Moisture Effect on Deformability of Epoxy/Montmorillonite Nanocomposite

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ABSTRACT: In this article the moisture effect on deformability of epoxy/montmorillonite nanocomposite was investigated. The change of fracture character and drop of elastic characteristics due to moisture absorption was observed. The estimation of filler morphological peculiarities (platelet stack constitution) in composite and its effect on nanocomposite elastic properties was undertaken. It is shown that the higher number of filler platelet per stack consistently leads to the decrease of nanocomposite elastic properties. Nevertheless prediction by micromechanical model is rough for moistened nanocomposite because of resin structural changes. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 493–498, 2010

Key words: nanoclay-composite; deformability; moisture effect; modeling

INTRODUCTION

The peculiarities of moisture absorption by epoxy/montmorillonite (MMT) nanocomposite (NC) were discussed in.[1] The enhanced barrier properties referred in the literature[2–8] were revealed. The sorption process in NC passed more slowly, for the highest filler content diffusivity was reduced about twice. This could be described by large aspect ratio and surface of the exfoliated silicate layers as they act as efficient barriers against moisture transport through the material and cause an increase in the path length for molecules diffusing through the polymer.[9]

Epoxy resins are quite attractive for structural applications because of their relatively high strength and stiffness, low creep, and shrinkage. However they have a major drawback of high moisture absorption, which in turn degrades the functional, structural and mechanical properties of the composites.[10–15] Since absorption of water reduces the elastic characteristics of hydrophilic polymers, the addition of nanoparticles to minimize the negative effects of water uptake is particularly useful.[5,14,15]

The emphasis of this article is made mainly to establish effect of moisture on deformability of epoxy/MMT NC taking into account filler morphological peculiarities and to verify if the negative effect of moisture on deformability of NC is minimized by introducing MMT clay nanoparticles.

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EXPERIMENTAL

The investigated material was provided by research institute SYNPO, Pardubice, Czech Republic. It was received in the shape of thin and wide plates with dimensions 2.0 × 130.0 × 130.0 (± 0.2) mm and then cut into bars with dimensions 2.0 × 8.0 × 130.0 (± 0.1) mm.

The NC consisted of bisphenol-A epoxy resin and octadecylamine modified MMT-based organoclay. Four filler weight fractions $c = 0$, 2, 4, and 6% were used to study the effect of moisture and filler weight fraction on the mechanical behavior of NC.

The homogeneity of the filler particles' dispersion could be approved by the transparency of all NC specimens. Additional microscopy methods, scanning electron (SEM) and transmission electron microscopy (TEM), were applied for the analysis.

Moisture sorption was performed in atmospheres with relative humidity $\varphi = 24$, 77, and 98% using desiccators with silica gel and saturated solution of salts NaCl and K_2SO_4, respectively.[1] According to the results obtained in Ref. 1, the average equilibrium moisture content reached in 437 days for NC was approximately −0.4, 1.7, and 3.2% for $\varphi = 24$, 77, and 98% with increase by approximately 7% for filler content changing from 0 to 6 wt %. It was experimentally confirmed that sorption process in NC passed more slowly than in pure epoxy resin, for the highest filler content diffusivity reduced about half of diffusivity as for epoxy resin. It could be caused by clay nanoparticles as they act as efficient barriers against moisture transport. The increase in equilibrium moisture content observed with the increase of clay weight content in NC was

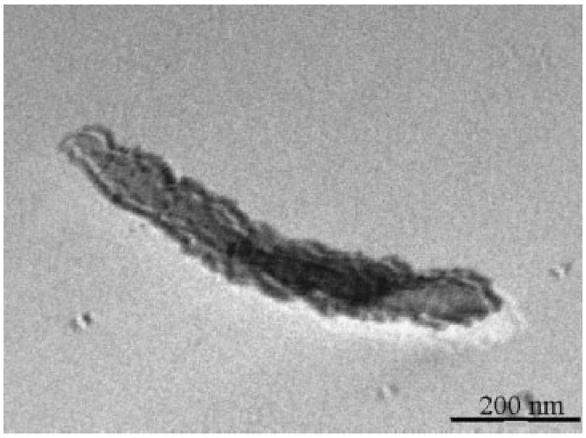

Figure 1 Typical TEM image of acetone suspension of clay nanoparticle. The nanoclay appears in black.

