Some Properties of Starch/Epoxy Composites

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Generally the fillers are used in order to diminish the amount of matrix for a certain composite structure but in the last period fillers are used to change also the basic properties of the material used as matrix, especially in the case of PMC (polymer matrix composites). The actual study is carried out in order to determine the influence of starch over the properties of epoxy resin and is based on the well known fact that starch is creating its own network inside of a matrix. In this case it is possible to talk about a nano-reinforcement of the matrix which might be used to form fiber reinforced materials with better mechanical or thermal properties. Due to its properties starch might be used also to ensure the dispersion of other fillers which generally tend to aggregate as CNT or ferrite and in this case it is necessary to know the upper limit of starch concentration for which the polymer properties are not changed or suffer negligible modifications. Not at least the presence of starch into the epoxy matrix might determine a higher alterability of the polymer making it easier to neutralize. Being easy to functionalize starch might be used as vector to transport positive and/or negative ions inside the polymer matrix via complex combinations which might lead to controllable electro-magnetic properties of the formed material or to multi-functional materials. The thermal, mechanical, tribological and electrical properties of starch/epoxy composites were studied using appropriate methods for materials with various starch concentrations.

KEY WORDS: starch, epoxy, physical properties, mechanical properties

The thermosetting matrix composites are largely used due to their properties even if they are difficult to neutralize. Unlike the thermoplastics, generally, they show a better thermal stability, better tribological behavior making them suitable for long life applications.

Filling the polymer with various substances in different forms (powders, whiskers, and flakes) was, at the beginning, a way to reduce the amount of polymer used to form a structure but this method became a way to modify the basic properties of the polymer leading to improvements regarding thermal, electro-magnetic or tribological properties.

The researchers had spent much time on modeling the properties of a particulate composite on the basis of its components properties and many solutions were purposed [1 – 5]. For all the models some simplifying assumptions had to be made limiting the models' predictions. For instance, there are not models regarding the connection between the nature and dimensions of dispersed particles and the nature and the properties of the polymer. In the case of thermoplastics the fillers are dispersed into the melt of the polymer and it is possible to control the dispersion conditions by controlling the temperature of the mixture [6]. In the case of thermosetting materials the powders (it is the most important case) are dispersed into a pre-polymer mixture allowing a possible chemical interaction between the polymer and powders molecules. Some of the powder materials could absorb some of the pre-polymer mixture (such as CNT) leading to more dense materials. Generally thermosetting materials are bi-component systems which have to be mixed in certain amounts to polymerize. This fact is making possible three different ways to disperse the powders – into a component, into the other, or in the pre-polymer mixture – leading to different properties of formed material [7].

Another aspect is more important regarding the powder fillers namely they may create nanostructures inside the matrix [8, 9] if they chemically interact with the thermosetting components. In this regard it has to be said that generally the powder particles tend to aggregate inside the polymer volume changing the polymer quasi-continuous structure and leading to worst mechanical properties. A way to solve this problem is to treat the powders in order to make them more dispersible inside the pre-polymer volume; another way is to use two fillers one as dispersant and the other one to change the intended properties. In this category talc and clay might be included with benefits regarding the fire resistance and wear resistance of formed polymers [10, 11].

The mixing rule [12, 13] is giving some information regarding the amplitude of a property if the properties of the components and their ratios are known. But the mixing rule works for micron dimensions of dispersed particles and in such dispersion the particles act as defects inside the polymer matrix leading to poor mechanical properties. Since the particles dimensions are decreased other aspects have to be taken into account. If at micron level it might be said that the interaction is solid-liquid type which may be described in terms of adhesion and cohesion forces at nano level the interaction might be at the level of molecules leading to nano-structures with significant changes of formed material properties.

As per starch many studies had emphasize its role as filler and in this regard is important to underline the opportunity to transform the epoxy resin in a more alterable matrix transforming it into an environmental friendly material. Also it has to be taken into account the fact that starch (natural one) contains nano-structures and might generate nano-structures inside the matrix [14].

