



STARCH EPOXY COMPOSITES A STUDY OF STARCH AMOUNT INFLUENCE

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Abstract: It is well known that starch reticulates when solved into a liquid. Based on this observation might be possible that starch to form its own network inside a thermosetting polymer volume (a network of polymeric chains) acting as a reinforcement if it is solved into the pre-polymer solution. Starting with this idea and taking into account the fact that starch may be easily functionalized it might be possible to use this powder to "place" other atoms or other chemical radicals inside the polymer to change its properties. These are the reasons for which this study is carried out in order to exhaustively characterize the starch epoxy materials realized from epoxy system EPIPHEN RE 4020 / EPIPHEN DE 4020 and corn starch (for food purposes) with weight rations starting with 1:100 till 50:100. For this paper dimensional stability and tribological behaviour are taken into account. The tribological tests were performed with pin-on-disk (with rectangular pins made of filled composites and steel disk) in order to identify the maxim amount of starch to be used without critical effects on the final materials properties.

Keywords: starch, epoxy, thermal behavior, tribological behavior, wear..

1. INTRODUCTION

Filling the polymer with various substances in various 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 modelling the properties of a particulate composite on the basis of its components' properties and many solutions were purposed [1-3]. 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 [4]. 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 [5].

Regarding the powder fillers another aspect is more important, namely they may create nanostructures inside the matrix [6, 7] if they chemically interact with the thermosetting components. In this regard it has to be said that generally the powder's particles tend to aggregate inside the polymer volume altering 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 de properties. In this category talc and clay might be included with benefits regarding the fire resistance and wear resistance of

formed polymers [8, 9].

The mixing rule [10, 11] 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 even to nano-structures with significant changes of formed material's properties.

2. MATERIALS

This study started with the idea that starch is a special compound which is developing its own structures when is dispersed into a liquid. Thinking this way it would be possible that starch to constitute a network inside the polymer network which means that the polymer is nano-reinforced. For such answers a SEM analysis is required and this is next level of the study.

Mean time starch is very easy to functionalize with different complex compounds. It is possible, this way, to use starch as vector to implant positive or negative ions inside the polymer network. The advantage of this receipt consists in easiness and elegance but involve a study regarding the amount of starch which might be placed into the polymer without changing its mechanical properties. Having ions inside the polymer it is possible to increase electrical conductivity, and even to control it. Another aspect is connected with the fact that starch is an excellent dispersant so it might be used to avoid aggregation of other powders' particles such as CNT, ferrite etc which are electro-magnetic active and could be used to control electro-magnetic response of the formed material.

The EPIPHEN RE 4020 – DE 4020 was used as matrix and corn starch as filler to form particulate composites with volume ratios starting with 1% and ending with 50%; from 1% to 5% the increment is one unit while from 5% to 50% the increment is five units. As dispersing technique in all the cases the amount of starch was mechanically dispersed for 30 minutes into the pre-polymer mixture (EPIPHEN RE 4020 – DE 4020). The named epoxy system has 45 minutes gel time so the mixture was moulded while its viscosity was not too high. After the polymerization (24 hours) the samples were extracted from moulds and they were thermally treated according to producer's recommendations in

order to reach their best properties (8 hours at 60 °C, 2 hours at 90 °C and 2 hours at 120 °C – to ensure a higher value of glass transition of the polymer).

Samples for thermal and tribological analysis were extracted from formed plates by using a high pressure water jet machine to avoid edge effects and thermal changes of the materials.

3. MEASUREMENTS AND RESULTS

Thermal properties of formed materials were investigated in order to identify the effects of starch filling over the epoxy matrix. Also a goal of this study is to determine the maximum starch concentration for which the basic properties of the epoxy resin are not changed allowing the use of starch as dispersant for other active powders. In this regard is not taken into account the initial dispersion technique which might influence the results.

The specific weight of formed materials is showed in Figure 1. Represented values are the ones after the thermal treatment. For the lowest starch ratios the material density is lower than epoxy's one due to the air which is introduced into the polymer volume together with the starch powder. At 10% the material density is just a little bit higher than the epoxy's one and at higher ratios the material specific weight becomes higher that the one of the base polymer.

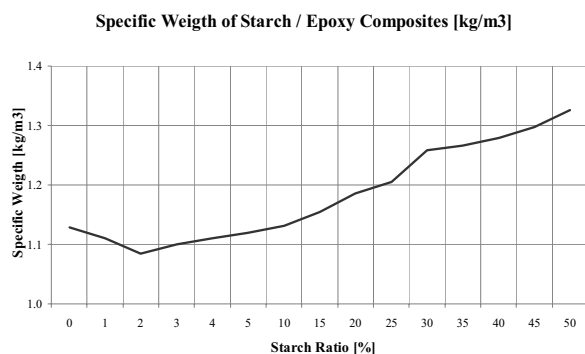


Figure 1. Specific Weighth of Starch/Epoxy Materials

The TMA-SDTA 840 from *Mettler Toledo* was used to determine the coefficient of thermal expansion by means of dedicated software *Stare* also from *Mettler Toledo*. 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°C signaling a structural change. Due to the air inside the polymer at low starch ratios the coefficient of thermal expansion is higher than the epoxy's one while for higher ratios it decreases. At 10% starch ratio the coefficient of thermal expansion shows almost the same value for epoxy and for starch/epoxy, Figure 2.

