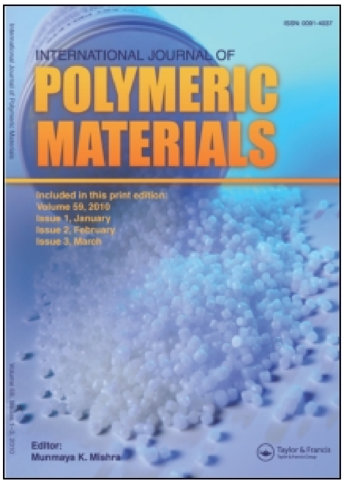

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Effects of the Treatment of $Al(OH)_3$ by a Silane Coupling Agent on the Tensile Properties of PVC/$Al(OH)_3$ Composite

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The present work deals with the study of a composite based on poly(vinyl chloride) (PVC) and aluminum hydroxide ($Al(OH)_3$) which is treated with different concentrations of the silane coupling agent N-(2-aminoethyl)-3-aminopropyltrimethoxysilane.

The composites containing untreated $Al(OH)_3$ and those treated with the coupling agent were prepared by melt mixing using a two-roll mill.

Analysis of the treated filler by means of Fourier Transform Infrared spectroscopy (FTIR) showed the formation of oligoaminosilanes resulting from the condensation of the silane coupling agent.

The tensile properties of the PVC/$Al(OH)_3$ composite reflected the effect of the addition of the mineral filler and also the influence of the chemical treatment on the interfacial adhesion. The incorporation of aluminum hydroxide into PVC resulted in an increase of Young's modulus and the yield stress.

From the calculation of a parameter B which was used to quantify the state of adhesion between the polymeric matrix and the filler, it was concluded that the surface chemical treatment of the filler with the silane coupling agent leads to higher reinforcement as a result of the interfacial interactions developed between PVC and $Al(OH)_3$.

Keywords: $Al(OH)_3$, composite, mechanical properties, PVC, silane coupling agent

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INTRODUCTION

Poly(vinyl chloride) (PVC)-based materials have been widely used in various application fields. But because of the PVC's poor thermal stability and low impact resistance, researchers have carried out many studies in order to modify and reinforce it through the addition of rubbers and fillers [1–3]. Composites based on PVC reinforced with calcium carbonate, kaolin, silica, and clay have been the subject of many works [4–6]. The addition of particulate fillers not only reduces the cost of the final product but also imparts certain rheological and mechanical properties. In order for calcium carbonate to act as a reinforcing filler it has to be treated. This chemical treatment can, in fact, improve the impact resistance of PVC and insure a good distribution through the matrix [7].

It has been established that the mechanical behavior of composite materials based on a thermoplastic matrix and an inorganic reinforcement depends much on the interactions that develop between the constituents of the composite [8]. The filler surface treatment seems to be an efficient way to improve the compatibility of the polymer and the filler [9]. In this context, Jancar et al. showed that the absence of adhesion between polypropylene (PP) and calcium carbonate ($CaCO_3$) leads to decrease in the yield stress of PP/$CaCO_3$ composites, but an improvement in the mechanical properties can be obtained through the addition of maleic anhydride-grafted polypropylene as a compatibilizer, which enhances the interactions, between PP and $CaCO_3$ [10]. Doufnoune and colleagues showed that the modification of $CaCO_3$ surface by a titanate coupling agent resulted in a better adhesion between $CaCO_3$ and PVC as evidenced by increases in Young's modulus and yield stress of PVC/$CaCO_3$ composite [11]. In another work, Doufnoune et al. found that the addition of $CaCO_3$ treated with silane coupling agents to PP improved the mechanical properties of PP/$CaCO_3$ composites [12]. Wu et al. found that the addition of $CaCO_3$ in the presence of chlorinated polyethylene resulted in an increase of both tensile strength and impact resistance of PVC/$CaCO_3$ composites [13]. Zhou et al. studied the relation between the thickness of the PMMA layer deposited on the talc surface and the mechanical properties of PVC/PMMA-g-talc composites and found that the PMMA grafted talc particles improve the dispersion of the filler particles throughout the PVC matrix and increase the interfacial adhesion [14]. Chen et al. also reported that the grafting of polymethylmethacrylate on $CaCO_3$ nanoparticles resulted in a strong interfacial adhesion as well as an improvement of the mechanical properties of PVC/$CaCO_3$ composites [15].

