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Stress relaxation behavior of starch powder-epoxy resin composites

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ABSTRACT: The purpose of the present study is to investigate the quasi-static and the viscoelastic behavior of epoxy resin reinforced with starch powder. An increase in the elastic modulus on the order of 42% was achieved; a behavior that was predicted by the modulus prediction model (MPM). Next, the composite was subjected to flexural relaxation experiments, in order to determine the relaxation modulus, at different filler-weight fractions and flexural deflections imposed. The viscoelastic models of the standard linear solid, the power law model and the residual property model (RPM) were applied in order to simulate/predict the stress relaxation curves. Predicted values derived from the application of the above models were compared to each-other as well as to respective experimental findings. From the above comparison it was proved the superiority of the RPM model in predicting both the linear and the nonlinear viscoelastic response of the materials investigated. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41697.

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INTRODUCTION

The last decade has become obvious that there is an increased interest on materials from renewable resources, the so called "Green Materials". The reasons for that are both ecological as much as economical. Ecological because unlike petroleum derived polymers, green polymers have a biodegradable nature. Economical, because the raw materials needed for green composites are very cheap. Also, the depletion of oil reserves has led to the inevitable increase in oil prices.[1,2]

Starch is one of the most abundant natural polymers and is considered as a promising raw material for the development of new, environmental friendly materials. Starch is a polysaccharide produced by many plants as a storage polymer. It is extracted from plants such as wheat, potato, tapioca, and rice, but the largest source of starch is corn (maize). It is comprised of glucose monomers joined by a-(1–4) linkages and it consists of two types of molecules: the linear and helical amylose and the branched amylopectin.[3] Depending on the plant, starch generally contains 20–25% amylose and 75–80% amylopectin. In its native form, starch is usually stored in granules.[4] The average granule size varies from source to source, with rice starch granules being roughly 3 μm in diameter, while potato starch granules are about 35 μm in diameter. Corn starch, the major and most common form of starch, has an average granule size of $\sim$10 μm.[5] There are many derivatives of starch, but the most well-known of them is thermoplastic starch or TPS. To this day, thermoplastic starch is estimated to represent 50–80% of the global bioplastic market and is the most significant and widely used bioplastic.[6] Starch itself is a very interesting material with multiple uses in industry. In the pharmaceutical industry starch is being used for the production of drug capsules.[7] Also, biocompatible, degradable starch based polymers are utilized to induce surrounding tissue ingrowth or to serve as temporary scaffolds for transplanted cells to attach, grow, and maintain differentiated functions.[8–10] However, the use of untreated starch granules as reinforcement, has not been studied thoroughly and specifically the effect of starch granules on the viscoelastic behavior of polymers. The reason for that is the hydrophilicity of starch, and that is why starch granules are treated before they are used as reinforcements.[11]

In the present investigation the quasi-static and viscoelastic behavior of untreated starch reinforced epoxy resin composites was studied. The composite produced is a semigreen composite and comprise a first attempt of reinforcing an epoxy matrix with untreated starch in order to study its behavior. In addition, four different models (MPM, RPM, PLM, and SLS models) were applied for the quasi-static and the viscoelastic

Table I. Physical Properties of Corn Starch

Amylose content (%)	16.9–21.3
Swelling power (g/g)	13.7–20.7
Solubility (%)	9.7–15
Water binding capacity (%)	82.1–97.7
Glass transition temperature (°C)	70

description/prediction of the semigreen materials manufactured and tested. It was found that predicted values were in good agreement with experimental results while the RPM model predicts well even in the case of nonlinear viscoelastic behavior where the rest of the models fail.

EXPERIMENTAL

Materials

Normal corn starch (Unmodified regular corn starch of industrial grade containing ~73% amylopectin and 27% amylose) was purchased from AKIS. The physical properties of corn starch are given in Table I as taken from Ref. 12. The epoxy system used as matrix material was resin RenLam CY219 (Bisphenol A) combined with a curing agent HY 5161 (amine) at a ratio 2 : 1 by weight. Gel time was 24 h at 50°C, and the density of cured polymer 1.1 g cm^{-3}. Viscosity of the amine was 0.9–1 Pas and for Bisphenol A was 1–1.2 at 25°C.

Specimens Manufacturing

Starch was placed in an oven in 50°C for 24 h in order to remove humidity. The materials were mixed by hand according to manufacturer's directions. Polymer resin and starch granules were carefully mixed in proper quantities to achieve uniform distribution of the fillers into the matrix. Then the hardener was added in the blend and was mechanically mixed for 5 min. Afterwards, the mixture was placed in a vacuum chamber for 5–6 min to reduce the amount of entrapped air. The final product was then poured in a proper metallic mold and subsequently cured in an oven at 50°C for 24 h. The final specimens had a total length of 100 mm, 12.8 mm in width, 2.5 mm in depth and a gauge length of 63 mm. Five or more specimens were tested for each case.

Quasi-Static Mechanical Tests

Pure epoxy resin specimens and polymer matrix composites reinforced with starch granules at different weight fractions of the filler particles (W_f%: 0, 5, 10, 15, 20, 25, 30, 40) were manufactured. A series of quasi-static three-point bending experiments (ASTM D790-99) in the universal mechanical testing machine Instron 4301, were performed at room temperature to investigate the mechanical properties of the manufactured composites. In all cases, a constant crosshead speed of 1 mm/min was applied.