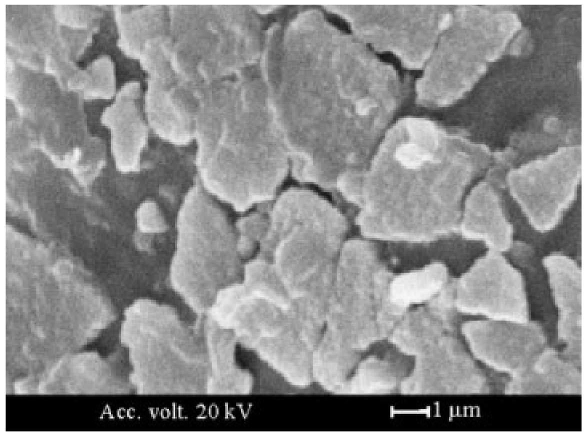

Figure 2 SEM micrograph of fracture surface of NC with $c = 2\%$.

explained by growth of interphase layer content. The sorption capacity of interphase layer in NC with 1% of filler was determined and the sorption isotherm of interphase was derived.

Quasi static tensile tests were performed on the specimens with different clay content in dry and wet state using Zwick 2.5 testing machine with a crosshead speed of 5 mm/min at room temperature. Tensile strength is defined as the maximal achieved value of stress in the specimen, and elastic modulus is calculated from the slope of a secant line between 0.05% and 0.25% strain on a stress–strain plot. Four specimens per each filler mass fraction were tested and the values given correspond to their arithmetic mean value.

RESULTS AND DISCUSSION

Microstructural characterization

The behavior and properties of NC are dependent not only on properties of its structural components but also on the material microstructure: the dispersion and orientation of filler particles, and the interactions between filler particles and polymer matrix.[16]

Nevertheless one of the main parameters that affect the behavior of the nanosystem is the effectiveness of dispersion of filler particles within the polymer matrix.[17]

One way to check the morphological peculiarities of clay nanoparticles in a solvent, before incorporating them to a matrix, is to observe their dispersion by TEM. A typical image of acetone suspension of clay nanoparticles is shown in Figure 1.

It is obvious from Figure 1 that the observed aggregate should be a stack of clay platelets having layered structure and high aspect (diameter to thickness) ratio (50). The aspect ratio of the platelet stack as observed from Figure 1 is about 7.

Moreover the platelet shape of the filler particles could be confirmed by SEM micrograph of fracture surface of NC specimen with $c = 2\%$ (Fig. 2). It could be seen that the transversal dimension of the filler aggregates is much smaller than longitudinal ones.

Mechanical properties

Experimentally measured stress–strain curves of NC with $c = 6\%$ moistened at $\varphi = 24$, 77, and 98% RH are shown in Figure 3. From these curves it could be observed that the effect of moisture on mechanical behavior is substantial. Absorbed moisture essentially plasticizes the NC and changes its fracture character from brittle in dry atmosphere to plastic one in wet atmospheres.

To examine the effect of organoclay content on mechanical properties, elastic modulus and tensile strength were plotted versus filler mass fraction (Figs. 4 and 5). From these figures it is clear that elastic modulus increases up to 20% and tensile strength of the NC decreases about the same value with the increase of organoclay content to 6%.

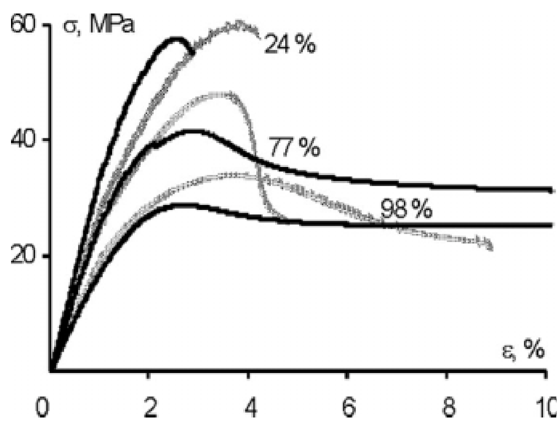

Figure 3 Typical stress–strain curves at a fixed rate of deformation ($v = 5$ mm/min) for neat epoxy resin (gray curves) and NC with $c = 6\%$ (black curves) and $\varphi = 24$, 77, and 98% RH.