The objective of this work is to study the effect of another type of mineral filler, namely aluminum hydroxide ($Al(OH)_3$), and its surface chemical treatment with a silane coupling agent on the mechanical properties of PVC-based composites.

EXPERIMENTAL

Materials

In this study a plasticized PVC formulation was prepared using the composition shown in Table 1.

The chemical composition of the aluminum hydroxide filler used is shown in Table 2.

The silane coupling agent used is N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, and was supplied by Dow Corning Corporation under the trade name of Z-6020.

Filler Surface Treatment

The chemical treatment of aluminum hydroxide filler was carried out by first dissolving the silane coupling agent, at the three concentrations of 0.4, 0.6, and 0.8% by weight with respect to the total weight of the filler, in distilled water and adjusting the pH of the solution to a value of 3 by means of acetic acid. The filler was then dispersed in these solutions and the mixtures were agitated for one hour to ensure a thorough impregnation. Finally, and in order to condensate the silane groups on the filler surface, the suspensions were washed and then filtered and dried at 105°C.

TABLE 1 Composition of the Plasticized PVC Formulation

Ingredient	phr	Supplier
PVC (grade 4000 M): K value = 67	100	ENIP – Algeria
Plasticizer (Plastimed 2001): Di-2-ethyl hexyl phtalate	30	SGP – Tunisia
Lubricant (KGOAD): Stearic acid	0.5	Henkel – Düsseldorf, Germany
Stabilizer (New stab): Barium/Cadmium/Zinc	2.5	EXIM – Germany
Filler: $Al(OH)_3$: Particle size = 40 µm, surface area = 0.5 m^2/g (Blaine method)	0–24	DIPROCHIM – Algeria

TABLE 2 Chemical Composition of the $Al(OH)_3$ Filler

Ingredient	%
Al_2O_3	63.13
SiO_2	2.92
CaO	1.62
Fe_2O_3	Traces
MgO	Traces
H_2O	30.26

Composite Material Preparation

The different ingredients for each formulation except the filler were first dry-blended for 10 min with PVC. Then melt mixing was carried out using a two-roll mill heated to 170°C by dispersing the filler onto the premelted batch and mixing for 10 min before sheeting out 2 mm-thick slabs.

Fourier Transform Infrared Spectroscopy (FTIR)

In order to confirm the chemical treatment of $Al(OH)_3$ surface by the silane coupling agent, a FTIR analysis was carried out. The untreated and treated samples were prepared using the KBr method: A small amount of the filler was mixed with potassium bromide, and the mixture was then compacted into thin pellets using a hydraulic press. PVC/$Al(OH)_3$ samples were also pressed into thin films in a hydraulic press at 200 Kg/cm^2 for about 5 min.

The infrared spectra were obtained using a Perkin Elmer apparatus.

Tensile Testing

Samples for tensile testing were cut out, in the longitudinal direction from the slabs obtained with the two-roll mill. Measurements were carried out, following ASTM D 638-72 procedure and using a Zwick instrument (model 1445), at a crosshead speed of 20 mm/min.

RESULTS AND DISCUSSION

Filler Treatment Characterization

Figure 1 shows the infrared spectra for the coupling agent (a), untreated filler (b), and that for aluminum hydroxide treated with 0.8% Z-6020 silane coupling agent (c). Two weak bands at 2924 cm^{-1}