Materials

The Epiphen RE 4020 – DE 4020 from Bostik was used as matrix and corn starch as filler to form materials to be studied. The named epoxy is a bi-component one with a mixing ratio of 3:1 between the two components and with

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a gel time of about 45 min. The mixing technique chosen for this study consisted in mixing the right amounts of the two components of epoxy system for about 20 min. The amount of starch was then added and the mixture pre-polymer/starch was mechanically mixed for other 15 min. The last step was to form rectangular shaped plates into glass moulds. The starch amounts are from 1% to 50% in volume ratios, with 1% increment from 1 to 5% and 5% increment from 5 to 50%.

After the polymerization (24 h) the samples were extracted from moulds and they were thermally treated according to producer recommendations in order to reach their best properties (8 h at 60 °C, 2 h at 90 °C and 2 h at 120 °C – to ensure a higher value of glass transition of the polymer).

The plates were used to analyze the electro-magnetic properties and after that samples were extracted for the tribological, bending and thermal analysis. The sample extraction was realized using a high pressure water jet machine to avoid edge effects and thermal degradation of the polymer.

Measurements and results

Electro-magnetic analysis

The electro-magnetic properties of formed materials were investigated using recommended methods [15, 16] and appropriate experimental fixture. As starch is not an electro-magnetic active ingredient it is expected that the values of the two parameters to not differ significantly. The electrical conductivity was evaluated from electrical resistance while the dielectric permittivity was evaluated on the basis of electrical capacitance. The experimental data (electrical resistance and electric capacitance) were achieved using an LCR-meter and there were 2000 values for each parameter. The recorded sets of values were statistically analyzed and the averaged values were computed for each significant parameter. For each parameter measurements were developed for two frequencies of measuring signal 10 kHz and 100 kHz to point out an eventual frequency dependent behaviour of materials.

Figure 1 and 2. show the results regarding the electrical conductivity of particulate composites and it might be noticed that the surface electrical conductivity is practically independent on starch amount while the bulk conductivity decreases for light concentrations of starch. In the case of bulk conductivity also it might be noticed the fact that higher starch concentrations (above 15%) lead to the same behavior as epoxy resin (denoted as 0% starch ratio). In the case of surface conductivity the behavior is understandable due to the fact that the entire surface of the sample is made of polymer and starch particles influence is lower. In the case of bulk conductivity the lowering concerns with the amount of air introduced into the polymer matrix together with the starch.

In the case of dielectric permittivity (both surface and bulk) as it might be observed in figure 3 and 4. the presence of starch does not change the polymer behavior. Using starch concentrations of about 15% to 40% the composites electro-magnetically act as epoxy acts.

Thermal analysis

The TMA-SDTA 840 from Mettler Toledo was used to determine the coefficient of thermal expansion by means of dedicated software Star**e** also from Mettler Toledo. The dilatation curves for few samples are presented in figure 5. It is noticeable that in the case of 10 and 20% starch ratios the peak corresponding to the glass transition of epoxy resin is moved to the right with about 5^{o}C signalizing a structural change. At higher concentration the presence of starch replaces more and more polymer chains and basic behavior of the matrix dilutes and the material acts as a granular aggregate.