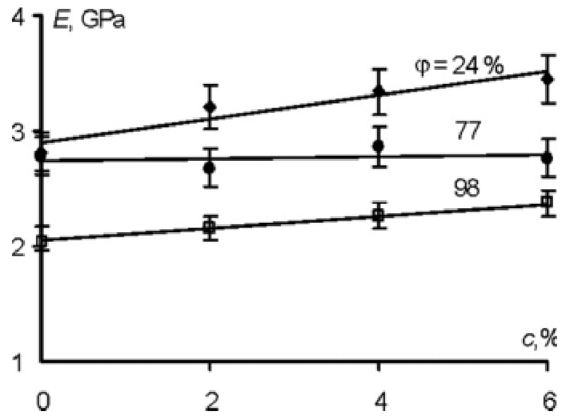

Figure 4 Elastic modulus of NC in atmospheres with different relative humidity versus filler weight fraction.

Figures 2 and 3 also show the quantitative effect of moisture on tensile strength and elastic modulus of NC. Tensile strength of moistened composite drops twice. Elastic modulus both of moistened pure epoxy resin and NC is reduced approximately 1/3 in comparison to initial state. Consequently, due to absorbed moisture both pure resin and NC with $c = 6\%$ show almost same degradation as for elastic modulus 1 GPa and for tensile strength 25 MPa, respectively. It should be noted that although the values themselves of elastic modulus and strength are improved with respect to filler content, the positive effect as moisture content increases (in atmosphere from 24% RH till 98% RH) was not revealed.

Efforts were being made to relate effective tensile elastic modulus of moistened NC with properties of its structural components. It should be emphasized that taking into account complicated structure of real composite material, only evaluative results could be obtained theoretically.[18]

The majority of micromechanical models are limited to characterization of linear elastic behavior of composites during static loading.[19–27] Another assumption is that the components are also linear elastic, and the composite is represented as nonhomogeneous linear-elastic medium.

In the structural hierarchy of polymer-clay NC at least two states can be assigned: (1) state of total exfoliation of clay platelets with characteristic parameters as thickness and dimensions in the plane of platelets, and (2) state of incomplete exfoliation of clay platelets and characteristic parameters as thickness and dimensions in the plane of intercalated layered stacks.[28] The aspect ratio and orientation of anisometric particles determine their reinforcement degree. Nevertheless, it is difficult to control the orientation of plane particles during processing of composite and the real distribution of their orientation could be rather complex, the determination of the effective elastic constants of transversely isotropic layers of a NC with coplanar orientation of such particles is of great importance. The data obtained in this case could serve as initial for a further analysis of the elastic properties of a composite with disoriented nanoparticles taking into account their orientational distribution in the material.[27]

Halpin-Tsai equations[27,25] obtained for isotropic polymer matrix filled with coplanar transversally isotropic cylindrical particles of arbitrary aspect ratio (Fig. 6) were used for the case of exfoliated NC. The elastic solution was obtained for the composite consited of a single fiber encased in a cylinder of matrix, both embedded in an unbounded homogeneous medium, which is macroscopically indistinguishable from the composite. The relations between the stress and strain components were averaged throughout the composite. The obtained formulas were curve fitted to exact elasticity solutions and confirmed by experimental measurements in order to get the solution for composite filled with particles of arbitrary aspect ratio.

