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## The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

### Acid-Base Interactions and Interphase Formation in Particulate-Filled Polymers

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Online publication date: 08 September 2010

**To cite this Article** Móczó, János, Fekete, Erika and Pukánszky, Béla (2010) 'Acid-Base Interactions and Interphase Formation in Particulate-Filled Polymers', *The Journal of Adhesion*, 78: 10, 861 – 875

**To link to this Article:** DOI: 10.1080/00218460214099

**URL:** <http://dx.doi.org/10.1080/00218460214099>

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## ACID-BASE INTERACTIONS AND INTERPHASE FORMATION IN PARTICULATE-FILLED POLYMERS

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*Particulate-filled composites were prepared from CaCO<sub>3</sub> and polymer matrices of various acid-base characters. Interfacial interaction of the components was characterized by the reversible work of adhesion, which was calculated either from dipole-dipole or acid-base interactions. The thickness of the spontaneously formed interlayer was derived from the tensile strength of the composites. The results proved that acid-base interactions play an important role in interphase formation. The strength of interfacial adhesion is determined by the joint effect of dispersion forces and acid-base interactions. Stronger interaction leads to a thicker interphase with decreased mobility. Treatment of CaCO<sub>3</sub> with an aliphatic fatty acid leads to a decrease in the strength of interaction, and to changes both in the thickness and properties of the interphase. In composites containing coated fillers, acid-base interactions influence composite properties less due to the neutral character of the surface.*

**Keywords:** Particulate-filled polymers; Interfacial interaction; Reversible work of adhesion; Acid-base interaction; Interphase thickness; Tensile strength; Contact angle; Inverse gas chromatography

Received 4 January 2002; in final form 4 April 2002.

This is one of a collection of papers honoring Hatsuo (Ken) Ishida, the recipient in February 2001 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*.

The National Scientific Research Fund of Hungary (Grants No. T 030579 and No. T 029719), the Institute of Chemistry of the Hungarian Academy of Sciences, and the Bolyai Scholarship are acknowledged for their financial support of this study. The authors are grateful to Horváthné Kovács-Sebestyén Andrea for carrying out some of the experiments.

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## INTRODUCTION

Interfacial interactions play an important role in the determination of the properties of all heterogeneous polymer systems, including particulate-filled polymers [1, 2]. These interactions lead to the formation of an interphase with specific properties [3, 4], determine the amount of filler which can be added to the polymer (maximum packing fraction) [5], result in the particle size dependence of properties [6, 7], and determine the prevailing micromechanical deformation mechanism of the composite [8, 9]. The amount of the polymer bonded in the interphase depends on the size of the contact surface between the polymer and the filler, *i.e.*, on the specific surface area of the filler and on the strength of the interaction. The thickness and properties of the interlayer cannot be measured directly. Spectroscopic methods may indicate the chemical composition of the interlayer or the limited mobility of the bonded chains [10–13], which occasionally can be detected by dynamic mechanical spectroscopy [14]. Recently, atomic force microscopy was used to characterize the interphase in fiber-reinforced composites, but the results need further considerations and checking [15, 16]. Moreover, the use of the technique is rather difficult for particulate-filled polymers. As a consequence, indirect methods and modeling are applied for the estimation of interfacial interactions and the thickness of the interphase [5, 16].

In particulate-filled polymers, interfacial adhesion of the polymer matrix and the filler results mostly from secondary van der Waals forces. Several forces may act between the components, including dispersion, dipole-dipole, induced dipole, etc. forces [2, 17]. The strength of the interaction is usually estimated by the reversible work of adhesion ( $W_{AB}$ ), which can be determined by one of two approaches. Dispersion forces are taken into account in both, while further interactions occurring in polar systems are described by dipole-dipole interactions in one [18] and by acid-base interactions in the other [18–20]. In an earlier paper, we found close correlation between the thickness of the interphase and the reversible work of adhesion calculated from dispersion and dipole-dipole interactions [21].  $\text{CaCO}_3$  was used as filler in that study and it was introduced into neutral and acidic polymers where significant attraction may develop between the components. However, in basic polymers unfavorable interactions may occur which might not be described by the approach used earlier.