Stress Relaxation Tests

Pure epoxy resin specimens and polymer matrix composites reinforced with starch granules at different weight fractions of the filler particles (W_f%: 0, 5, 15, 25) were manufactured according to the previously mentioned specifications. Relaxation experiments took place in the universal testing machine Instron 4301. The specimens ware placed on the support rollers, with a span of 63 mm. Initially the machine started and continued to operate until the desirable displacement was reached. Then the machine was stopped at the desirable displacement (2, 3, 4, 5, and 7 mm). The values of the applied load were monitored every 20 s.

THEORETICAL BACKGROUND

In the current investigation four models were applied in total. Before presenting the MPM model and its application for the modulus prediction of the composites manufactured and tested, it is important to preliminary analyze some of the parameters affecting the mechanical behavior of particulates, which have also been taken into account in the development of the model. These parameters include the particle size, the filler-matrix interfacial adhesion bond, particle volume fraction, and the degree of mixing that defines the extent of dispersion of fillers into the polymeric matrix.

Effect of Particle-Matrix Interphase

In the area between polymeric matrix and filler, polymer surface layers are created at the boundary interface, which are of essential importance for the increase in modulus with filler concentration. In such thin films, the polymer is subjected to bulk deformation. It is well known,[13] that bulk modulus is much higher than shear modulus, and therefore the increase in polymer fraction in surface layers leads to a general increase in modulus of the filled system.

Effect of Particle–Matrix Bond Strength

A very important parameter is the bond strength between the particle and the polymeric matrix. One of the key damage phenomena in particle-reinforced composite materials is particle-matrix debonding. Because of the effect of dewetting, voids are created, leading to the initiation, and propagation of cracks in composites. Three different cases of bond strength can be identified.

1. Very weak bond strength: For very weak (or zero) bond strength, the filler-polymer bond fails immediately upon straining, and small holes (or vacuoles) are created next to a particle. Since there is no physical reinforcement, the material is weak and highly extensible.
2. Very high bond strength: Alternatively, if the bonds are strong, the filled material exhibits a relatively high modulus with considerable reduction in the ultimate elongation. This statement is valid for brittle matrices like epoxies.
3. Adhesive bond of intermediate value: It is in those systems where the adhesive bond is of intermediate value; however, that the problem of localized failure appears. As the specimen undergoes loading, the weakest bond strengths are first exceeded. The filler particles are then released, transmitting a higher stress to the neighboring polymer–particle bonds. The effect observed is that of a line of released particle perpendicular to the direction of strain. If the applied load occurring after this phenomenon does not exceed the bond strength of the remaining intact bonds, the polymer along this line experiences very high strain and eventually fails.[14,15]

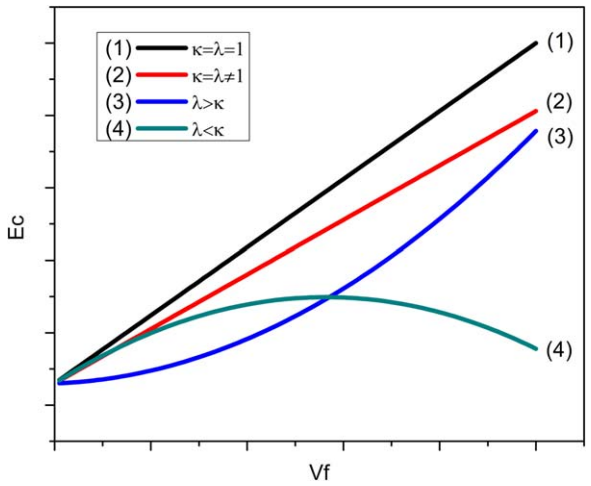

Figure 1. Schematic representation of modulus variation with the filler-volume fraction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of High Filler Content

In the case of particulate composites, we prefer low filler volume fraction (<0.50), in order to ensure that we have a good dispersion of the particles and assume that the resin acts as the continuous phase.[16] In case of higher volume fractions, usually >50%, we can deduce two additional microstructures as well. In the first case, the resin is completely entrapped within the filler aggregates or clusters, with particles touching each other.[17] In the second case the composite exhibits a microstructure with a mixture of regions of resin entrapped within particle clusters. So, in this case there are randomly dispersed particles, but each region contains a different volume of filler.[18]

Effect of the Degree of Mixing

As "degree of mixing" is defined the extent of homogeneity for the dispersion of given filler in the polymer matrix. So far the method of trial and error is still used, since so far no methods exist to deal with the effect of the degree of mixing on the properties of filled polymers. A good degree of mixing is required in order to have better properties in the manufactured specimen. Mechanical mixing of particulate composites can lead to different properties, because of the dispersion of the particles within the polymeric matrix, which depends on the mixing time period.[19]

The Modulus Prediction Model (MPM)

The MPM model for particulate composites is a semi-empirical model developed by the first author and it predicts the variation of the modulus as a function of the volume fraction of the filler. It is based on the assumption that the modulus is affected by two main parameters: λ and κ; namely: The *particles dispersion parameter* λ, and the *particle-matrix adhesion parameter* κ, denoting the adhesion between fillers and the polymer matrix.