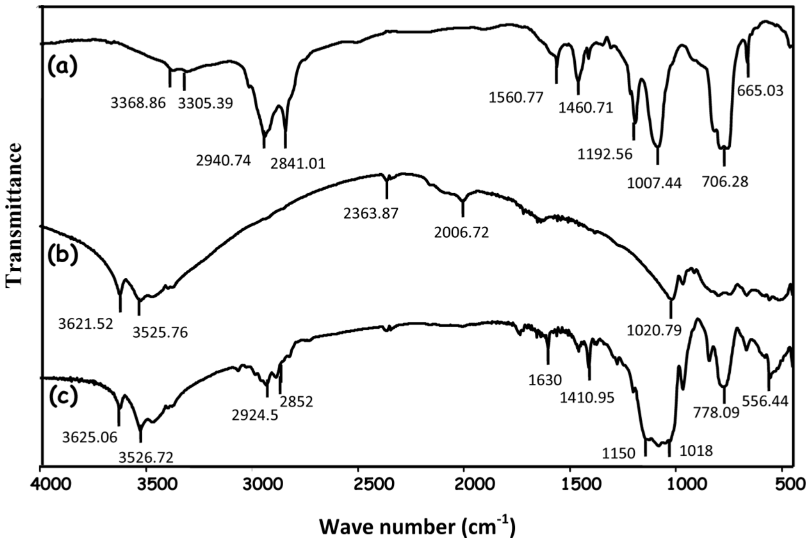

FIGURE 1 FTIR spectrum of (**a**) Z-6020 coupling agent, (**b**) untreated $Al(OH)_3$, (**c**) $Al(OH)_3$ treated with 0.8% of Z-6020.

and $2852\,cm^{-1}$ can be seen on spectrum (c), and correspond to the C–H bond stretch of the aminoethyl or aminopropyl segment of the silane coupling agent. A strong band situated between $1150\,cm^{-1}$ and $1018\,cm^{-1}$ can be distinguished and is attributed to the Si-O-Si bonds formed as a result of the condensation of the silane to a polysiloxane. On the other hand, the presence of the C=O group of the ester functional group which is manifested by the band at $1630\,cm^{-1}$, suggests that the methyl alcohol resulting from the hydrolysis of the aminosilane was not fully created.

Tensile Properties

The stress/elongation curves for PVC composites based on untreated aluminum hydroxide and those treated with 0.8% coupling agent are shown in Figures 2 and 3, respectively. These plots show that the deformations are lower for the composites than those for the matrix. This seems to be the consequence of the introduction of nondeformable solid particles. A slight improvement in the stress at break is noted for the composites prepared from the aluminum hydroxide treated with 0.8% of the Z-6020 coupling agent. This is attributed to the compatibility imparted by the organometallic molecules that resulted in more interfacial adhesion between PVC and $Al(OH)_3$.

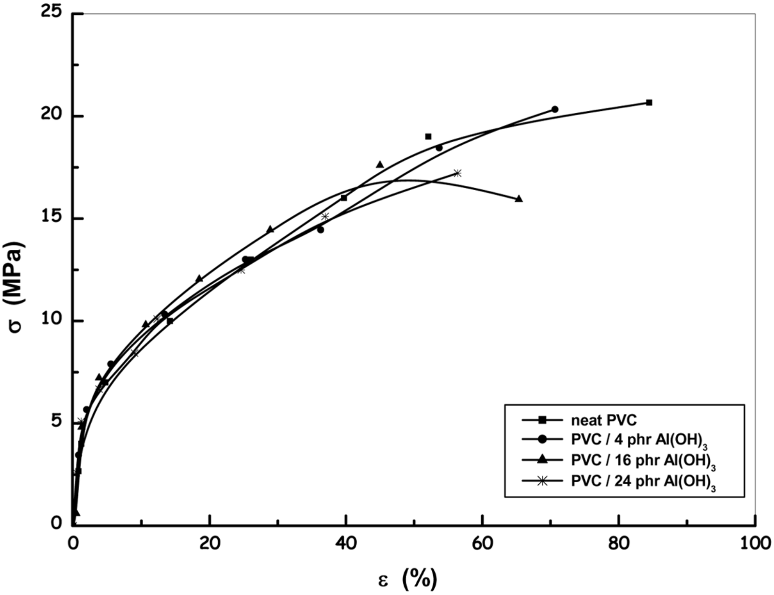

FIGURE 2 The stress/elongation curves for PVC/untreated $Al(OH)_3$ composites.