The goal of this study was to check the effect of specific interactions on interphase formation in particulate-filled polymers. Uncoated and surface-treated  $\text{CaCO}_3$  was introduced both into acidic and basic polymers, and the reversible work of adhesion was calculated by both

approaches mentioned above. The thickness of the interphase was deduced from mechanical properties and compared with  $W_{AB}$ . The results obtained by the different approaches are discussed in the paper.

## BACKGROUND

Previous studies proved that in particulate-filled polymers the best estimate for the strength of interfacial interaction is the reversible work of adhesion [2, 22]. This quantity can be divided into two components,

$$W_{AB} = W_{AB}^d + W_{AB}^{sp}, \quad (1)$$

where  $d$  and  $sp$  indicate the dispersion and the specific component of  $W_{AB}$ . According to Fowkes [23, 24], the dispersion component is calculated by

$$W_{AB}^d = 2(\gamma_p^d \gamma_f^d)^{1/2}, \quad (2)$$

where  $\gamma_p^d$  and  $\gamma_f^d$  are the dispersion components of the surface tension of the polymer and the filler, and subscripts  $p$  and  $f$  stand for the polymer and the filler, respectively. Equation (2) is used for the calculation of the dispersion component of  $W_{AB}$  by both theories.

The two approaches differ in the determination of the specific component of the work of adhesion. If we assume that dipole-dipole interactions define adhesion,  $W_{AB}^{sp}$  can be calculated as

$$W_{AB}^{sp} = W_{AB}^p = 2(\gamma_p^p \gamma_f^p)^{1/2}, \quad (3)$$

where superscript  $p$  indicates the dipole-dipole component of surface tension. If acid-base interactions develop between the components, the specific part of the work of adhesion can be determined as [19, 20]

$$W_{AB}^{sp} = W_{AB}^{ab} = n f \Delta H^{ab}, \quad (4)$$

where  $n$  is the surface concentration of interaction sites,  $f$  is a conversion factor to transform enthalpy to free energy, and  $\Delta H^{ab}$  is the heat of acid-base interaction. According to Guttmann [25] this latter quantity can be determined from acceptor ( $AN$ ) and donor ( $DN$ ) numbers by the following correlation:

$$\Delta H^{ab} = (AN_f DN_p + AN_p DN_f)/100. \quad (5)$$

The strength of interaction calculated by the two approaches must be compared with its effect, with the thickness of the interphase

forming spontaneously in the composite. This quantity can be derived from mechanical properties by a simple semiempirical model developed earlier [6, 7]. This model expresses the composition dependence of tensile strength in the following way [7]:

$$\sigma_T = \sigma_{T0} \lambda^m \frac{1 - \varphi}{1 + 2.5 \varphi} \exp(B\varphi), \quad (6)$$

where  $\sigma_T$  and  $\sigma_{T0}$  are the true tensile strength of the composite and the matrix, respectively ( $\sigma_T = \sigma\lambda$ , where  $\sigma$  is the measured engineering tensile strength),  $\lambda$  is relative elongation ( $\lambda = L/L_0$ , where  $L_0$  is gauge length and  $L$  the length measured at the moment of failure),  $m$  expresses the strain-hardening character of the polymer,  $\varphi$  is the volume fraction of the filler in the composite, and  $B$  expresses the load-bearing capacity of the filler, *i.e.*, it is closely related to interaction.  $B$  depends both on the thickness and the strength of the interphase:

$$B = (1 + A_f \rho_f \ell) \ln \frac{\sigma_{Ti}}{\sigma_{T0}}, \quad (7)$$

where  $A_f$  and  $\rho_f$  are the specific surface area and density of the filler,  $\ell$  is the thickness, and  $\sigma_{Ti}$  is the strength of the interface. Further details about the model can be found elsewhere [6, 7, 26]. If the tensile strength of the composites is determined as a function of composition, parameter  $B$  can be determined easily and the use of fillers with the same chemical composition but different specific surface area leads to the thickness of the interphase through Equation (7).

