

Quantitative estimation of the reinforcing effect of layered silicates in PP nanocomposites

László Százdi^{a,b}, Béla Pukánszky Jr^{a,b,c}, G. Julius Vancso^c, Béla Pukánszky^{a,b,*}

^a Department of Plastics and Rubber Technology, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 91, Hungary

^b Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary

^c Department of Materials Science and Technology of Polymers, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 Enschede, The Netherlands

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Abstract

Various polypropylene/layered silicate composites were prepared with different silicate contents. Montmorillonites with and without organophilization as well as three maleinated polypropylenes were used to change the extent of exfoliation and hence the properties of the composites. Structure was characterized by X-ray diffraction (XRD), scanning (SEM) as well as transmission electron microscopy (TEM) and tensile properties were also measured. The analysis of the tensile yield stress values of a large number of composites showed a broad range of variation in mechanical properties. XRD and TEM results do not reflect the differences in properties and they usually do not give quantitative information about the extent of exfoliation either. PP/clay composites containing maleinated PP, which do not exhibit a silicate reflection in XRD, may have very poor mechanical properties indicating small extent of exfoliation. The composition dependence of tensile yield stress of these composites may be described and evaluated quantitatively by a simple model developed earlier for particulate filled polymers. The use of a few simple assumptions most of which are supported by previous results allows us to estimate the extent of exfoliation quantitatively. The tensile yield stress of about 40 composites was analyzed with the model. Some of the composites were prepared by us, while results on others were taken from papers published in the literature. The analysis indicated that the extent of exfoliation is very low in most composites; it reaches maximum 8% of the theoretically possible value in the best case. This result is in agreement with our observation that complete exfoliation can be seldom reached in thermoplastic/clay composites; the structure is complex and hierarchical including large particles and individual silicate layers. The results prove that further efforts must be done to increase the extent of exfoliation in order to achieve reinforcement levels forecasted earlier.

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1. Introduction

Layered silicate polymer nanocomposites created much interest recently. Practically all papers published on this new class of materials emphasize their potential advantages in various applications [1] including high modulus, increased strength and heat resistance, decreased gas permeability and flammability, etc. [2,3]. One of their potential advantages is high level of reinforcement at low silicate content leading to stronger and lighter parts [2–10]. The basic idea behind this

expectation is the extremely large interface created by the exfoliation of the layered silicate, which is a precondition of improved properties [11,12]. A large contact surface coupled with strong interaction of the components must lead to a significant increase in strength and stiffness [13–19]. As a consequence, good interaction is expected to exist between the finely dispersed silicate layers and the polymer matrix [1,4,20–22]. Naturally, orientation of the platelets parallel to the direction of the load is an additional condition to achieve considerable reinforcement [1]. Although an extremely large number of papers are published on the structure, properties, and advantages of layered silicate nanocomposites, very few of them contain information, which unambiguously proves the validity of this concept.

Among the numerous papers published on these materials only a few present information about composite properties measured at large deformations. Dynamic mechanical spectra

* Corresponding author. Address: Department of Plastics and Rubber Technology, Budapest University of Technology and Economics, H-1521 Budapest, P.O. Box 91, Hungary. Fax: +36 1 463 3474.

E-mail address: bpukanszky@mail.bme.hu (B. Pukánszky).

and modulus values are published in numerous publications [23–31], since stiffness is expected to be the best indicator of the extent of reinforcement [21]. Several, rather successful attempts were made to model the modulus of layered silicate nanocomposites [8,15,32–34]. Structure is taken into account by the aspect ratio of the silicate particles and the extent of exfoliation is estimated from the results [35]. All these calculations assume that property improvement generally and reinforcement particularly is proportional to and increases with the extent of exfoliation [8,15,21,32–35]. However, stiffness always increases when inorganic fillers are added to the polymer [36–38]. Moreover, models describing the composition dependence of stiffness rarely include particle size, specific surface area or interfacial interaction. As a consequence, the extent of exfoliation estimated in this way may not give information about the strength of the composites. Properties measured at larger deformations, like tensile yield stress, tensile strength, or fracture resistance, are more sensitive to structure and interaction [39–41], but reports containing such results for layered silicate nanocomposites are scarce. Among the more than 100 papers collected by us on layered silicate PP nanocomposites, only about eight contained information about tensile characteristics measured at more than one silicate content.