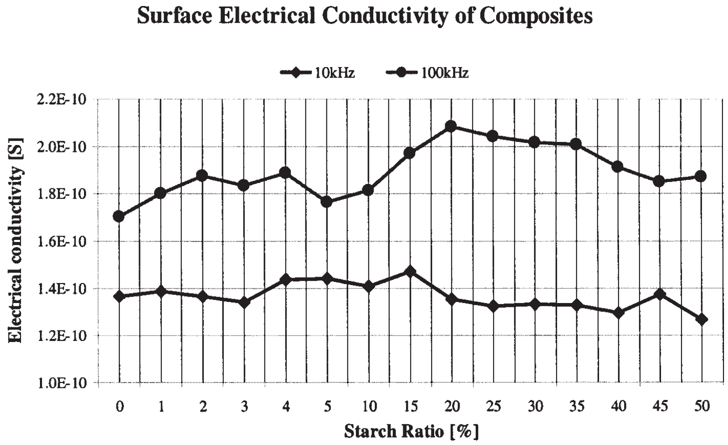

Fig. 1. Surface electrical conductivity of particulate starch/epoxy composites

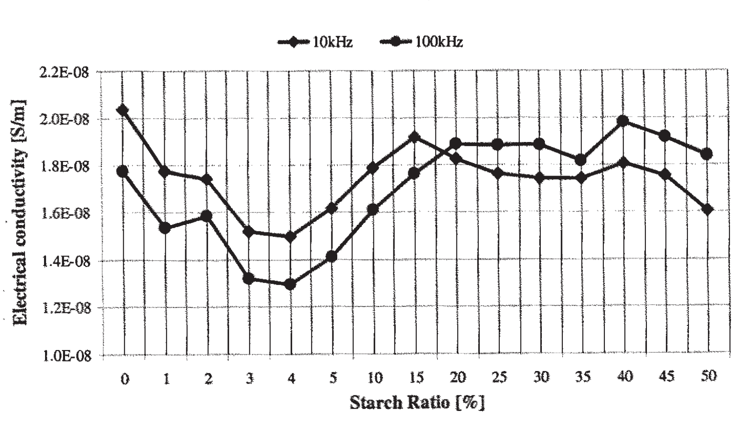

Fig. 2. Bulk electrical conductivity of particulate starch/epoxy composites

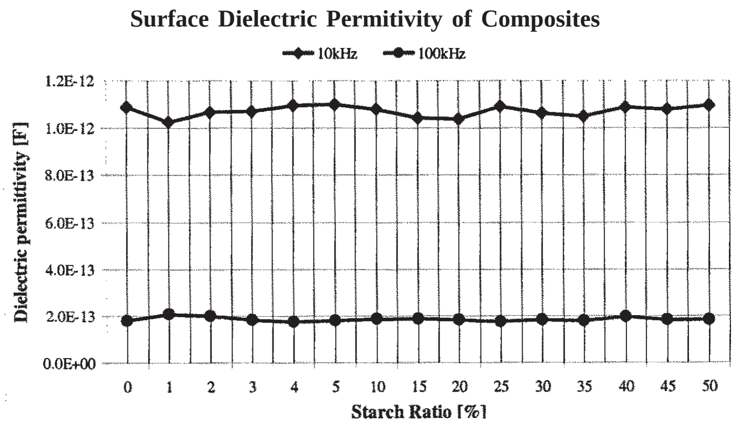

Fig. 3. Surface dielectric permittivity of particulate starch/epoxy composites

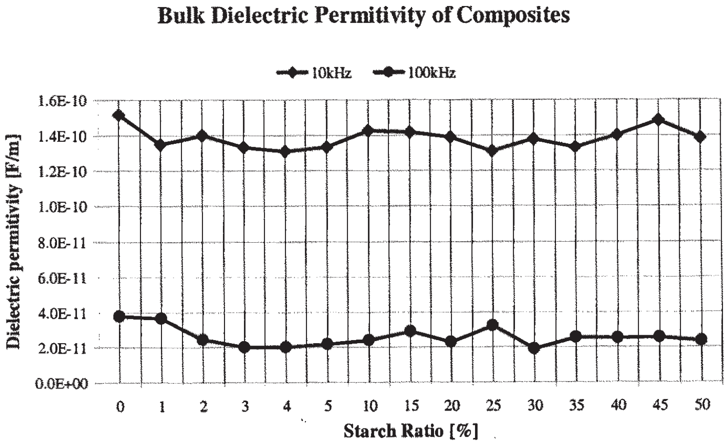

Fig. 4. Bulk dielectric permittivity of particulate starch/epoxy composites

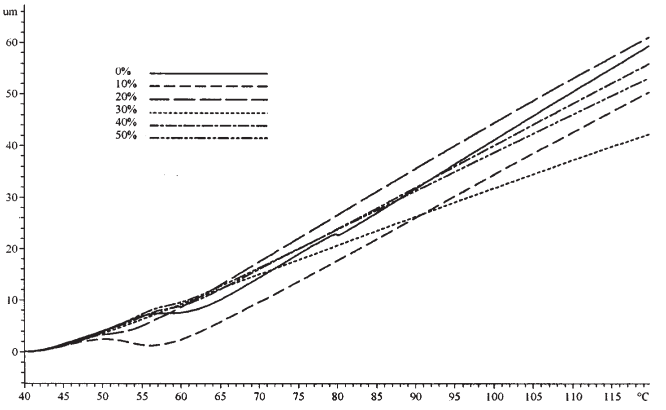

Fig. 5. Dilatation curves of some particulate composites (thickness variation vs temperature)