## EXPERIMENTAL

CaCO<sub>3</sub> fillers obtained from various sources were used as fillers in the study. Their most important characteristics are listed in Table 1. Polyethylene (PE) (Tipolen FB 2223, TVK, Hungary), Polypropylene (PP) (Tipplen H 543F, TVK, Hungary), unplasticized Poly(vinyl chloride) (PVC) (PVC 5061, BC, Hungary), and Poly(methyl methacrylate) (PMMA) (Diacon APAL, ICI, UK) were used as matrices. Filler content was changed between 0 and 0.3 volume fraction in 0.05 volume fraction steps. The composites were prepared in an internal mixer. Set temperatures were 170°C for LDPE and 190°C for the other polymers. Homogenization was carried out at 50 rpm for 10 min, then 1 mm thick plates were compression molded from the composites at 170°C (LDPE) and 190°C (PP, PVC, PMMA). Tensile bars were cut from the plates for further testing.

The surface tension of the polymers was determined by contact angle measurements. Four liquids were used ( $\alpha$ -bromonaphtalene,

**TABLE 1** Origin and Characteristics of the Ground  $\text{CaCO}_3$  Fillers Used in the Study

Trade name	Abbreviation	Producer	Particle size ( $\mu\text{m}$ )	Specific surface ( $\text{m}^2/\text{g}$ )
Calcilit 100	C100	Alpha Calcit	120	0.5
Millicarb	M	Omya	3.6	2.2
Omyacarb 2 GU	2GU	Omya	2.5	3.6
Polcarb	P	ECC (Imerys)	1.3	5.0

water, ethylene glycol, formamide), and both the dispersion and the polar component of  $\gamma_p$  were calculated. The surface tension of the fillers ( $\gamma_f$ ) was determined by finite concentration IGC. The dispersion component was derived from adsorption isotherms measured with n-octane, while benzene was used to determine its polar component. The details of the measurement can be found in Fekete et al. [27]. The donor and acceptor numbers published by Schreiber [28] were used for the calculation of  $\Delta H^{ab}$  and  $W_{AB}^{ab}$ .

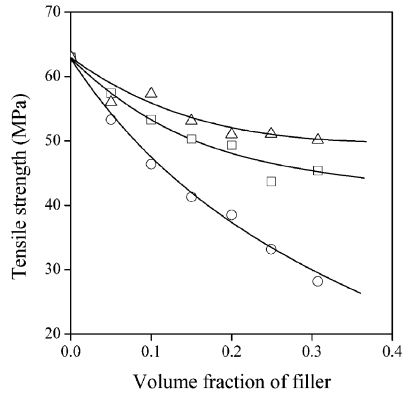
The tensile properties of the matrix polymers and the composites were measured at 5 mm/min cross-head speed and 50 mm gauge length using a Zwick 1445 machine. Young's modulus, yield stress and strain, as well as tensile strength ( $\sigma$ ) and elongation-at-break ( $\varepsilon$ ) were derived from measured force *versus* elongation traces. Only tensile strength data are presented in this paper, since they were used for the determination of interphase thickness.

## RESULTS

The results are presented in three sections. First, those obtained on the uncoated filler are reported, then the effect of surface treatment on interaction is discussed. The third section compares interphase thicknesses obtained in composites prepared with coated and uncoated fillers and gives a tentative explanation for the observed differences.

### Uncoated Filler

The determination of interphase thickness from tensile yield stress is more reliable than from tensile strength, since the standard deviation of yield stress is smaller and the strain hardening of the polymer can be neglected. As mentioned before, a close linear correlation was found between  $W_{AB}$  and the interphase thickness derived from yield stress in our earlier study [21, 22]. Unfortunately, the composites prepared from the polymer—drawn into this study due to its definite basicity,



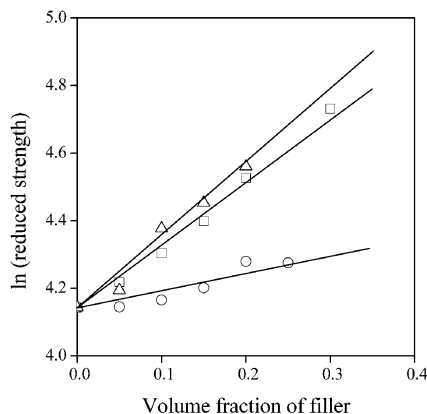
**FIGURE 1** Composition dependence of the tensile strength of PMMA/CaCO<sub>3</sub> composites containing fillers with different specific surface area: (○) 0.5 m<sup>2</sup>/g, (□) 3.6 m<sup>2</sup>/g, (△) 5 m<sup>2</sup>/g.

