}} \qquad (1)$$

considering the modificating function ψ in the form

$$\psi = 1 + \frac{1 - v_{fa}^{\max}}{(v_{fa}^{\max})^2} v_{fa} \qquad (2)$$

where A and B are constants, M_c and M_m are, respectively, the composite or matrix moduli, v_{fa} is an apparent filler volume fraction taking into account interfacial interactions, and $v_{fa}^{\max}$ is the maximum apparent filler volume fraction [7]. For the PP/$CaCO_3$ 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]

$$v_{fa} = (1 + b)\, v_f \qquad (3)$$

where b is the "degree" of matrix immobilization. This means the product $(bv_f) = v_i$ 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 $v_{fa}^{\max} = 1$ at which all remaining matrix is immobilized. Hence

$$v_{fa}^{\max} = v_f^{\max} + v_i = 1 \qquad (4)$$

where $v_f^{\max}$a 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]

$$t_{eff} = \frac{b}{S_f \varrho_f} \qquad (5)$$

where S_f is the specific surface area of the filler, and ϱ_f is its density.

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

$$\frac{M_c^{L,T}}{M_m} = \frac{1 + A_{L,T}B_{L,T}v_{fa}}{1 - B_{L,T}v_{fa}} \qquad (6)$$

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/$CaCO_3$ composites. The simple Tsai approximation [6] was used for calculation of the modulus, M, of composites with randomly oriented particles from transversal, M_T, and longitudinal, M_L, values of composites with unidirectionally aligned filler particles

$$M = \tfrac{3}{8}M_L + \tfrac{5}{8}M_T \qquad (7)$$

3.1.2. Unfilled polypropylene modified with maleated PP

The increase in E' and G' moduli of unfilled PP with the MPP volume fraction, $v_{MPP} = 0.4$ (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 I Characteristics of fillers used

Chemical nature	Grade	Specific area ($m^2 g^{-1}$)	Density ($g cm^{-3}$)	Young's modulus (GPa)	Shear modulus (GPa)	Average aspect ratio, $\bar{p}$
$CaCO_3$	Durcal 2	3.3	2.71	72	28	irregular approximately spherical $p \approx 1$
$Mg(OH)_2$	Kisuma 5B	7	2.36	64*	25*	hexagonal lamellae $p \approx 5$
	Reachim	6.8	2.36	64	25	hexagonal lamellae $p \approx 5$
	Kisuma 7B	37	2.36	64	25	needles $p \approx 25$

*The values E and G moduli of $Mg(OH)_2$ were estimated from the relation between elastic moduli and hardness of materials.

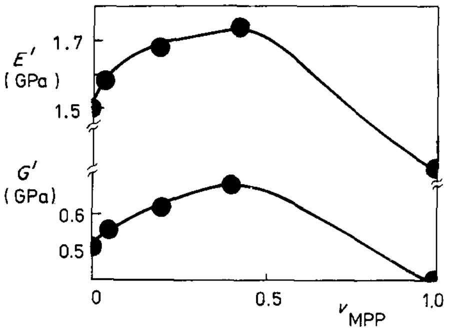

Figure 1 Dependence of the Young's and shear elastic moduli on the volume fraction of maleated PP (v_{MPP}) in unfilled PP matrix.

TABLE III Maximum relative increase of E' and G' moduli with MPP content†

Composite	Maximum relative increase†	
	E'	G'
	(%)	
PP/CaCO$_3$	5.0	10.0
PP/Mg(OH)$_2$ plates	4.3	31.6
PP/Mg(OH)$_2$ needles	3.2	19.0
PP	23.0	40.0

* Related to the E' and G' moduli of corresponding samples without MPP.

†The values were determined at $v_{MPP} = 0.05$.

the concentration interval mentioned above, MPP causes crystallinity and the number of spherulites to increase (Table II), while at the same time the diameters of the spherulites steeply decrease (Fig. 2). Because MPP strongly affects the crystallization kinetics due to the additional nucleating centre activation, the lamellar thickness also changes (Table II).