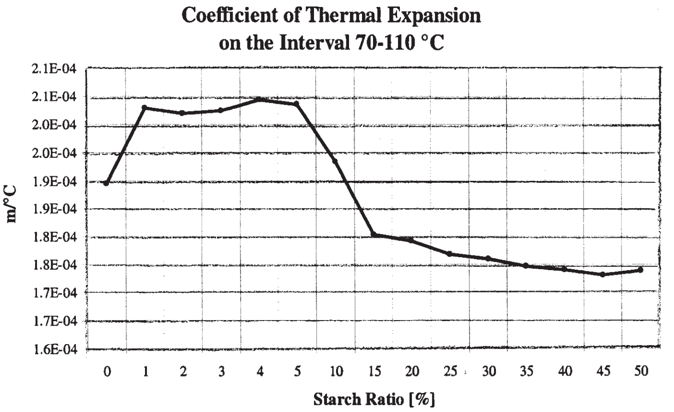

Fig. 6. Coefficient of thermal expansion for formed materials

As per coefficient of thermal expansion one may notice from figure 6 that at lower values of starch ratio the amount of air inside the matrix is higher and the air presence determines a foam like behaviour of the particulate composite. At higher values of starch ratio the materials become more dimensionally stable.

The specific heat of formed materials was investigated using DSC 1 from Mettler Toledo and the above mentioned software. In figure 7 averaged values of the specific heat in the interval [70°C – 110°C] are presented. As expected, the specific heat has a smooth variation on the entire interval (it increases with the temperature) but to characterize the global behavior the average value is good enough.

In figure 8. the heat absorption curves for few materials are showed. The differences are due to the weight of each sample but the specific heat value is not affected. For low ratios the specific heat decreases reaching the lowest value at 3% while for higher ratios the specific heat shows almost the same value as epoxy.

Both dimensional analysis and specific heat analysis were developed on three samples of each material and the presented results are averaged values. The curves showed in figure 5 and 7 are actually the curves as they results from software usage but from the 15 obtained curves for each analysis the most significant were placed on the same graph with re-scaling such as all of them to start on zero. That is why in figure 5 the thickness variation is represented and not the thickness itself, actually the samples are not identical and they have different thickness at the start of the measurement.

Tribological analysis

The tribological behavior and the wear behavior had been studied on the same machine *Multi-Specimen Test System - UMT from CETR* in the fixture pin-on-disk with pin made of formed material and steel disk. For abrasive tests the disk was covered with abrasive paper P 400.

The friction conditions for the tribological study were set at: normal loading 10 N, sliding distance 1700 m and

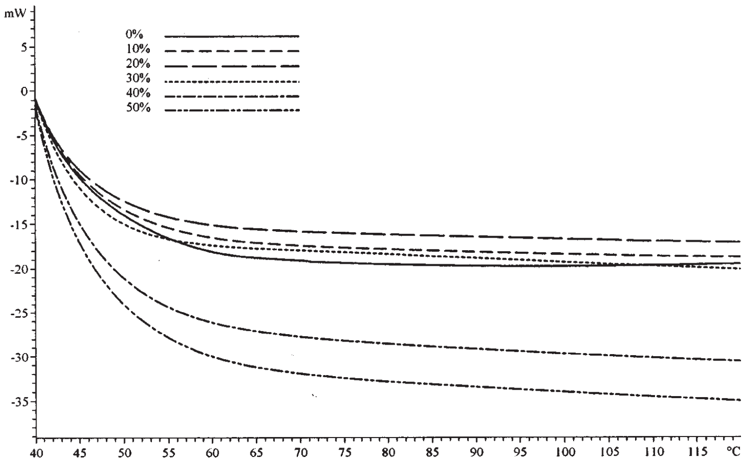

Fig. 7. Heat flow for some of the materials (heat flow vs temperature)