PMMA—fail without yielding, and thus tensile strength had to be used for the calculation of interlayer thickness. Figure 1 shows the composition dependence of tensile strength of PMMA composites prepared with three fillers. The effect of the changing specific surface area of the filler is clearly seen in the figure. The amount of the polymer bonded in the interlayer increases with increasing  $A_f$ . The thickness of the interphase is assumed to be the same, since the composites were prepared from CaCO<sub>3</sub> and the same polymer in all cases. Parameter  $B$  can be derived from the primary data by simple calculations. Reduced tensile strength can be expressed from Equation (6) by eliminating the effect of changing effective load-bearing cross-section of the matrix and the strain-hardening tendency of the polymer:

$$\sigma_{\text{Tred}} = \frac{\sigma_T}{\lambda^m} \frac{1 + 2.5\varphi}{1 - \varphi} = \sigma_{T0} \exp(B\varphi). \quad (8)$$

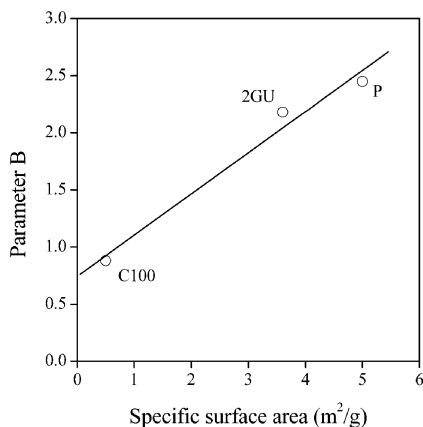
If we plot the natural logarithm of  $\sigma_{\text{Tred}}$  as a function of filler content, a straight line should be obtained with the slope of  $B$ . The results of Figure 1 are plotted in this way in Figure 2. A very good linear correlation is obtained in each case, thus parameter  $B$  characterizing stress transfer and interaction can be determined with a high accuracy. The slope is changing with the specific surface area of the filler, as expected.

The thickness of the interphase can be determined from the  $B$  values by using Equation (7). According to the equation,  $B$  should



**FIGURE 2** Linear representation of the data of Figure 1 according to Equation (8); effect of specific surface area.

show linear dependence on  $A_f$ . The correlation is presented in Figure 3. A straight line is obtained, indeed, proving the validity of the approach. The  $B$  values obtained for all combinations of fillers and polymers is compiled in Table 2 together with the interphase thicknesses derived from them. The largest interlayer thickness was obtained for PVC as expected. The interaction of this acidic polymer with the basic filler is strong, leading to a thick interphase. A much thinner interlayer develops in the apolar polymers, in PP and PE.



**FIGURE 3** Determination of interphase thickness according to Equation (7) for PMMA/CaCO<sub>3</sub> composites.



**TABLE 2** *B* Values and Interlayer Thicknesses (*l*) Determined for Composites Containing Uncoated Fillers

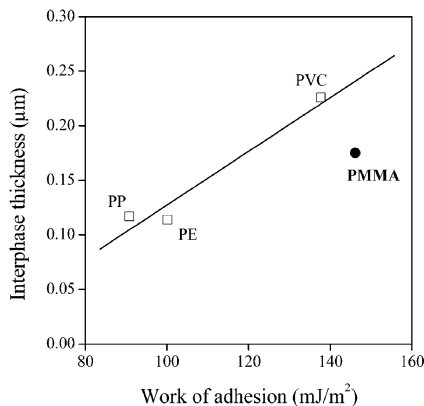
Polymer	Parameter <i>B</i> for filler			<i>l</i> (μm)
	Calcilit 100	Omyacarb 2 GU	Polcarb	
PMMA	0.88	2.18	2.45	0.175
PE	3.44	6.07	—	0.114
PP	1.00	1.84	—	0.117
PVC	1.18	2.87	3.37	0.226

However, the influence of specific interactions cannot be determined unambiguously from the data in the table; we must compare the thickness of the interphase to the strength of the interaction.