Although further increase of the MPP content (above $v_{MPP} = 0.4$) causes a lamellar thickness decrease leading to an increase in lamellar aspect ratio, the crystallinity reduction is much more prominent. This the most probable reason for the decrease in the matrix moduli (Fig. 1). An additional reason which may be considered is the decrease in the average molecular weight of the matrix even up to one-half of the formal PP at $v_{MPP} = 1$. The values of elastic moduli are then the result of competition between these contradictory mechanisms.

3.1.3. Composites PP/CaCO$_3$ and PP/Mg(OH)$_2$ with randomly oriented particles

The increase in E' and G' of any blends studied with MPP content (Figs 3 to 5) cannot be explained only as a consequence of the matrix rigidity improvement discussed above. Other effects must also be taken into account and the value of the elastic modulus results from competition between the different processes.

The maximum relative increase of composite moduli is always lower than that of the unfilled matrix, and it appears at lower MPP content (Table III). Hence, the filler probably restricts, in some manner, the reinforcing effects of MPP on the matrix, compared to the unfilled matrix. This process is probably connected with the fact that the filler itself affects the matrix morphology. PP morphology is characterized by the extinction of spherulites and by transition to the lamellar structure in the composites PP/CaCO$_3$ and PP/Mg(OH)$_2$ containing 18 vol/vol% filler [11]. MPP, accelerating the matrix crystallization due to additional nucleating centres activation, probably causes the more prominent decay of the spherulites. We also assume that the majority of MPP interacts preferentially with the filler surface centres while the nucleating centres activation in the matrix bulk is a minor effect. Unfortunately, no available structural data could be obtained to verify this proposed explanation.

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* Related to the E' and G' moduli of corresponding samples without MPP.

†The values were determined at $v_{MPP} = 0.05$.

In the PP/CaCO$_3$ composite the maximum is reached at $v_{MPP} = 0.01$, in the PP/Mg(OH)$_2$ plate composites at $v_{MPP} = 0.05$, and in the PP/Mg(OH)$_2$ needles at $v_{MPP} = 0.1$ (Figs 3 to 5). Increase in elastic moduli is thus the consequence of matrix immobilization on the filler surface due to the extensive interfacial interactions between acid carboxyl groups of MPP and base centres on the filler surface. Further important contribution to the elastic moduli increase enhances the matrix rigidity in the bulk. To reduce the different surface properties of CaCO$_3$ and Mg(OH)$_2$, the fillers were surface treated (hydrophobized). Therefore, the different behaviour of the composites with distinct fillers is caused by the increase in specific surface area

TABLE IV Effective thickness of the interlayer on the filler surface*

Composite	MPP volume fraction, v_{MPP}		Effective interlayer thickness, t_{eff} (nm)	
			Tensile test	Shear test
PP/CaCO$_3$	0	surf. tr.	11	61
	0	untreated	37	82
PP/CaCO$_3$	0.04	surf. tr.	17	72
	0.04	untreated	53	92
PP/Mg(OH)$_2$ plates	0	surf. tr.	8†	–
	0	untreated	10†	–
PP/Mg(OH)$_2$ plates	0.04	surf. tr.	12†	24†
	0.04	untreated	20†	37†
PP/Mg(OH)$_2$ needles	0	surf. tr.	5‡	–
PP/Mg(OH)$_2$ needles	0.04	surf. tr.	10‡	–

*Values t_{eff} were calculated from Equation 5.

†Values of t_{eff} for composites with Mg(OH)$_2$ plates were calculated without considering the decrease in average aspect ratio.

‡Values t_{eff} were estimated from temperature dependences of E modulus.