PP nanocomposites cannot be prepared by the simple mixing of the polymer and the organophilic silicate; only micro-composites can be created in this way. Maleinated polypropylene (MAPP) is added in order to improve component interaction leading to a more homogeneous structure with an enhanced degree of exfoliation [19,23–25,42–48]. In such composites the X-ray diffraction (XRD) peak, which is characteristic for the silicate disappears from the diffractogram and individual silicate layers can be detected by transmission electron microscopy (TEM) [23,25,47–49]. The strength and stiffness of the composites also surpass the corresponding properties of microcomposites indicating stronger interaction and possible exfoliation, which are prerequisites for improved reinforcement [45,47].

In an attempt to estimate the reinforcing effect of layered silicates in PP matrices, a relatively large number of PP composites containing neither sodium or organophilic montmorillonite were prepared and investigated in this study. The silicates were organophilized with different surfactants and MAPP was added to some of the composites to promote exfoliation. We also tried to collect and evaluate data available in the open literature. Using a simple model developed earlier [39,40], we compared the load-bearing capacity of various silicates in different PP matrices and estimated the extent of reinforcement using the theoretical surface area of completely exfoliated silicate [5,50,51].

2. Background

The mechanical properties of composites, including tensile yield stress, depend on composition, component properties, structure and interaction [19,41–48,52]. Usually, homogeneous distribution of the dispersed particles is assumed in particulate

filled composites. If the particles have anisometric geometry, their orientation and orientation distribution must be also taken into account in order to estimate reinforcement. The effect of interaction depends on its strength and on the size of the contact surface. Strong interaction is assumed to prevail in polymer/layered silicate composites [1,4,20,22] in spite of the fact that the surface of the silicate is covered with a surfactant. Such treatment was shown to decrease interaction significantly in all composites containing traditional fillers [53–55]. On the other hand, the interface between the phases can be extremely large in nanocomposites, the specific surface area of the silicate is about 750 m²/g [5,50,51] compared to the 3–5 m²/g value of usual particulate fillers [56–59], which may compensate the effect of any occasional decrease in interaction.

A simple model was developed earlier to describe the composition dependence of the tensile yield stress of particulate filled composites [39,40,60]. The model is based on the fact that an interphase forms spontaneously in composites and it assumes that yield stress changes proportionally to its actual value as a function of composition. Accordingly, the composition dependence of tensile yield stress can be described by the following equation [39,40,60]

$$\sigma_y = \sigma_{y0} \frac{1 - \varphi}{1 + 2.5\varphi} \exp(B\varphi) \quad (1)$$

where σ_y and σ_{y0} are the yield stress of the composite and the matrix, respectively, φ the volume fraction of the filler in the composite and B is related to the load carried by the dispersed component, i.e. it depends on interaction [39–41,53,54]. The term $(1 - \varphi)/(1 + 2.5\varphi)$ expresses the effective load-bearing cross-section of the matrix. At zero interaction all the load is carried by the polymer and the load-bearing cross-section decreases with increasing filler content. The same correlation can be used to describe the composition dependence of tensile strength, if the elongation of the composite is small, usually less than 100% [40].

The value of parameter B depends on all factors influencing the load-bearing capacity of the filler, i.e. on the strength of interaction and on the size of the contact surface. The effect of these factors on B is expressed as

$$B = (1 + A_f \rho_f l) \ln \frac{\sigma_{yi}}{\sigma_{y0}} \quad (2)$$

where A_f is the specific surface area of the filler (contact surface), ρ_f is its density, while l and σ_{yi} are the thickness and corresponding property of the interphase. The latter two parameters were shown to depend on the strength of matrix/filler interaction [61,62]. A detailed study of numerous composites proved that in composites containing stiff fillers or reinforcements a hard interphase forms, which increases the load-bearing capacity of the filler and contributes to reinforcement [63–65]. Only the formation of such a hard interphase explains that composite yield stresses exceeding the yield stress of the matrix are achieved occasionally [39]. Moreover, we must assume that such an interphase forms also in layered silicate nanocomposites leading to the observed

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