The model can be described by the following single equation

$$E_c=(\lambda-\kappa)E_f V_f^2+\kappa(E_f-E_m)V_f+E_m \quad (1)$$

Next, the quantities K (*degree of adhesion*) and L (*degree of dispersion*) that are associated with the parameters κ and λ of the model are defined as:

$$K=\left|\frac{\kappa}{2-\kappa}\right| \quad (2)$$

and

$$L=\left|\frac{\lambda}{2-\lambda}\right| \quad (3)$$

Knowing two experimental points S_1 (V_{f1}, E_1) and S_2 (V_{f2}, E_2), the values of the parameters κ, λ and therefore the values of the degrees K, L can be determined as:

$$\kappa=\frac{\mathrm{B}}{(E_f-E_m)} \quad (4)$$

$$\lambda=\frac{\mathrm{A}}{E_\mathrm{f}}+\kappa \quad (5)$$

where:

$$\mathrm{A}=\frac{-\frac{V_{f2}}{V_{f1}}(E_1-E_\mathrm{m})+(E_2-E_\mathrm{m})}{V_{\mathrm{f}2}^2(1-\frac{V_{f1}}{V_{f2}})} \quad (6)$$

and

$$\mathrm{B}=\frac{\frac{V_{f2}}{V_{f1}}(E_1-E_\mathrm{m})-\frac{V_{f1}}{V_{f2}}(E_2-E_\mathrm{m})}{V_{\mathrm{f}2}\left(1-\frac{V_{f1}}{V_{f2}}\right)} \quad (7)$$

Since at very low filler volume fractions particle dispersion is almost perfect, one should select the first experimental point at concentrations close to 1% while the second one should correspond to the highest filler-volume fraction studied. For granular starch E_f = 15 GPa.[20,21]

Investigating the physical meaning of the adhesion parameter κ and the dispersion parameter λ, the following cases can be distinguished:

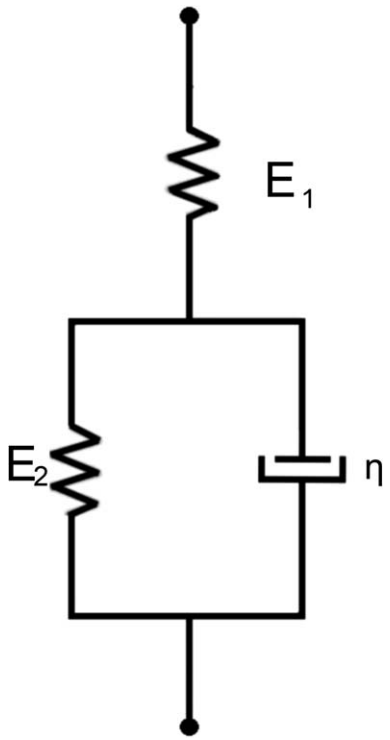

Figure 2. Standard linear solid model.

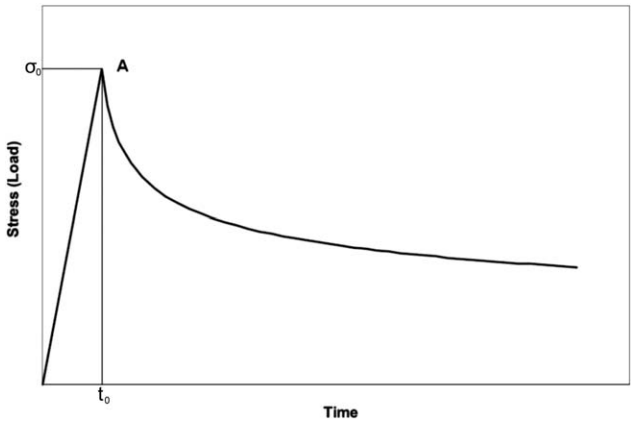

Figure 3. Schematic representation of a typical stress relaxation curve.

1. For $\kappa = \lambda = 1$ (perfect adhesion and perfect dispersion):

$$E_c = E_f V_f + E_m(1 - V_f) \quad (8)$$

In this case the variation of the modulus as a function of the filler volume fraction is linear and follows the well-known "**Rule of Mixtures**" (Figure 1, curve 1).

2. For $\kappa = \lambda \neq 1$ (Equal degree of adhesion and dispersion):

$$E_c = E_f kV_f + E_m(1 - kV_f) \quad (9)$$

In this case, variation of the modulus as a function of the volume fraction is linear, but the modulus for the same volume fraction will have a lower value than the value of the rule of mixtures (Figure 1, curve 2). In this case the MPM gets a modified version of the rule of mixtures where the volume content has been replaced by the "*active volume fraction*", kV_f.

3. $\lambda - \kappa > 0$ (Low degree of adhesion and high degree of dispersion):
   In this case variation of the modulus as a function of the volume fraction takes the form of an ascending parabolic curve with the concave upwards, (Figure 1, curve 3). This type of variation has the following physical meaning: Initially, as the filler volume fraction increases, due to the low degree of particle adhesion, a slow increase in modulus is observed. On the other hand, due to the high degree of dispersion, aggregation does not exist in a high extent so that the filler-matrix contact area increases with increasing filler-volume fraction leading to a continually increasing modulus. Thus, the overall behavior observed is characterized by an initial slow increase in modulus, followed by a subsequent increase with a higher rate.
4. For $\lambda - \kappa < 0$ (High degree of adhesion and low degree of dispersion):
   In this case variation of the modulus as a function of the volume fraction takes the form of a parabolic curve with the concave downwards, (Figure 1, curve 4). This type of variation has the following physical meaning: As the filler volume fraction increases, due to the low degree of particle dispersion, aggregation becomes a parameter of crucial importance leading to a reduction of the total filler-particle contact area. Thus, at low filler loadings and due to the high degree of adhesion an initial increase in modulus is observed. However, as the filler-volume fraction increases, high degree of agglomeration is observed due to the low degree of dispersion, leading to a total reduction of the filler-particle contact area. Thus, the overall behavior observed is characterized by an initial increase in modulus up to a certain limit, followed by a subsequent decrease of its value.[19]