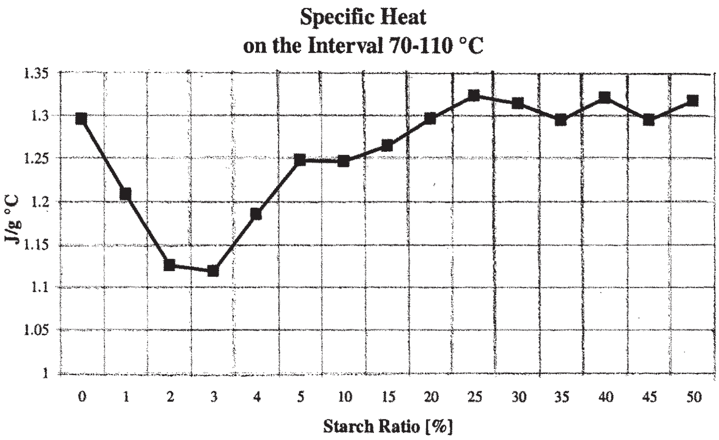

Fig. 8. Specific heat of formed materials

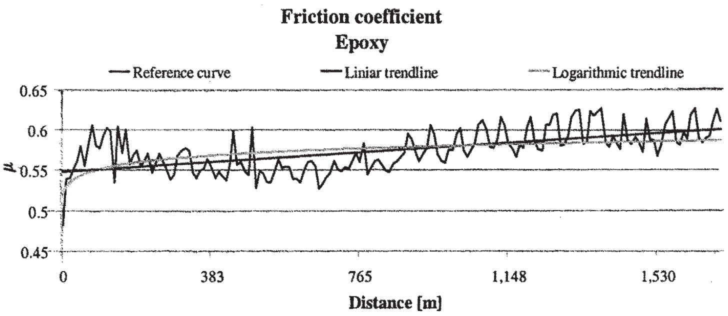

Fig. 9. Friction coefficient for epoxy (matrix material)

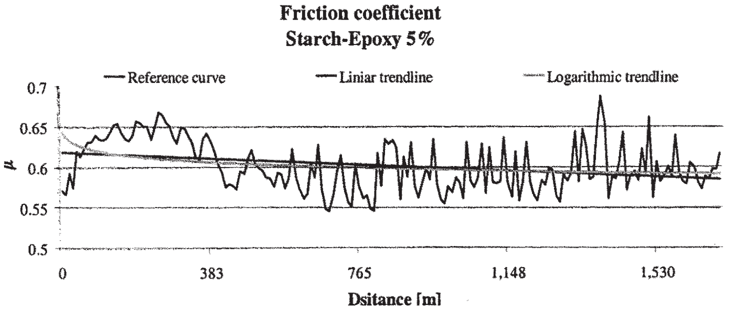

Fig. 10. Friction coefficient 5% starch-epoxy composite

sliding speed 0.942 m/s for all the materials and in figures 3 to 6 some of acquired data and their trends are presented.

Generally, the averaged friction coefficient shows three tendencies: decreasing during tests (for low starch concentrations (1% to 5%) - figure 10; remaining almost constant during tests (10% to 25% starch ratio) – figure 11; increasing during the tests (for concentrations of 30% and above) – figure 12, to make a comparison the frictional coefficient of epoxy resin is presented in figure 9.

For studied materials the frictional wear rate was evaluated according to [17] and the results are presented in figure 13. The best friction wear resistance is reached in the case of 10% material but is noticeable that adding starch into the matrix the frictional wear rate decreases. Taking into account also the specific weight of materials it is expected that at high concentrations the frictional wear rate to be higher due to the large amount of material which is lost during test. The high resistance means that adding starch the frictional properties are improved by ensuring a better package of the polymer chains and limiting the weight loss by making the matrix less breakable.