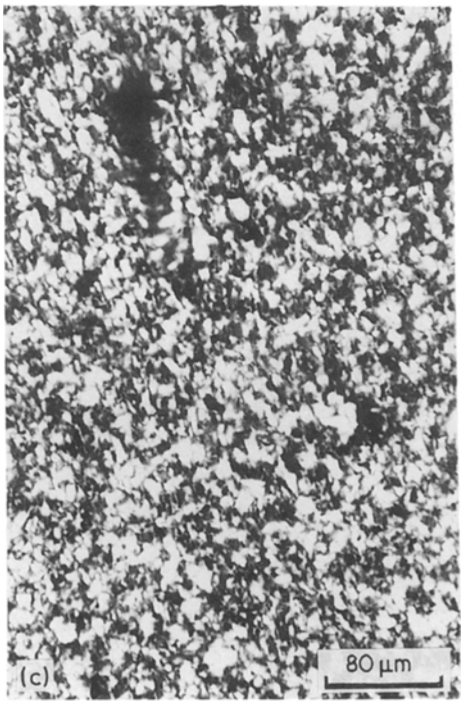

Figure 2 Spherulitic structure of the matrix as seen by optical microscopy using polarized light. (a) Unmodified PP, (b) MPP volume fraction, $v_{\mathrm{MPP}} = 0.003$, (c) $v_{\mathrm{MPP}} = 0.4$.

increase (Table IV) and by the increase in average aspect ratio of the filler in the sequence $CaCO_3$ < $Mg(OH)_2$ plates < $Mg(OH)_2$ needles. Some evidence exists about the strong influence of the fillers used on the PP morphology in the bulk (Fig. 6). In addition, the critical length, L_c, decreases with MPP content in the composites containing $Mg(OH)_2$ needles [6]. This causes an apparent increase in the number of reinforcing particles with $L > L_c$ oriented parallel to the loading direction.

Non-monotonic dependence of the elastic moduli on the MPP content with its further increase is then a result of the competition between the two kinds of process. Firstly, in the same way as in the low concentration region, the mechanisms act tending to increase the moduli. Secondary, the decrease of both the matrix crystallinity and its average molecular weight with MPP content leads to a reduction in the moduli. The competition between the two processes determines the resulting values of the composite moduli.

Additionally, the reduction of the PP/$Mg(OH)_2$ composite moduli can partly be the consequence of hyperstructure creation. For a given filler, hyperstructure formation depends on the effective "thickness" of the interlayer adhering to the filler surface. Therefore, increase of the effective interlayer "thickness" with increasing amount of MPP could be the reason for the formation of a physical network of filler particles at

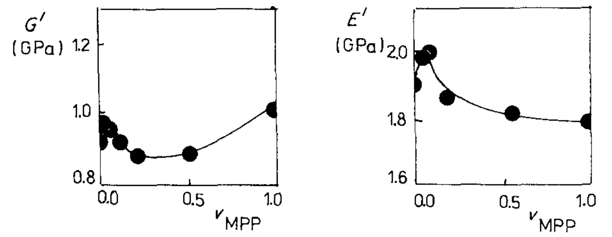

Figure 3 Dependence of Young's shear elastic moduli of PP/$CaCO_3$ composites on the MPP volume fraction, v_{MPP}, at constant filler volume fraction, $v_f = 0.18$. $CaCO_3$ was surface treated with 0.3 wt/wt% of stearic acid before compounding.

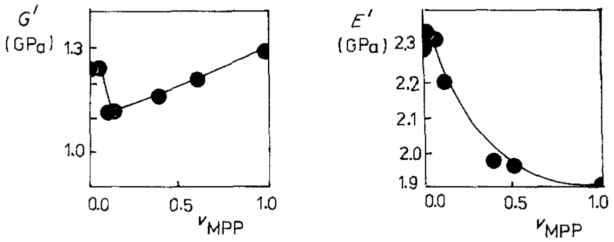

Figure 4 Dependence of Young's and shear elastic moduli of PP/$Mg(OH)_2$ plate composites on the MPP volume fraction, v_{MPP}, at constant filler volume fraction, $v_f = 0.18$. $Mg(OH)_2$ was surface treated by the producer.