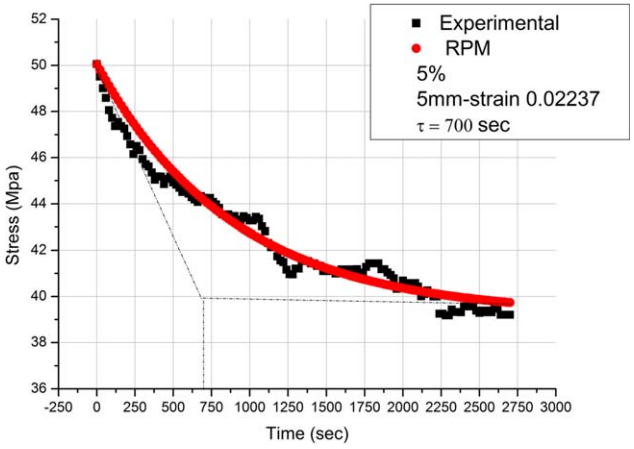

Figure 4. τ_{rel} found as the time corresponding to the intersection point of the two tangents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

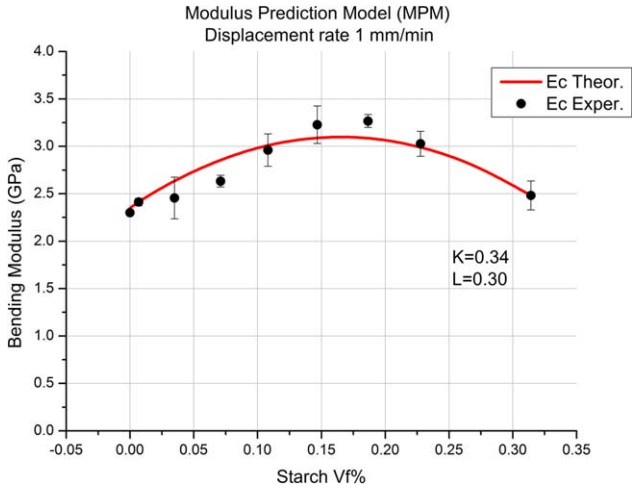

Figure 5. Comparison between experimental values and theoretical predictions as derived from modulus prediction model (MPM) for the bending modulus of the starch particle-epoxy matrix composites investigated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Standard Linear Solid Model (Zener)

The behavior of a viscoelastic material is modeled using a linear combination of springs and dashpots to represent elastic and viscous components, respectively. The standard linear solid (SLS) model or Zener model is the combination of two elements, a spring and a Voigt model (Figure 2).

The model is based on the *Boltzmann Superposition Principle*, which describes the response of a material to different loading histories. The Boltzmann superposition principle states that the

Table II. Ultimate Strength Values and Comparison Between Experimental Values and Theoretical Predictions as Derived from Modulus Prediction Model for the Bending Modulus of the Starch Particle-Epoxy Matrix Composites Investigated

W_f (%)	Ultimate strength (MPa)	Exp. bending modulus (GPa)	Theor. bending modulus (GPa)	Deviation (%)
0	51.6	2.3	2.35	2.12
5	57.07	2.45	2.63	6.76
10	60.98	2.63	2.85	7.78
15	63.87	2.96	3.01	1.65
20	59.88	3.23	3.08	4.48
25	59.24	3.26	3.08	5.88
30	51.59	3.02	2.99	1.25
40	33.75	2.48	2.48	0

response of a material to a given load is independent of the response of the material to any load, which is already on the material. The deformation of a specimen is directly proportional to the applied stress, when all deformations are compared to equivalent times and it is only valid in linear viscoelastic region. Because of the fact that SLS model is based on this principle it is not expected to predict the nonlinear viscoelastic behavior.[22]

The constitutive equation of the model is:

$$\frac{d\varepsilon}{dt}+\frac{\varepsilon}{\tau_2}=\frac{\sigma}{\tau_1\cdot E_1}+\frac{1}{E_1}\cdot\frac{d\sigma}{dt} \tag{10}$$

where the characteristic times τ_1 and τ_2 are given by:

$$\tau_1=\frac{\eta}{E_1+E_2} \tag{11}$$

and

$$\tau_2=\frac{\eta}{E_2} \tag{12}$$

In a stress relaxation experiment a constant strain ε_0 is the imposed on the specimen at $t=0$ and maintained for $t\geq 0$ while the stress σ is observed as a function of time; so that:

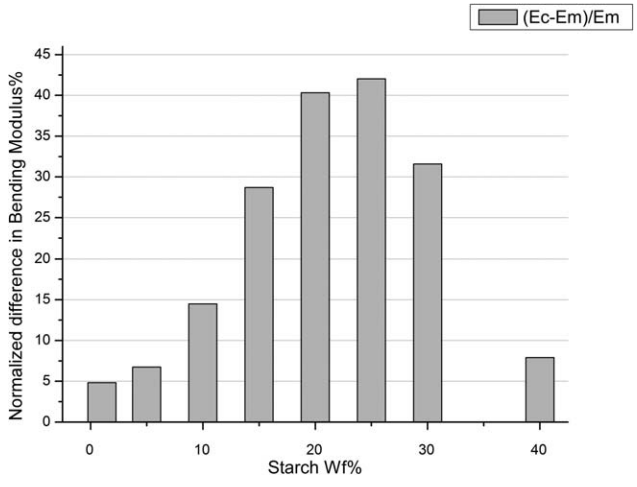

Figure 6. Normalized diagram of the bending modulus as a function of the filler weight fraction.