The reversible work of adhesion values calculated according to the two approaches presented in a previous section are listed in Table 3.  $W_{AB}$  is small for the two polyolefins; much larger values were obtained for PMMA and PVC. Attention must be called here to the fact that considerably differing interactions are calculated by the two methods for the two polar polymers. When dipole-dipole interactions are taken into account, the adhesion of PMMA to the filler is stronger than that of PVC, while the latter polymer should adhere better to  $\text{CaCO}_3$  if acid-base interactions dominate in the composite. The correlation of interlayer thickness and the reversible work of adhesion is plotted in Figure 4 for the case when we assume that dipole-dipole interactions determine the strength of adhesion and interphase formation. A good linear correlation is obtained for the neutral and acidic polymers just as before [21, 22], but the value obtained for PMMA considerably deviates from it. If layer thickness is plotted against  $W_{AB}$  calculated from acid-base interactions (Figure 5), all the points, including that of

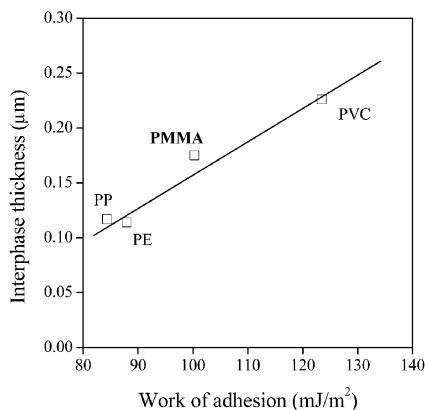
**TABLE 3** Comparison of Reversible Work of Adhesion ( $W_{AB}$ ) Values Calculated by the Two Approaches (See Equations (1) to (5))

Polymer	Work of adhesion, $W_{AB}$ (mJ/m <sup>2</sup> )	
	Dipole-dipole	Acid-base
PP	90.75	84.33
PE	100.80	87.93
PVC	137.65	123.42
PMMA	146.05	100.27



**FIGURE 4** Correlation of interphase thickness and  $W_{AB}$  calculated by considering dipole-dipole interactions.

PMMA, fit a general correlation; significant deviation from it cannot be observed. The two figures and the results presented in them clearly prove that in particulate-filled polymers acid-base interactions play a significant role in interphase formation and thus also in the determination of composite properties. Finally, attention must be called here to the fact that because of the indirect character of the determination of interphase thickness the obtained result depends on the method used. Dissolution experiments [29, 30] and atomistic modeling [31] yielded interlayer thicknesses of a few nanometers, while the use of



**FIGURE 5** Effect of acid-base interactions on the thickness of the interlayer.

**TABLE 4** Comparison of Interphase Thicknesses Calculated for Composites Containing Uncoated and Coated Fillers

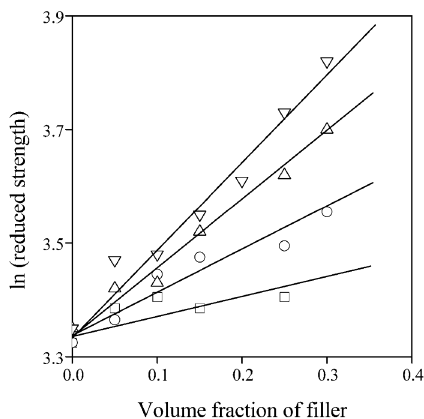
Polymer	Interphase thickness ( $\mu\text{m}$ ) for filler	
	Uncoated	Coated
PP	0.117	0.150
PE	0.114	0.183
PMMA	0.175	0.386
PVC	0.226	0.400

mechanical properties leads to thicknesses in the micrometer range [32–34], just as in the present case (see Tables 2 and 4). The range of secondary forces is short and they affect only a small volume (dissolution, modeling), but in the case of large deformations (tensile) a larger volume is involved because of the decreased mobility of the chains attached to the filler surface [2]. Nevertheless, the same factors determine the thickness of the interphase in both cases, as shown by the present paper.