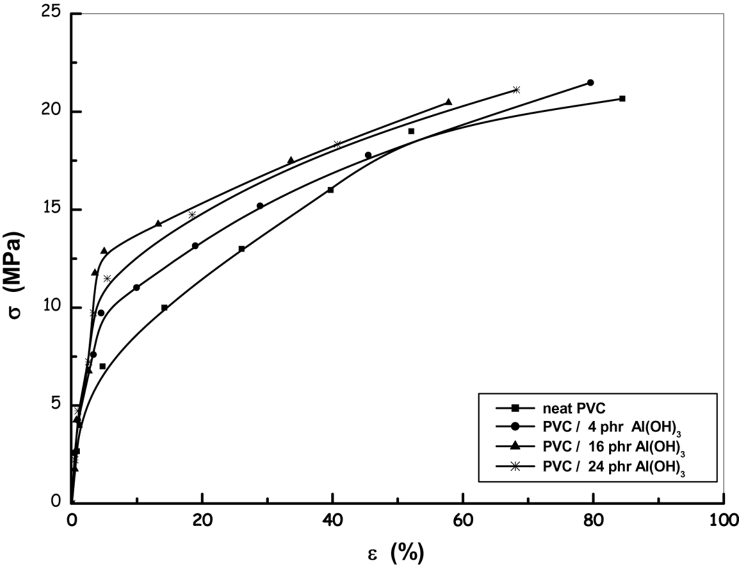

FIGURE 3 The stress/elongation curves for the composites of PVC/$Al(OH)_3$ treated with 0.8% Z-6020 silane coupling agent.

Similar results were found in a study on PVC/glass beads composites by Masao et al. who also reported a decrease of the deformation and the stress at break when increasing filler concentration from 2 to 20 phr [16].

Figure 4 presents the variation of Young's modulus with filler concentration. It shows that the incorporation of aluminum hydroxide into PVC resin resulted in an increase in the modulus. It is also shown that the composites based on treated Al(OH)$_3$ have higher moduli than those made with untreated filler. This is explained by the improvement of the adhesion between PVC and the filler through the formation of chemical bonds.

In order to point out the reinforcing effect of the filler, the results have also been expressed in terms of the relative modulus which is defined as the ratio of the composite modulus to that of the neat matrix. The variations of the relative modulus for the different composites studied are shown in Figure 5. It can be seen that the rigidity of the materials increases with filler loading. This increase is more pronounced with chemically treated Al(OH)$_3$ composites. Figure 6 indicates a decrease of the stress at break when increasing the filler

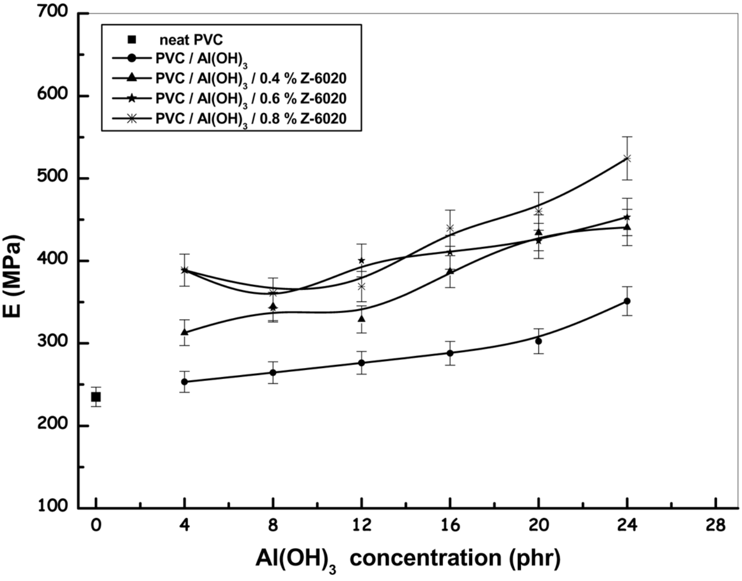

FIGURE 4 Variation of Young's modulus with filler concentration for the composites of PVC/Al(OH)$_3$ treated with different concentrations of the Z-6020 silane coupling agent.