If the exfoliation of filler platelets is incomplete the composite system is considered to consist of matrix and pseudoparticles (stacks of individual platelets). Figure 7 shows sheme of filler particles that are forming a stack (a pseudoparticle). N is the number

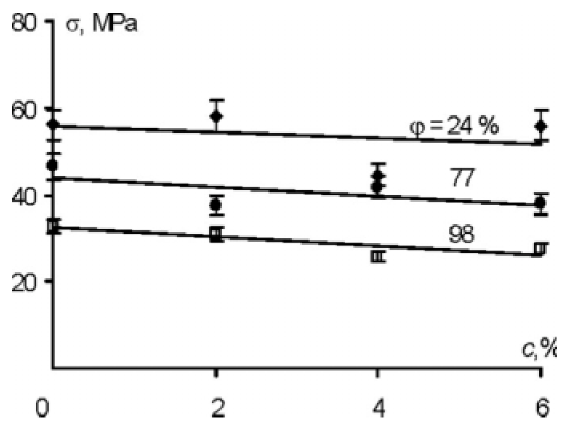

Figure 5 Tensile strength of NC in atmospheres with different relative humidity versus filler weight fraction.

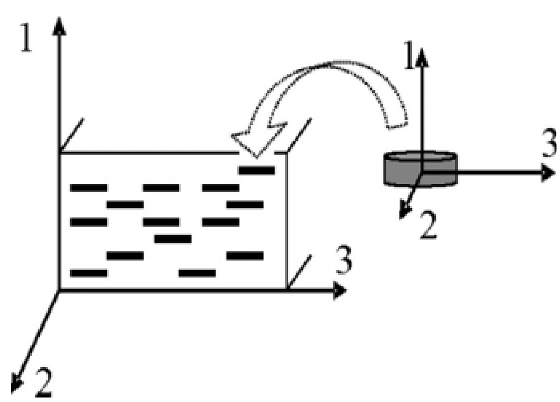

Figure 6 Schematic representation of cylindrical filler particles embedded in polymer matrix.

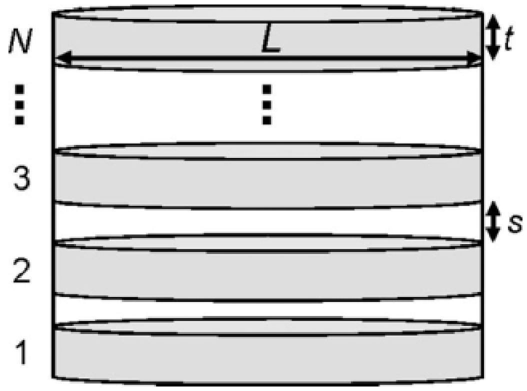

Figure 7 Representation of pseudoparticle (platelet stack).

of platelets per stack, L – length (width), t – thickness of the platelet, s – interplatelet spacing.

The Halpin-Tsai equations that were used[27] to characterize the case of incomplete exfoliation of filler platelets within the composite are as follows

$$E_1 = E_m \frac{1 + 2\eta_1'\phi'}{1 - \eta_1'\phi'}, \quad (1)$$

where

$$\eta_1' = \frac{R_1' - 1}{R_1' + 2},\ R_1' = \frac{E_{p1}}{E_m}, E_{p1} = \frac{E_{f1}E_m(Nt + (N-1)s)}{E_mNt + E_{f1}(N-1)s},$$
$$\phi' = \phi\left(1 + \left(1 - \frac{1}{N}\right)\frac{s}{t}\right).$$

Here E_1, E_m, E_{p1}, E_{f1} are elastic moduli of given composite, matrix, filler platelet stack and single filler platelet, accordingly, for axis direction shown in Fig. 6; φ and φ' are the volume fraction of filler particles and filler platelets. The case of complete exfoliation of filler platelets within composite could be easily obtained for $N = 1$, $s = 0$.