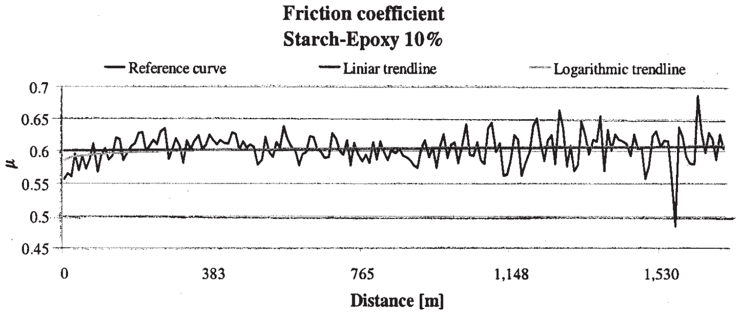

Fig. 11. Friction coefficient 10% starch-epoxy composite

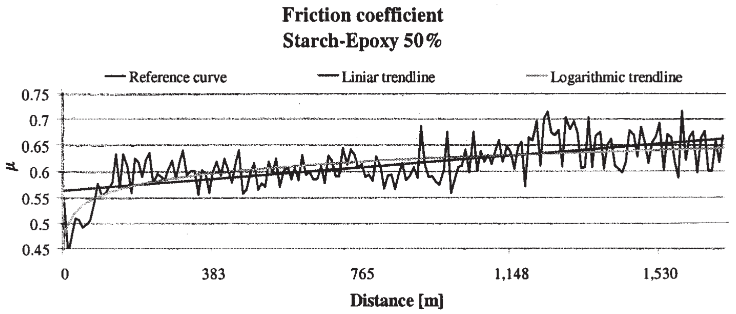

Fig. 12. Friction coefficient 50% starch-epoxy composite

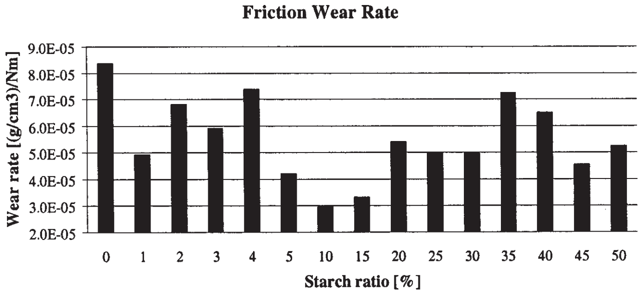

Fig. 13. Friction wear rate of formed composites

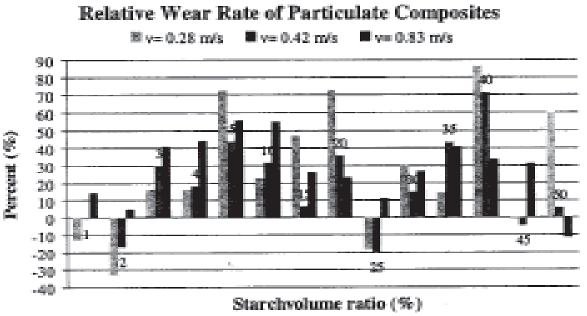

Fig. 14. Relative abrasive wear rate of formed composites

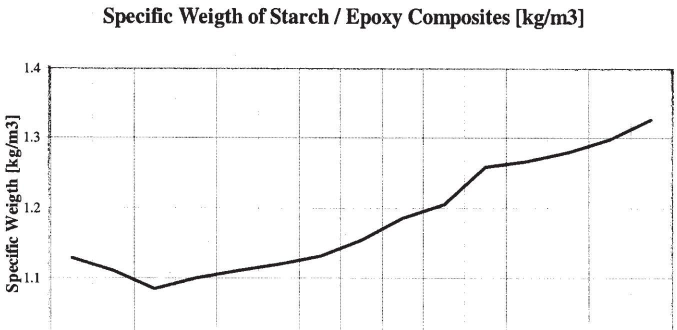

Fig. 15. Specific weigth of formed materials

The abrasive tests [18] were performed at a normal loading of 2 N and three different sliding speeds as it might be noticed in figure 14. Almost all the materials show abrasive wear rates higher than epoxy one the few exceptions appear randomly and are explainable just by defects inside the matrix. These defects may appear as a consequence of forming technique or may be caused by mechanical defects of samples as cracks. The relative abrasive rate was evaluated as the difference between the value of the rate for particulate composite and the value of the rate for epoxy reported to the abrasive wear rate of epoxy resin.

Since both frictional and abrasive wear rates depend on materials specific weight in figure15 are presented the measured values of this parameter. For lower concentration of starch the density of materials decreases because of the air inside the epoxy matrix but starting with 10% (when the density is almost the same as for epoxy) the values are increasing as expected.