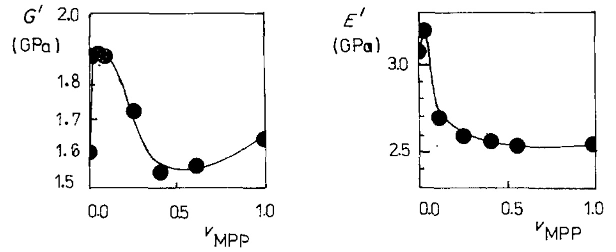

Figure 5 Dependence of Young's and shear elastic moduli of PP/$Mg(OH)_2$ needle composites on the MPP volume fraction, v_{MPP}, at constant filler volume fraction, $v_f = 0.18$ $Mg(OH)_2$ was surface treated by the producer.

filler contents lower than in the systems with "zero" adhesion.

3.1.4. PP/$Mg(OH)_2$ composites with unidirectionally aligned filler particles

The simple way of orientation used does not cause any alignment of the $Mg(OH)_2$ plates, as in composites with "zero" adhesion [12]. On the other hand, effects of the filler particle orientation lead to a prominent difference between parallel and perpendicularly measured moduli, E'_L and E'_T in the PP/$Mg(OH)_2$ needle composites (Fig. 7). As shown in Fig. 7, the observed differences are strongly dependent on the MPP content. The E'_T modulus exhibited a monotonic fall with MPP content, while the E'_L modulus had a prominent maximum at $v_{MPP} = 0.05$. This maximum appears at lower MPP content than in the composites with randomly oriented $Mg(OH)_2$ needles (Fig. 5).

Theoretically, the E'_T modulus of the composite with perfectly aligned fibrous filler particles is the lowest boundary. Every disorder of the alignment leads to the E'_T modulus increase [13]. Therefore, the observed decrease of the E'_T modulus must be the consequence of either changes in matrix morphology or particle alignment improvement. Matrix morphology changes have been described above, but we have no available structural data to discuss the second effect. A further alternative explanation of the E'_T modulus decrease may be proposed considering the formation of the bundles of needles. These bundles act as reinforcing elements and their number evidently depends on the needle volume fraction and, when v_f is held constant, on the effective interlayer "thickness". As the effective elastic moduli of such a "filler" are lower than that of $Mg(OH)_2$ due to the matrix presence in the bundles, the constant B in Equaton 6 is necessarily lower than the formerly assumed. This "filler softening" leads to a lowering of the elastic modulus at the same filler content.

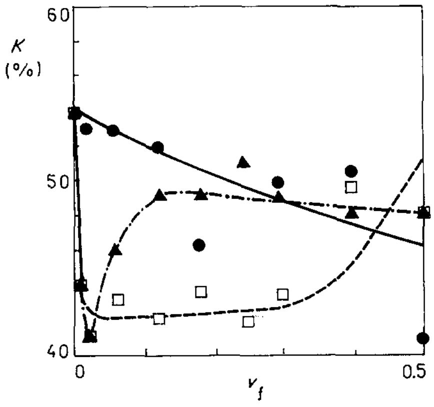

Figure 6 Dependence of the crystallinity, α, on the filler volume fraction v_f. (●) PP/$CaCO_3$, (□) PP/$Mg(OH)_2$ plates, (▲) PP/$Mg(OH)_2$ needles. Crystallinity was determined from X-ray diffraction measurements. (Published by permission of Dr Baldrian, Institute of Macromolecular Chemistry, Czechoslovakian Academy of Sciences, Prague.)