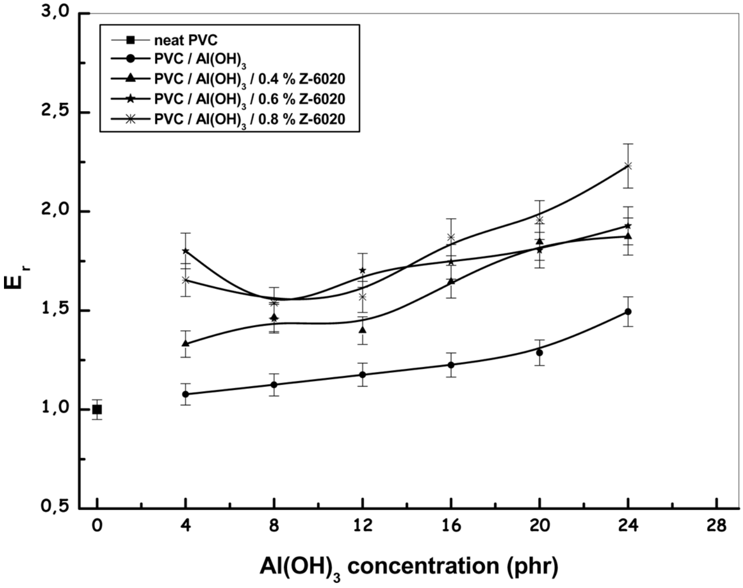

FIGURE 5 Variation of the relative modulus with filler concentration for the composites of PVC/Al$(OH)_3$ treated with different concentrations of the Z-6020 silane coupling agent.

concentration. The stress at break for the composites with treated aluminum hydroxide, being much higher than that of the composites with untreated filler, proves that there is a better affinity between the filler and the matrix owing to the surface treatment of the former.

The effect of Al$(OH)_3$ and its surface treatment by the silane coupling agent on the elongation at break is shown in Figure 7. It can be observed that there is a decrease of the elongation at break. This is attributed to the incorporation of non-deformable solid Al$(OH)_3$ particles into the flexible PVC matrix and to the presence of an interfacial zone with strong interactions between the filler and the matrix.

Interface Characterization

As mentioned above, the mechanical resistance of filled polymers is much influenced by the interfacial interactions between the polymer and the reinforcing filler. Yet, there are only a few studies reported about the quantitative characterization of the interface. For this purpose, some researchers have used the approach of the yield stress [17]. For its definition, they show the presence of two stress maxima: the

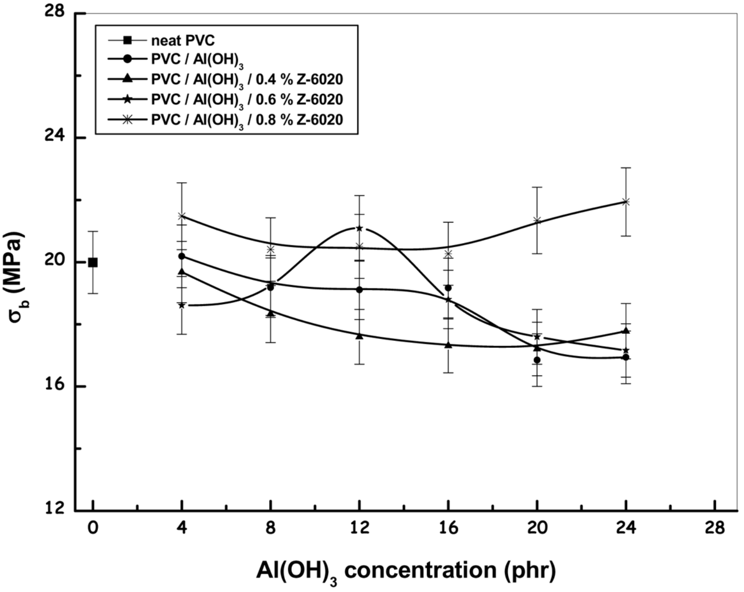

FIGURE 6 Variation of the stress at break with filler concentration for the composites of PVC/Al(OH)$_3$ treated with different concentrations of the Z-6020 silane coupling agent.

first is in the polymeric matrix above the particle and the second is at the interface next to the location of the maximum stress. It is therefore interesting to consider how local mechanisms participate in the macroscopic response of a filled polymer subjected to an increasing stressing. The simplest approach is to consider the passage to the yield point. It is assumed that the yield stress for a filled polymer is proportional to the amount of material that passes to the plastic deformation. The calculations reported by Pukanszky and coworkers [17] lead to Eq. 1 where the yield stress is determined assuming a perfect interfacial adhesion:

$$\frac{\sigma_{\mathrm{yc}}}{\sigma_{\mathrm{ym}}} = 1 + 0.33 \cdot \mathrm{F}(c) \cdot \mathrm{V}_{\mathrm{f}}^{2} \tag{1}$$

where σ_{yc} and σ_{ym} are the yield stress for the composite, and the yield stress for the matrix respectively. $\mathrm{V_f}$ is the volume fraction of the filler, and $\mathrm{F}(c)$ is a function of the extent of the deformation around each particle. The evolution of this function could reflect the non-ductile nature of the matrix assuming no load transfer between the