$$\varepsilon_{(t)}=\varepsilon_0=\text{const.}\rightarrow\frac{d\varepsilon}{dt}=0$$

and

$$\sigma(t)=\varepsilon_0\left[E_1-\frac{{E_1}^2}{E_1+E_2}\left(1-e^{-\frac{t}{\tau_1}}\right)\right] \tag{13}$$

The Power Law Model

A typical stress relaxation curve for most viscoelastic materials is shown in Figure 3. A signifies the position where the loading process was just stopped and the stress relaxation begins. The values σ_0 and ε_0 are the stress and strain at position A, respectively. Obviously, the total strain, ε_0, can be regarded as being consisted of three components; namely, the elastic strain, ε_{el}, the plastic strain, ε_{pl}, and the viscoplastic strain, ε_{visc}, occurred during the loading process. At every moment of the relaxation period, ε_0 remains unchanged and is always equal to the sum of the three components mentioned above.[23]

On the basis of the above considerations, the final expression for the (PLM) model is:

$$\frac{1}{\sigma^{m-1}}=\frac{1}{\sigma_0^{m-1}}\left[1+(m-1)\frac{t}{\tau_{rel}}\right] \tag{14}$$

Table III. Normalized Values of the Bending Modulus and Ultimate Strength as a Function of the Filler Weight Fraction

W_f (%)	Normalized bending modulus (%) $(E_c-E_m)/E_m$	Normalized ultimate strength (%) $(\sigma_{uc}-\sigma_{um})/\sigma_{um}$
0	0	0
5	6.75	10.6
10	14.49	18.17
15	28.69	23.78
20	40.31	16.04
25	42.01	14.80
30	31.58	−0.019
40	7.89	−34.58

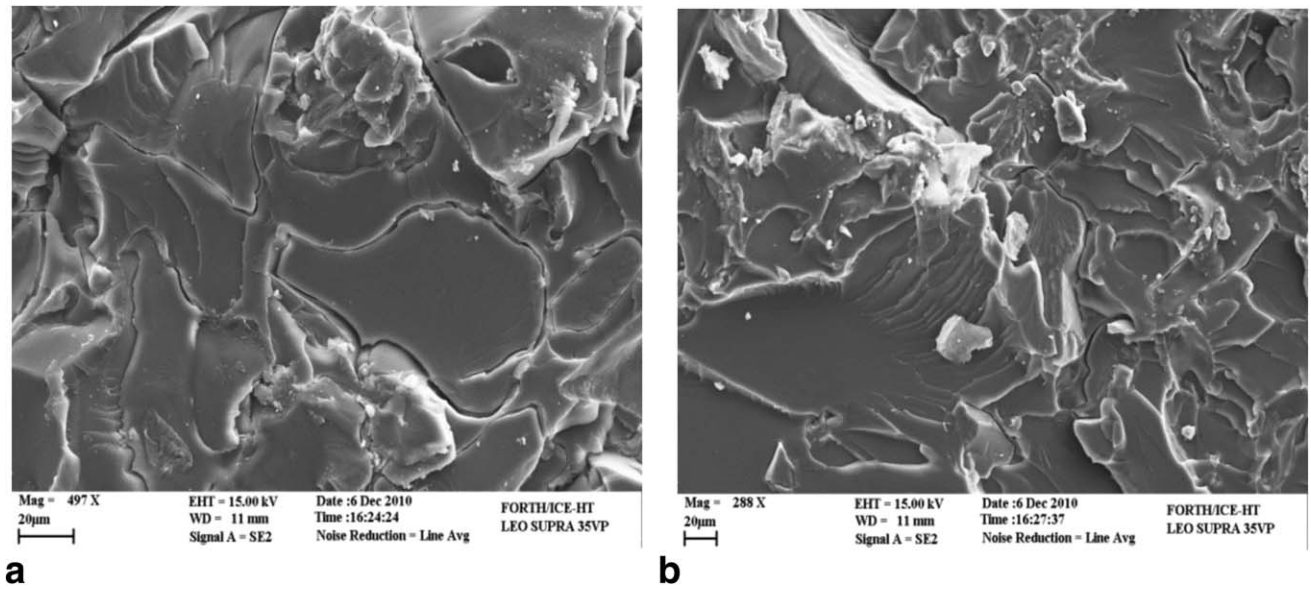

Figure 7. SEM micrographs of corn starch/epoxy composites at: (a) 10 W_f % and (b) 40 W_f % corn starch.

where[20]

$$m = \frac{\ln\left(-\frac{\tau_{rel}}{\sigma}\frac{d\sigma}{dt}\right)}{\ln\left(\frac{\sigma}{\sigma_0}\right)} + 1 \quad (15)$$

and

$$\tau_{rel} = \frac{-t}{\ln\left(\frac{\sigma}{\sigma_0}\right)} \quad (16)$$

The Residual Property Model (RPM)

The RPM model is a model developed by the CMG group, in the University of Patras, and it is used for the description of the residual behavior of polymers and polymer-matrix composites, after damage. As it has been shown[24,25], the model gives accurate predictions for the residual materials properties variation irrespective of the cause of damage and of the type of material considered at the time.[26]

The final expression for the RPM model is:

$$\frac{P_r}{P_0} = s + (1-s)\cdot e^{-SM} \quad (17)$$

where

$$s = \frac{P_\infty}{P_0} \quad (18)$$

where P_r is the current value of the mechanical property considered at any time of the damage process, P_0 is the value of the same property for the virgin material (i.e., for the undamaged material), and M is a function depended on the source of damage, and the property considered at the time. In the present case, where three-point bending tests were performed on specimens, P_0 represents the initial stress at the beginning of relaxation and P_r represents the stress at any given time t. Also