### Surface Treatment

$\text{CaCO}_3$  fillers are routinely treated with stearic acid to decrease aggregation. The treatment results in decreased interaction with the matrix, *i.e.*, smaller surface tension and work of adhesion [5]. As a consequence, in composites containing the treated filler the role of acid-base interaction should decrease compared with those prepared with uncoated  $\text{CaCO}_3$ , and the interphase should be thinner as well. To check these assumptions, the fillers were coated with stearic acid and composites were prepared with the coated filler. The amount of stearic acid was selected to give 100% surface coverage, which was identified as the amount of irreversibly bonded surfactant [2, 27, 35].

The reduced tensile strength of PP composites containing the coated filler is plotted in Figure 6 in the linear representation. Straight lines are obtained again with relatively small deviations, which indicates that the semiempirical model used for the description of the composition dependence of tensile strength can be used also for the composites containing the coated filler. The data presented in the figure also demonstrate well the effect of the specific surface area of the filler. The slope of the straight lines, *i.e.*, parameter  $B$ , increases with increasing  $A_f$ .  $B$  parameters obtained for the various composites are collected in Table 5. In order to facilitate comparison the values derived for



**FIGURE 6** Reduced tensile strength plotted against filler content for PP composites prepared with coated fillers of different specific surface area: (□)  $0.5 \text{ m}^2/\text{g}$ , (○)  $2.2 \text{ m}^2/\text{g}$ , (△)  $3.6 \text{ m}^2/\text{g}$ , (▽)  $5 \text{ m}^2/\text{g}$ .

composites containing the uncoated filler are also listed in the table. The direct evaluation of the results is rather difficult, and far-reaching conclusions about interfacial interactions cannot be drawn from them.

**TABLE 5** Effect of Surface Treatment on Stress Transfer and Interaction in Particulate-Filled Composites; Comparison of Coated and Uncoated Fillers

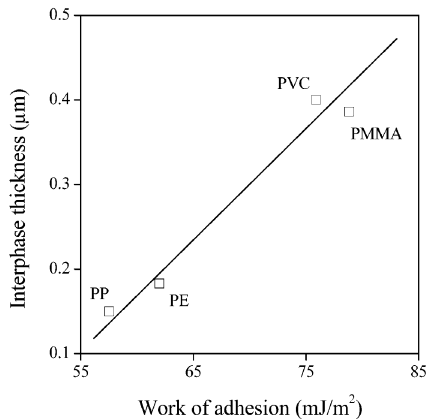
Polymer	Filler	Parameter <i>B</i> for fillers	
		Uncoated	Coated
PMMA	Calcilit 100	0.88	0.46
	Millicarb	—	—
	Omyacarb 2 GU	2.18	1.74
	Polcarb	2.45	1.98
PE	Calcilit 100	3.44	1.99
	Millicarb	—	1.87
	Omyacarb 2 GU	6.07	4.04
	Polcarb	—	4.50
PP	Calcilit 100	1.00	0.23
	Millicarb	—	0.71
	Omyacarb 2 GU	1.84	1.12
	Polcarb	—	1.40
PVC	Calcilit 100	1.18	—
	Millicarb	—	1.38
	Omyacarb 2 GU	2.87	2.00
	Polcarb	3.37	2.21

We can establish, however, that surface treatment decreases the strength of the interaction. Indeed, parameter  $B$  is always smaller for the composite containing the treated filler than for the one prepared with uncoated  $\text{CaCO}_3$ .

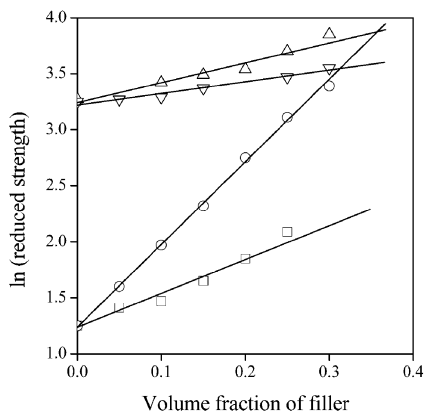
In order to check the possible effect of acid-base interactions, interphase thicknesses determined for composites containing the coated filler are plotted against the reversible work of adhesion in Figure 7. The strength of interaction, *i.e.*,  $W_{AB}$ , was calculated by assuming that only dipole-dipole interactions act in the composite. A straight line is obtained with very small deviation from the general tendency; the point obtained for PMMA also fits the line. This proves that the role of acid-base interactions is much smaller for the treated filler, indeed. We must note here, though, that acceptor and donor numbers are not available for the coated filler, thus  $W_{AB}^{ab}$  could not be calculated in order to check the validity of the second approach. These values must be determined in the future in order to verify the conclusions drawn here.