Taking into account the anisotropy of considered filler particles and as consequence of the composite material two additional Halpin-Tsai equations could be applied

$$E_2 = E_3 = E_m \frac{1 + 2A_f'\eta_2'\phi'}{1 - \eta_2'\phi'}, \quad (2)$$

where

$$\eta_2' = \frac{R_2' - 1}{R_2' + 2A_f'},\ R_2' = \frac{E_{p2}}{E_m}, E_{p2} = \frac{E_{f2}Nt + E_m(N-1)s}{Nt + (N-1)s},$$
$$A_f' = \frac{A_f}{N}\left(\frac{1}{1 + (1 - \frac{1}{N})\frac{s}{t}}\right).$$

In these equations E_{p2}, E_{f2} are elastic moduli of filler platelet stack and single filler platelet for the axis direction shown in Figure 6. A_f and A_f' are the aspect ratios of single filler platelet and platelet stack (>1 since it equals to the diameter divided by thickness for cylindrical platelets). Again the case of complete exfoliation of filler platelets within composite could be easily obtained assuming that $N = 1$, $s = 0$.

Using known values of elastic modulus of matrix in atmospheres with different relative humidity it is possible to determine elastic moduli of NC by equations (1) and (2). The elastic moduli of montmorillonite clay platelets are ranging from 40 GPa[29] to 180 GPa[23,30–32] based on the literature values for layered-structure clay minerals, an empirical modulus-density relation for alumina, silica and their compounds and values obtained by simulation for the product of elastic modulus and thickness of the platelets. In this study elastic moduli of filler are assumed to be $E_{f1} = 55$ GPa, $E_{f2} = E_{f3} = 178$GPa, aspect ratio of filler platelet $A_f = 50$, number of platelets per stack N is changed from 1 to 6, $s/t = 1$.

Comparing results of evaluation by eq. (1) with experimental data of quasistatic tensile tests of specimens conditioned in dry atmosphere ($\varphi = 24\%$ RH) provided in Figure 8 it is obvious that evaluation results for elastic modulus of NC with exfoliated filler particles are higher than experimental ones. Increasing the number of platelets per stack gives the opportunity to get better agreement between them. Although it is rather arguable, as it is assumed in the model that filler particles obey coplanar orientation in polymer matrix. On the other hand evaluation by eq. (2) (low bound) is much lower than experimental results even for the case of exfoliated platelets. It means that real orientation distribution of clay platelets is somewhere in between these limits and could be rather complicated.

Nevertheless using obtained results (the same parameters N, t, s) for moistened NC it is possible to estimate structural changes of the polymer resin because of moisture absorption.

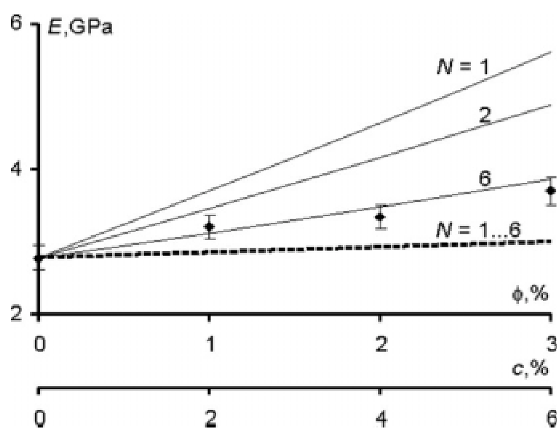

Figure 8 Elastic modulus of NC versus filler volume content. Evaluation by (1) (solid line) and (3) (dashed line) for different number of elementary layers N (numbers on the curves) in a platelet stack. Dots – experimental data for $\varphi = 24\%$ RH.

The resulting evaluation of elastic modulus of moistened NC by eq. (1) shows the deviation from results obtained experimentally (Fig. 9). As it can be seen taking into account platelet stack layered structure (increasing the number of platelets in stack till 6) improves the congruence of results with experimental data. Apparently it could be described by the change of elastic properties of the platelet stacks. It should be emphasized that while elastic modulus of impermeable clay platelets is not dependent on moisture content, the matrix phase that is located in the interplatelet spacing absorbs moisture. Therefore, the elastic properties of the platelet stacks are dependent on absorbed moisture content and cause more significant decrease of moistened NC elastic modulus as presented in Figure 9.

The change of elastic modulus under effect of moisture e.g. NC with $c = 6\%$ proves that moisture which exists in the interplatelet spacing significantly influences the elastic modulus. Logically enough, the higher content of filler leads to higher content of interplatelet spacing and as a result to greater moisture absorption and greater change of NC properties that are sensitive to moisture.