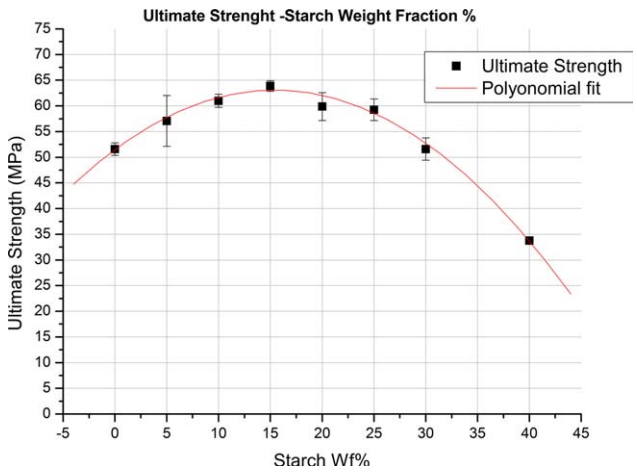

Figure 8. Ultimate strengths variation as a function of W_f of the starch particle-epoxy matrix composites investigated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

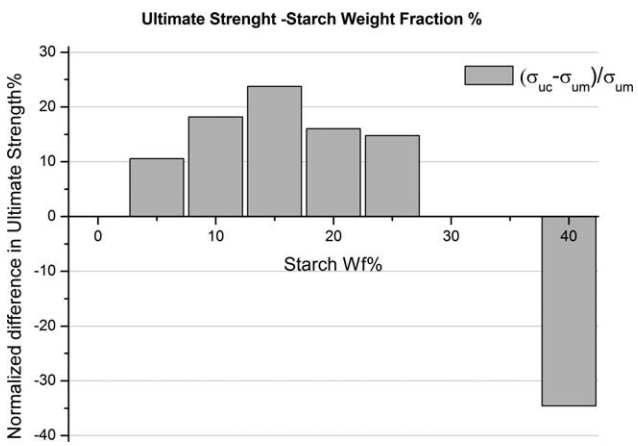

Figure 9. Normalized diagram of ultimate strength as a function of the filler weight fraction.

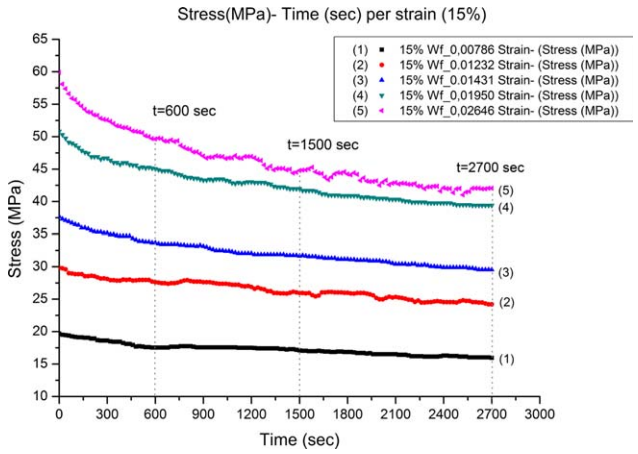

Figure 10. Stress relaxation curves for the same starch weight fraction (15% W_f) and for different strain levels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

P_∞ is the value of the property under damage saturation conditions.

Concerning the function M, in the present case, this is given by:

$$M = \frac{t}{\tau_{rel}} \tag{19}$$

Wherein t is any given time during the experiment while τ_{rel} is the characteristic relaxation time. Only two experimental points are needed, for the determination of the two parameters, s and τ_{rel}. It has been observed that, τ_{rel} can be evaluated from the stress relaxation curve by determining the point where the extrapolated tangents at P_0 and P_∞ intersect. The time corresponding to the intersection point is termed the relaxation time (Figure 4).

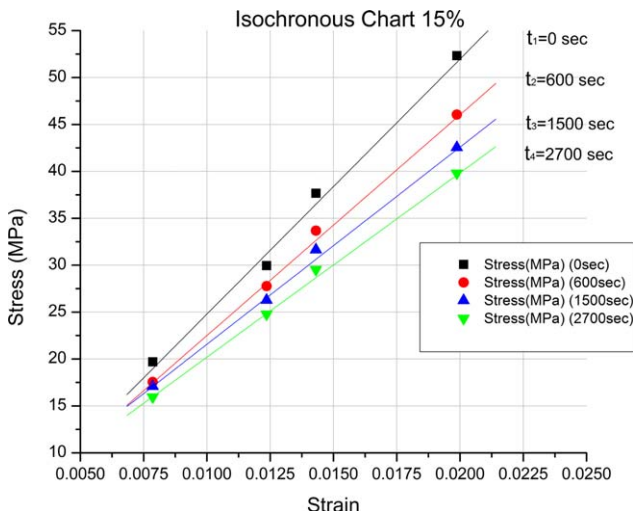

Figure 11. Isochronous curves for epoxy-starch composite with $W_f = 15\%$ and different values of imposed strain up to 2.0%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