## Comparison and Discussion

The results presented in the previous sections corroborated our earlier experience and preliminary assumption that surface treatment leads to a decrease in the strength of interaction. This conclusion is further supported by Figure 8, where the reduced tensile strength of several



**FIGURE 7** Effect of the strength of interaction on the thickness of the interlayer for composites prepared with coated fillers; lack of acid-base interactions.



**FIGURE 8** Influence of matrix properties and surface treatment on the load-bearing capacity of the filler (parameter  $B$ ); (○) PE/uncoated  $\text{CaCO}_3$ , (□) PE/coated filler, (△) PP/uncoated  $\text{CaCO}_3$ , (▽) PP/coated filler. The filler was Omycarb 2GU in all four cases.

composites is plotted as a function of composition in the linear representation. The figure shows that the extent of stress transfer (*i.e.*, interaction) expressed by parameter  $B$  depends on the properties of the matrix polymer and on the coating. The surface treatment of the filler by stearic acid results in a decrease of surface tension, work of adhesion, and parameter  $B$ , as expected. On the other hand, our other assumption that the thickness of the interlayer also decreases as a consequence of treatment was contradicted by the results, as shown by the values listed in Table 4. The interphase thickness obtained in the composites containing the treated filler significantly exceeds the values determined with uncoated fillers. This result needs further consideration and explanation.

We may assume that the long aliphatic chains of the fatty acid also take part in the formation of the interlayer. At 100% surface coverage they are oriented vertically to the surface [22, 27] and even the interdiffusion of the surfactant and the matrix might occur. However, if interdiffusion leads to the development of entanglements, it should improve stress transfer, which would lead to increased strength. The results presented in Figure 8 and Table 5 strongly contradict this assumption; parameter  $B$  always decreased as an effect of surface treatment. Moreover, the stearic acid chain is much shorter than the difference in the thickness of the interlayers determined in the composites containing the two kinds of fillers, thus it cannot contribute to the increased layer thickness either. Although interdiffusion might

occur, it definitely does not lead to the formation of entanglements and improved stress transfer.

Another explanation for the phenomenon may be supplied by the analysis of the simple theory used for the calculation of interphase thickness. In addition to the thickness of the interphase, Equation (7) contains other parameters as well. The density of the filler is naturally constant, but the properties of the interlayer may change significantly as an effect of treatment. Because of the weaker interaction and possible interdiffusion, a looser, less stiff interphase may form in composites containing the coated filler. Because of the looser structure and the lower stresses developing in the composite, chains attached to the surface of the filler may have increased deformability, and thus larger apparent interlayer thicknesses are obtained as a consequence. Naturally, both of the above-presented tentative explanations need verification; further study must be carried out to reveal the reason for increased interlayer thickness in the composites containing the treated filler.

## CONCLUSIONS

Experiments carried out with polymer matrices of various acid-base characters proved that such interactions play an important role in the development of a spontaneously forming interphase in particulate-filled polymers. If the acid-base character of the filler and the polymer is similar, only the consideration of acid-base interactions gives an acceptable estimate of interfacial adhesion. The strength of this latter is determined by the joint effect of dispersion forces and specific interactions. Stronger interfacial adhesion leads to an increase in the thickness of the polymer layer with decreased mobility. The treatment of  $\text{CaCO}_3$  with an aliphatic fatty acid decreases the strength of interaction and changes both the thickness and the properties of the interphase. Acid-base interactions are less important in composites containing coated fillers due to their neutral surface character. In such cases, the consideration of dipole-dipole interactions, which can be easily obtained from infinite concentration IGC measurements, can be also applied for the estimation of interfacial interactions. Further experiments must be carried out to confirm the conclusions presented here. The changes in the thickness and properties of the interlayer as an effect of surface treatment must be studied in more detail as well.

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