Bending analysis

Bending measurement was performed using a M350-5AT testing machine and the evaluations were made using dedicated software both from Testometric. In figure 16. the bending modulus of formed materials is presented and it might be noticed that starch presence is not changing the ending elasticity of materials. The same result is observable from figure 17 regarding the energy to break of materials. These results together might be intrepreted as there is a high compatibility between the starch and epoxy resin leading to high quality interfaces which balances the

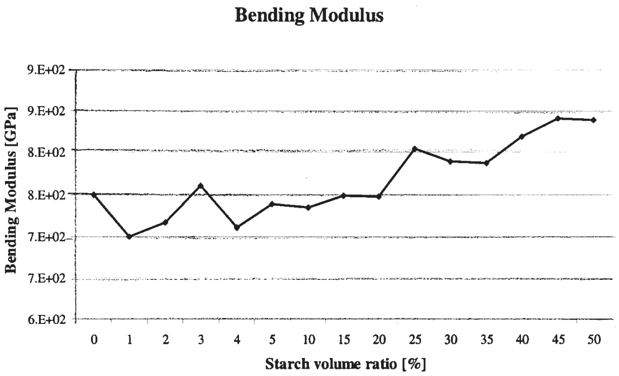

Fig. 16. Bending modulus of formed materials

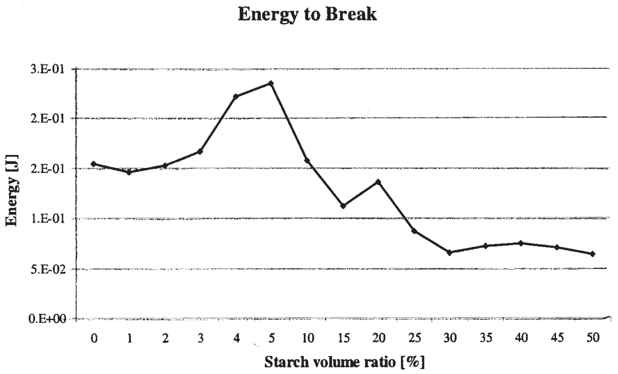

Fig. 17. Energy to break of formed materials

granular structure of particulate composites or the forming technique leads to some structures which are not corresponding to matrix or starch, practically a new material.

Conclusions

The attempt of dispersing some active powders inside the polymer matrix is obstructed by the tendency to aggregate of the particles. To avoid that dispersants are used to ensure the uniform dispersion of powder particles inside the liquid polymer or pre-polymer. Adding chemical compounds to the polymer in order to solve the problem might lead to poor properties of the matrix so a better solution is to disperse into the polymer or pre-polymer another powder with dispersive effect (starch, clay, talc) or a mixture of this dispersive powder and the active one.

This study emphasizes the fact that filling the epoxy pre-polymer with an amount 10% volume ratio of starch practically the properties of the matrix are not changed and that means that is possible to use not epoxy system as matrix but the starch-epoxy composite without damaging the final properties of intended materials. It is possible to obtain CNT-epoxy composites or ferrite-epoxy composites avoiding their clusterization if instead of epoxy the starch-epoxy is used.

Of course the same combination might be used to form reinforced materials with the advantage of controlling the final properties (not only mechanical ones). Other studies might be developed to point out the influence of dispersion technique (in the case of thermosetting polymers) and to analyze the properties of particulate composites with epoxy matrix and a mixture of starch and other powders as filler.

Microscopic and structural analysis might be performed by means of SEM and X-Ray to identify eventual nano-structures inside the starch-epoxy composites or inside the particulate composites with starch-epoxy matrix.

Since the mixing rule is giving acceptable answers for microscopic spherical particles uniformly dispersed into the matrix and clearly is not able to describe the presented results a modeling based on neural network had been developed. The neural networks were trained using a partial set of the above results and the validation was done by querying the values for the other values. It seems that the model works.

In the attempt of controlling the properties of a composite and to transform it into a multi-functional material the starch-epoxy system might be a reliable solution to form layered materials not only from the reinforcement point of view but also from the polymer (matrix) layers point of view. Each layer might be used to solve one or two properties as the assembly to fit all the required and desired properties. For instance the external layers of a composite structure as to present three major properties: high electrical conductivity, high wear resistance and high corrosion resistance the other properties as magnetic, mechanical or thermal ones might be placed inside the material or structure, being protected by the external layers.

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