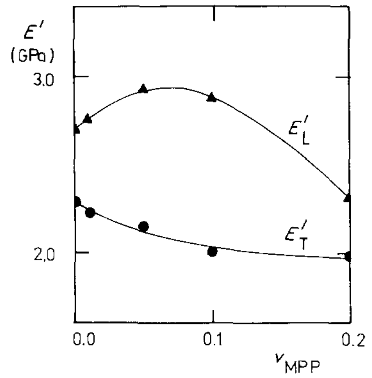

Figure 7 Dependence of the transverse, E'_T, and longitudinal, E'_L, elastic moduli of PP/$Mg(OH)_2$ neddle composites with unidirectionally aligned filler particles on the MPP volume fraction, v_{MPP}. $T = 296$ K, $f = 1$ Hz.

As the dependence of E'_L modulus on the MPP amount exhibits a maximum, two kinds of contradictory processes must operate. Firstly, an increase in the amount of immobilized matrix and the increase of the matrix modulus in the bulk cause the composite modulus to increase. The apparent improvement, described above, in the degree of orientation due to reduction of the critical length, L_c, also leads to an increase in the E'_L modulus [14]. Secondly, on the other hand, bundle formation and molecular weight and crystallinity reduction cause the E'_L modulus to decrease. The balance between the prominence of these two processes evidently depends on the MPP content and consequently the shape of E'_L (v_{MPP}) dependence results from their competition. It is worthwhile to note that the expected increase in the effective interlayer "thickness" with MPP content causes the occurrence of conditions necessary for hyperstructure formation at lower filler volume fractions than in the system without adhesion.

3.2. Concentration dependence of elastic moduli of composites with enhanced interfacial adhesion

3.2.1. PP/$CaCO_3$ composites with isometric particles

The character of the concentration dependence of E' and G' moduli of PP/$CaCO_3$ composites did not change when the interfacial adhesion is increased (Fig. 8). Significantly higher values of elastic moduli of the composite with untreated $CaCO_3$ compared to the system with treated filler, is the consequence of the higher value of adhesive energy of untreated $CaCO_3$ (at the same conditions and composition). In accordance with theoretical expectations, the value of b in Equation 3 is greater when $CaCO_3$ is untreated, thus the amount of immobilized matrix is greater in the

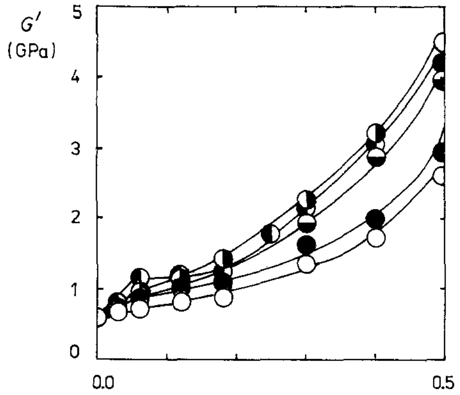

Figure 8 Concentration dependence of the composite's elastic moduli at enhanced interfacial adhesion. The ratio between MPP and filler volume fraction is held constant ($v_{MPP}/v_f = 0.02$). (●) PP/CaCO$_3$ (untreated), (○) PP/CaCO$_3$ (treated), (◑) PP/Mg(OH)$_2$ (plates, untreated), (◒) PP/Mg (OH)$_2$ (plates treated), (◐) PP/Mg(OH)$_2$ (needles). $f = 1$ Hz, $T = 296$ K, $v_{MPP} = 0.004$.

system with untreated filler due to the more intensive interactions between basic centres on the CaCO$_3$ surface and carboxyl groups grafted on PP molecules (MPP).