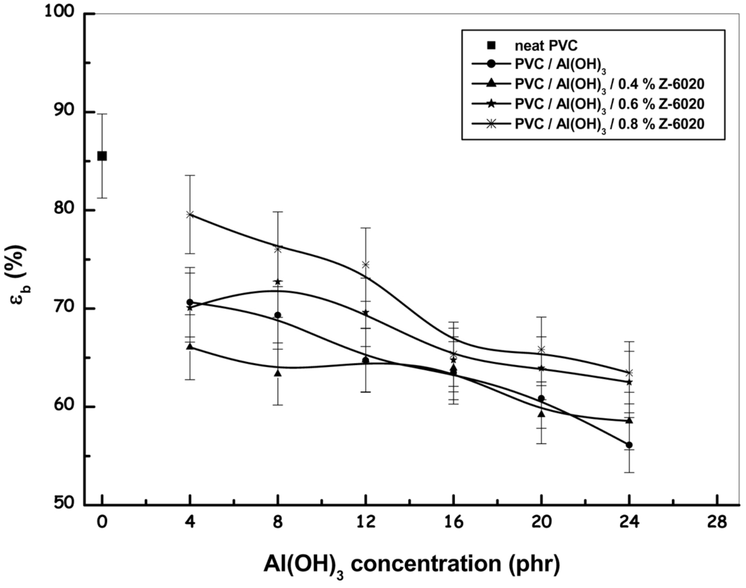

FIGURE 7 Variation of the elongation at break with filler concentration for the composites of PVC/Al(OH)$_3$ treated with different concentrations of the Z-6020 silane coupling agent.

matrix and the filler particle and that the entire deformation will be supported by the efficient polymer matrix.

Many authors [18–20] have developed a model to predict the variation of the yield stress with the filler volume fraction using the following equation:

$$\sigma_{\mathrm{yc}} = \sigma_{\mathrm{ym}} \frac{1 - \mathrm{V_f}}{1 + 2,5 \cdot \mathrm{V_f}} \exp(\mathrm{B} \cdot \mathrm{V_f}) \tag{2}$$

where B, which will be referred to as factor B, is a semi-empirical factor through which the interface can be quantified. A high value of this factor represents strong and efficient interfacial interactions. This factor depends also on other parameters that have an effect on the reinforcing capacity of the filler. The relationship between factor B and these parameters is given by Eq. 3:

$$\mathrm{B} = (1 + l \cdot \rho_{\mathrm{f}} \cdot \mathrm{A_f}) \ln \frac{\sigma_{\mathrm{yi}}}{\sigma_{\mathrm{ym}}} \tag{3}$$

where $\mathrm{A_f}$ is the filler surface area, ρ_{f} is its density, l is the interface thickness, and σ_{yi} is the yield stress of the interface. The last two parameters (l and σ_{yi}) express the dependency of the yield stress and the polymer/filler interfacial interactions [21,22].

Following this model, and defining the relative yield stress as the ratio of yield stress of the composite to that of the neat matrix, the variation of the logarithm of the relative yield stress (σ_{yr}) with the filler volume fraction should give a straight line whose slope gives the value of factor B according to Eq. 4:

$$\ln \sigma_{yr} = \ln \sigma_{yc} \frac{1 + 2.5 \cdot V_f}{1 - V_f} = \ln \sigma_{ym} + B \cdot V_f \qquad (4)$$

The validity of this model should also be consistent with experimental results such as the increase of factor B with the decrease of filler particle size or with the increase of the interface layer thickness [19,22–24].