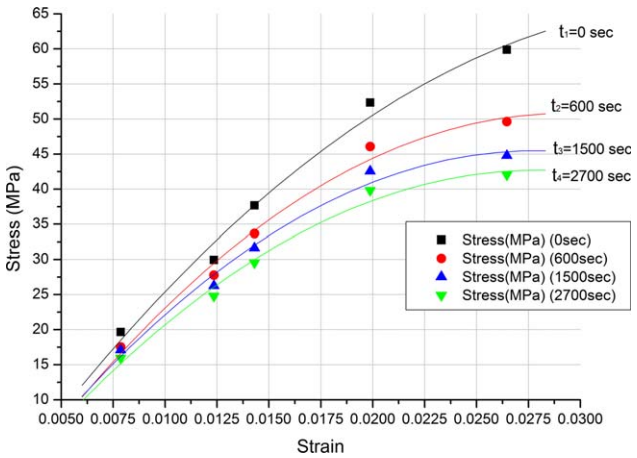

Figure 12. Isochronous curves for epoxy-starch composite with $W_f = 15\%$ and different values of imposed strain up to 2.6%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Quasi-Static Mechanical Results

Initially, results for the quasi-static three point bending experiments will be presented. The variation of the bending modulus of the composite under investigation with the filler volume fraction is shown in Figure 5. Also the MPM modulus predictions were plotted together with respective experimental results in the same diagram. It can be seen that the model predicts very well the variation of the bending modulus as a function of the filler volume fraction. As it is shown in Table II the deviation between experimental results and respective theoretical predictions, never exceeds 8%. In addition, following the procedure presented in paragraph 3, the values for the degree of adhesion K and the degree of dispersion L for the materials under investigation were calculated as: $K = 0.34$ and $L = 0.30$.

In Figure 6 is presented the percentage variation of the bending modulus as a function of the filler weight fraction. An increase

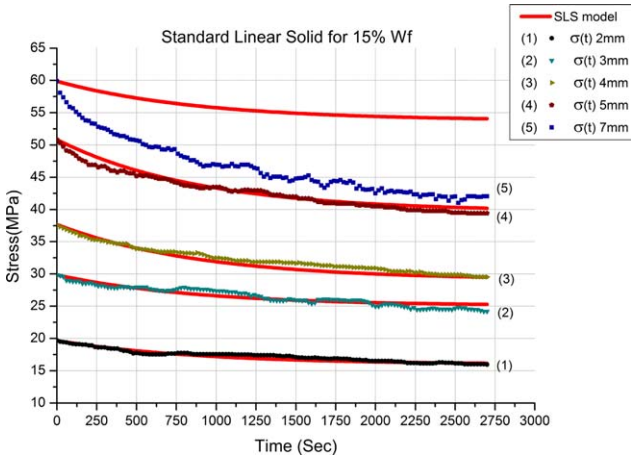

Figure 13. Comparison between experimental values and theoretical predictions as derived from standard linear solid (SLS) model for stress relaxation, of the starch particle-epoxy matrix composites investigated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

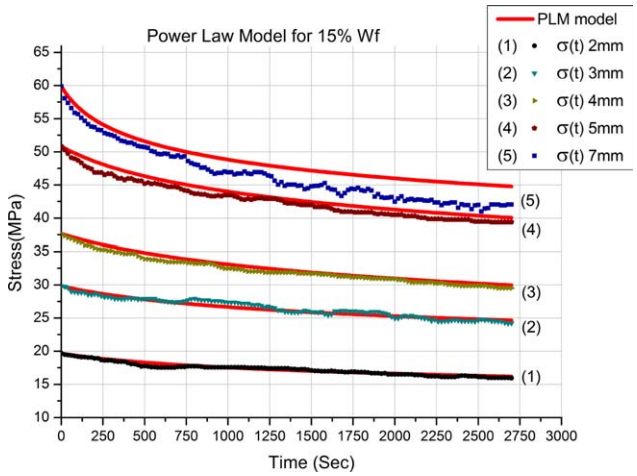

Figure 14. Comparison between experimental values and theoretical predictions as derived from the power law model (PLM) for stress relaxation, of the starch particle-epoxy matrix composites investigated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of 42% in bending modulus (Table III) was observed due to the reinforcement; however, after the threshold of 25% W_f, the bending modulus decreases due to filler agglomeration and bad adhesion as this is shown in both Figures 5 and 6. Also this effect can be attributed to a bad degree of mixing, since with the increase of starch volume fraction the viscosity of the mixture decreases, affecting the stirring process. Furthermore, as aforementioned, MPM model predicted a low degree of adhesion ($K = 0.34$) and a low degree of dispersion ($L = 0.30$), which is in accordance with observations made through SEM photomicrographs shown in Figures 7(a,b) as well as with respective data found in Refs. 21,27.

Morphology of flexural-fractured surface of corn starch-epoxy resin composites reveals the incompatibility of starch with the synthetic epoxy resin. As observed clearly in Figure 7(a) the adhesion between the filler and the matrix is bad. In general, the main disadvantage of natural filers as reinforcements to polymer matrices is the poor compatibility between filler and matrix and their relative high moisture absorption.[24]

In Figure 8 the variation of the ultimate strength as a function of starch weight fraction is depicted, while in Figure 9 the respective normalized diagram is presented. The same behavior as before is observed. Namely, there is an initial increase on the order of 23% in ultimate strength (Table III) due to the reinforcement; however, beyond the threshold of 15% W_f, the strength decreases due to the formation of aggregates as well as to the reduced adhesion between the matrix and the filler. Furthermore, for specimens with filler concentration 30% W_f the ultimate flexural strength is almost equal to that of the pure resin, meaning that the effect of aggregation is totally balanced by the particle reinforcement effect. For concentrations higher than 30% W_f, the normalized ultimate strength decreases even further reaching the value of −34% mainly due to extensive aggregations as well as to voids formation created when mixing the constituents.