3.2.2. PP/Mg(OH)$_2$ composites with anisometric particles

Similar to the PP/CaCO$_3$ composites, the elastic moduli of PP/Mg(OH)$_2$ blends increased with MPP content, but the character of the concentration dependence did not change (Fig. 8). Greater values of the elastic moduli were observed in composites with untreated filler. The increase in the strength of adhesion, σ_a, between the matrix and the Mg(OH)$_2$ surface causes a greater effective "thickness" of immobilized interlayer and therefore this effect is more prominent when untreated Mg(OH)$_2$ is used (Fig. 8). Again, the influence of the Mg(OH)$_2$ surface hydrophobization on the interlayer "thickness" lies in the reduction of the thermodynamic energy of adhesion. Some of the adsorption centres on the treated surface are occupied by the long-chain fatty acid molecules, so that the MPP–Mg(OH)$_2$ acid – base interactions are weaker. Therefore, the number of bonded MPP molecules is lower and, consequently, the effective thickness of the strongly adsorbed interlayer is also lower. The relatively high value of the parameter *b* of the PP/Mg(OH)$_2$ needle composite is probably the consequence of both the five-fold greater specific surface area than that of Mg(OH)$_2$ plates and the effects of the fibrous shape of the particles.

These differences in the needles cause the appearance of effects connected with the hyperstructure of physically bonded needle formation. Higher "thickness" of immobilized interlayer on the needle surface is probably the main reason for the physical network creation at a lower filler content compared to the systems with "zero" adhesion. The simple analysis considered assumes a constant value of *b* (constant effective interlayer "thickness") within the concentration region studied. However, it seems evident that the analysis used cannot describe the concentration dependence of the elastic moduli sufficiently. In addition, it must be taken into account that the creation of bundles of needles, now acting as reinforcing elements, causes a reduction of both average aspect ratio and effective moduli of this "filler". The elastic moduli of the composite with a "filler" so composed are inevitably lower than those of a system with separated needles at the same filler content. Unfortunately, the simple model used does not consider the effects of physically bonded space network of Mg(OH)$_2$ particles in such a simple manner as in the blends with "zero" adhesion. A detailed study of the hyperstructure formation and its influence on the elastic response of the PP/Mg(OH)$_2$ needle composites is now being completed ready for publication.

4. Conclusions

Enhancing the interfacial adhesion with maleated PP content led to an increase in the moduli for all composites studied containing constant volume fraction of fillers. The essence of this increase is that the matrix moduli increase in the bulk and the amount of immobilized matrix in the interlayer on the filler surface also increases. The increase in matrix moduli was due to the changes in the kinetics of PP crystallization caused by the presence of MPP. Acid–base interactions between basic centres on the filler surface and carboxyl acid groups grafted onto PP molecules caused an increase in the amount of matrix immobilized in the interlayer. Contradictory effects which reduced the composite moduli also operated. These effects were caused by both the average molecular weight and crystallinity of the matrix decreasing with the MPP content. The nonmonotonic shapes of the dependences of the elastic moduli of composites studied on the MPP content were therefore the consequence of competition between the two processes.

The character of the concentration dependences of the elastic moduli did not change in the presence of MPP, but their values were higher compared to the composites with "zero" adhesion. This dependence was, for the PP/CaCO$_3$ composites, plausibly described using the Kerner–Nielsen equation considering the apparent filler volume fraction. The value of parameter *b* which expresses the quantity of immobilized matrix, increased with MPP content. This increase was more prominent when CaCO$_3$ was not surface treated with low molecular fatty acid due to the more intensive acid–base interactions. In the PP/Mg(OH)$_2$ composites, the required accordance between theoretical and experimental data was reached using the Halpin–Tsai equation. The PP/Mg(OH)$_2$ plate composites exhibited similar behaviour to PP/CaCO$_3$ blends, except that the values of moduli were higher under the same conditions and composition. The differences were caused by both higher specific surface area and anisometric particle shape.

Some peculiarities were observed for the PP/Mg(OH)$_2$ needle composites. Firstly, an increase in the amount of MPP led to an increase in effective interlayer "thickness" in the composite with constant filler volume fraction, which may have caused creation of the hyperstructure of physically bonded needles. This hyperstructure consists of bundles of needles created at lower filler content, compared to the blends with "zero" adhesion. The presence of the hyperstructure caused a reduction in composite moduli due to a decrease in both the average aspect ratio and effective moduli of the composed "filler".

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