In our study, this model has been used in order to characterize and quantify the PVC/Al(OH)$_3$ interface. As shown in Figure 8, the stress at yield increases with increasing Al(OH)$_3$ concentration. This increase is more pronounced at higher concentrations of the coupling agent. The treatment of the filler with 0.8% of the silane coupling agent allows the surface to be rich in functional groups by which the

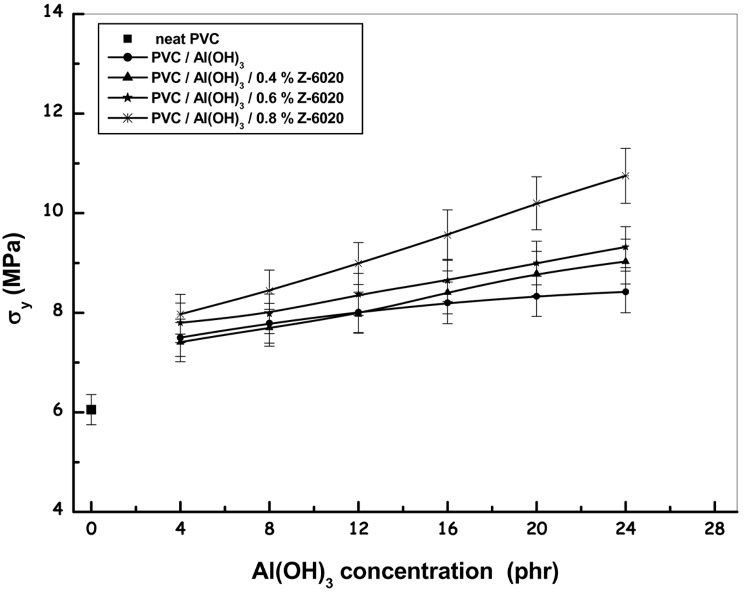

FIGURE 8 Variation of the stress at yield with filler concentration for the composites of PVC/Al(OH)$_3$ treated with different concentrations of the Z-6020 silane coupling agent.

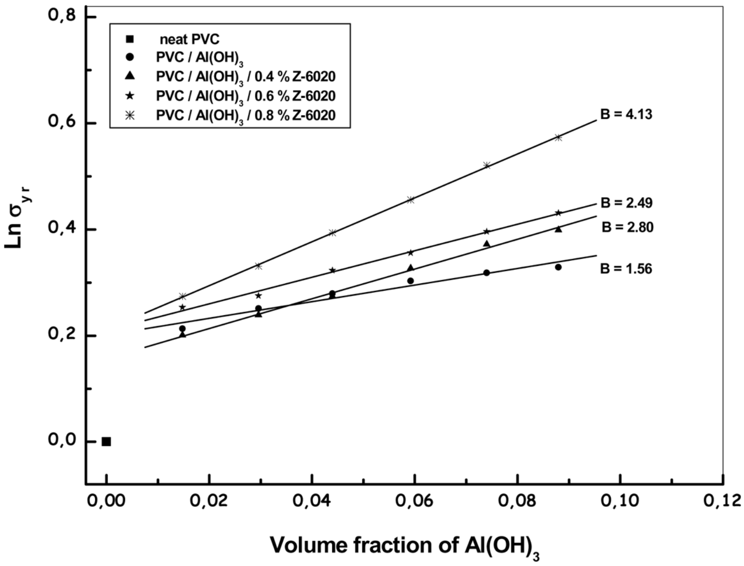

FIGURE 9 Variation of the logarithm of the relative stress at yield with filler concentration for the composites of PVC/Al(OH)$_3$ treated with different concentrations of the Z-6020 silane coupling agent.

mineral filler gets attached to PVC matrix resulting in a strong interface. From the logarithmic plot of the variation of the relative stress at yield as a function of the filler volume fraction for PVC/Al(OH)$_3$ composites, the values of factor B were calculated for the different coupling agent concentrations. As shown in Figure 9, higher values of this factor were obtained at higher concentrations of the silane coupling agent, confirming hence the higher extent of reinforcement due to the chemically treated filler.

CONCLUSIONS

The objective of this study was to investigate the effect of the reinforcement of plasticized PVC by aluminum hydroxide and its chemical surface treatment with a silane coupling agent.

Infrared spectroscopy indicated the presence of oligoaminosilanes resulting from the condensation of the silane molecules into polysiloxanes.

The tensile properties of the composite have also been measured in order to study the effect of the addition of mineral particles and their chemical treatment. The most remarkable improvements were noted for the chemically treated filler as manifested by an increase in Young's modulus and yield stress.

For a better approach to characterize quantitatively the interface, factor B which had already been used for this purpose, was calculated. The results showed an increase of this factor reflecting, hence, a better interfacial adhesion as a consequence of the strong interactions developed between the polymer and the treated filler.

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