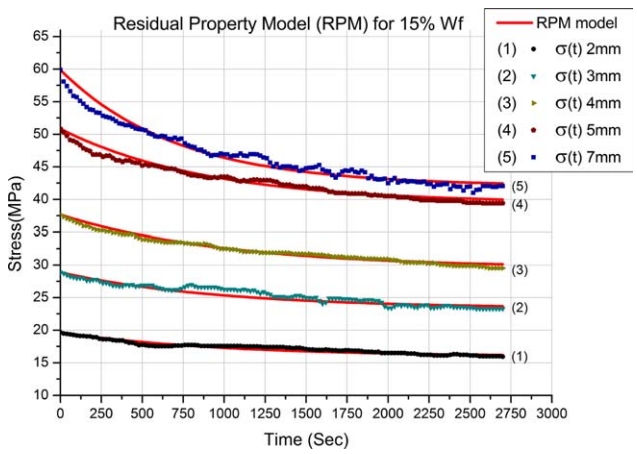

Figure 15. Comparison between experimental values and theoretical predictions as derived from residual property model (RPM) for the stress relaxation, of the starch particle-epoxy matrix composites investigated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Stress Relaxation Results

Three different theoretical models were applied in order to predict and/or describe the stress relaxation behavior of the epoxy-starch reinforced composites. Predicted values were compared with respective experimental results. These models are: the SLS model proposed by Zener, the power law model (PLM), and the RPM developed by the first author, at the University of Patras. Also, the isochronus curves were plotted, in order to determine whether or not the observed viscoelastic behavior is a linear or a nonlinear one.

In Figure 10, representative stress relaxation curves for a specific starch weight fraction (15% W_f) and for different imposed strain levels are presented. An important cross-plot is a section for a constant time, or *isochronous curve*, which results in a stress–strain curve for each time (Figures 11 and 12). It is observed that for the same filler weight fraction (Figure 10), as the imposed strain increases, the stress also increases in the various stress relaxation curves, as expected.

The isochronous curves plotted and presented in Figures 11 and 12 differ in the maximum strain imposed. More precisely, in Figure 11 the maximum strain imposed was 2% while the maximum strain for the curves shown in Figure 12 was 2.6%. Isochronous curves presented in Figure 11 show a linear viscoelastic behavior, while curves illustrated in Figure 12 show a nonlinear viscoelastic behavior. Thus, it can be deduced that

Table IV. Relaxation Time Predicted by Residual Property Model

τ_{rel} (s)	0%	5%	15%	25%
2 mm	800	800	800	650
3 mm	800	800	800	650
4 mm	800	800	800	600
5 mm	700	700	700	550
7 mm	-	500	450	-

the linear-nonlinear viscoelasticity threshold can be found in the range between the strain levels of 2% and 2.6%, corresponding to imposed displacements of 5 and 7 mm, respectively.

In the next three figures (Figures 13–15) experimental curves for the 15% starch weight fraction specimens, along with the predictions made through modeling are shown. As aforementioned, from the isochronous curves and for imposed displacements up to 5 mm, a linear viscoelastic behavior can be observed. On the other hand, for 7 mm imposed displacement it can be safely stated that the specimen exhibits a nonlinear viscoelastic behavior.

In Figure 13 a comparison between experimental and theoretical values, as derived from SLS model for stress relaxation, are shown. Although the model describes sufficiently well the linear viscoelastic behavior, it cannot describe the nonlinear viscoelastic behavior, as expected. This was expected since the SLS model is based on Boltzmann's superposition principal. In Figure 14 the corresponding comparison between experimental values and theoretical predictions as derived from PLM for stress relaxation is presented. The PLM model predicts sufficiently well the linear viscoelastic behavior; however it fails to predict well the nonlinear viscoelastic behavior. Finally, in Figure 15 the RPM model is applied on our experimental results, and as can be seen it predicts extremely well both linear and nonlinear viscoelastic behaviors.

Finally, relaxation times as derived from the application of the RPM are given in Table IV. As depicted in Table IV the relaxation time depends both on the applied deflection and the filler weight fraction.

CONCLUSIONS

In the present investigation the quasi-static and viscoelastic behavior of starch reinforced epoxy resin composites was thoroughly studied. The modulus prediction model (MPM), which is developed by the first author, was applied in order to predict the variation of the bending modulus as a function of the filler volume fraction. Also, for the viscoelastic behavior, existing models were applied and as compared with respective experimental findings and the RPM predictions. The RPM model was developed by the first author, for the description of the residual behavior of polymers and polymer-matrix composites, after any type of damage. From the whole work the following conclusions can be derived:

- A 42% increase in stiffness, and a 23.8% in strength was achieved. Results have shown that there is an optimum filler loading corresponding to the maximum quasi-static properties, beyond which a decrease of the properties was observed due to agglomeration.
- The modulus prediction model was successfully applied and predicted extremely well the variation of the bending modulus. From the application of the same model a low degree of adhesion ($K = 0.34$) and a low degree of dispersion ($L = 0.3$) for the materials manufactured and tested were calculated. These findings were experimentally verified through both SEM photography and relevant sources as taken from Refs. 24,25.
- It was proved that the RPM model predicted perfectly well and much better than the two other models the stress relaxation behavior of the composites investigated and above all it can predict well both the linear and the nonlinear viscoelastic behavior.
- Finally, it was found that the relaxation times as calculated from the RPM model application, depend both on the applied deflection and the filler weight fraction.

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