The isotherm shown in Figure 10 concludes the proposed analysis of moisture and filler effect on deformability of epoxy/MMT NC taking into account filler morphological peculiarities. Using this figure it is possible to estimate NC elastic modulus of any filler content in atmosphere with any relative humidity. It is obvious that because of moisture absorption elastic modulus of NC is substantially decreased. Since the value of elastic modulus of epoxy resin is improved with respect to filler content in spite of no positive effect for the decrease of elastic modulus of NC, due to moisture absorption (in atmosphere from 24% RH till 98% RH) epoxy resin modified by impenetrable stiff MMT clay nanoparticles could be applied in environments with higher-operating relative humidity.

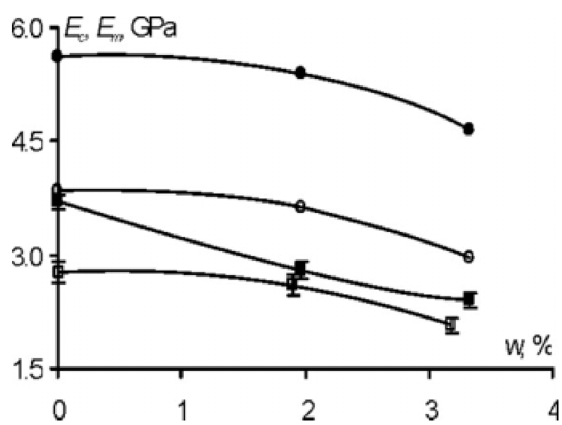

Figure 9 Elastic modulus of epoxy resin and NC with $c = 6\%$ versus absorbed moisture content. Experimental data (NC with $c = 6\%$ (–■–), epoxy resin (–□–)), evaluation by (3) for NC with $c = 6\%$ and $N = 1$ (–●–) and $N= 6$(–○–).

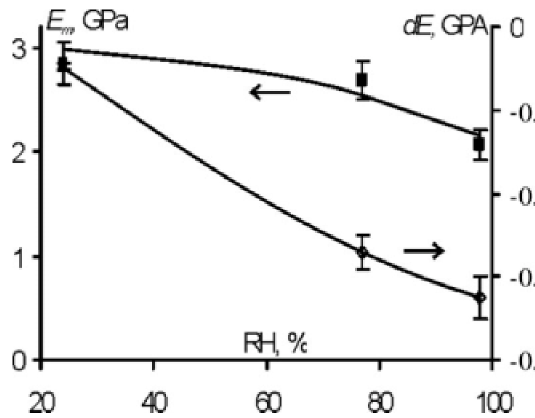

Figure 10 Elastic modulus of epoxy resin (■) and normalized to 1 wt % of filler deviation of NC elastic modulus (◇) versus relative humidity of the atmosphere.

CONCLUSIONS

In this article the effect of moisture absorption on the mechanical properties of NC was examined. Quasistatic tensile tests were carried out for evaluation of the mechanical properties. Finally, an attempt was made to estimate the effect of moisture on elastic modulus of platelet stack and moistened NC. From the above investigation the following conclusions may be derived:

- Shown effect of moisture on mechanical properties is substantial. Absorbed moisture essentially plasticizes the composite changing the fracture character. Tensile strength of moistened composite drops twice. Elastic modulus both of moistened pure epoxy resin and NC is reduced approximately 1/3 in comparison to initial state.
- Halpin-Tsai equations were applied to estimate effective elastic modulus of NC conditioned in atmospheres of different relative humidity. The results obtained for specimens conditioned in dry atmosphere were used for moistened NC and provided opportunity to estimate structural changes of the polymer resin because of moisture absorption.
- Based on obtained results it could be concluded that incorporation of impenetrable clay nanoparticles with high mechanical characteristics did not reduce the negative effect of absorbed moisture on mechanical properties of NC. But since the value of elastic modulus of epoxy resin is improved with respect to filler content up to 20% epoxy resin modified by impenetrable stiff

MMT clay nanoparticles could be applied in environments with higher-operating relative humidity.

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