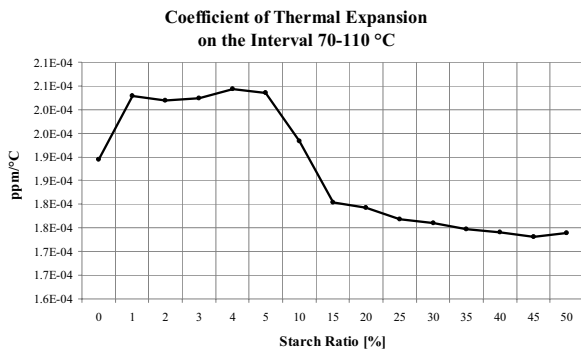


Figure 2. Coefficient of thermal expansion

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

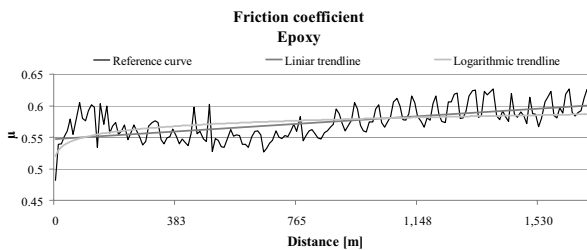


Figure 3. Friction coefficient of epoxy resin

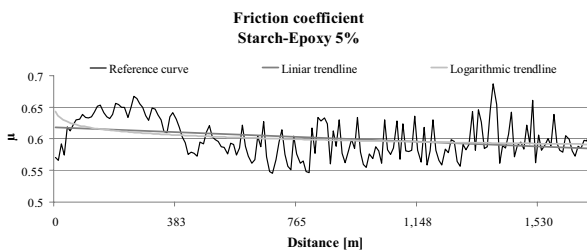


Figure 4. Friction coefficient of starch/epoxy (5%)

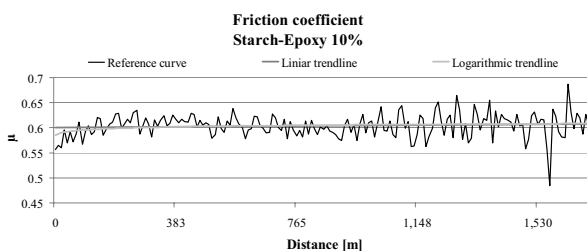


Figure 5. Friction coefficient of starch/epoxy (10%)

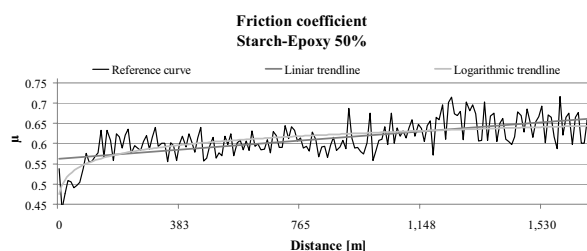


Figure 6. Friction coefficient of starch/epoxy (50%)

The friction condition for the tribological study were set at: normal loading 10 N, sliding distance 1700 m and 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%); remaining almost constant during tests (10% to 25% starch ratio); increasing during the tests (for concentrations of 30% and above).

For studied materials the frictional wear rate was evaluated and the results are presented in fig. 7.

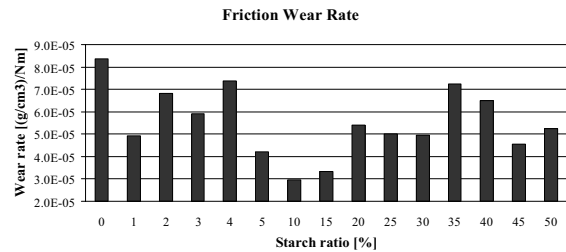


Figure 7. Friction wear rate of starch/epoxy composites

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.

The abrasive tests were performed at a normal loading of 2 N and three different sliding speeds as it might be noticed in fig. 8.

Almost all the materials show abrasive wear rates higher than epoxy's 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.

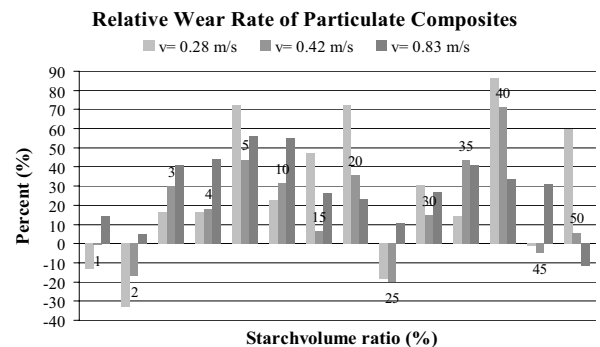


Figure 8. Relative abrasive wear rate

4. CONCLUSIONS

Even the design problem is a complex one the presented results are encouraging further studies regarding filled polymers and reinforced materials with filled polymer matrix to achieve more advantages when forming a material. Another aspect is connected with the description of particulate composite's properties in terms of powder and polymer properties. The mixing rule does work for micron dimensions and is not taking into account possible interaction between fillers' particles and polymer's components. For this study the starch was dispersed directly into the pre-polymer mixture and it is expected that none interaction took place, the starch particles were covered by polymer chains. In this hypothesis the air (or other gaseous chemical compounds) presence inside the matrix is normal but this situation could be improved by using anti-foaming products or by changing the way of dispersion.

The aim of this study was to establish the highest starch concentration which is not changing the epoxy's basic properties. It seems that the answer is 10% from specific weight, thermal stability and frictional properties but is not good enough from the abrasive behaviour point of view. Anyway the study is just a preliminary analysis before using starch just to disperse other fillers which generally tend to aggregate as CNT or ferrite or to use functionalized starch to transport at the polymer chains level some positive or negative ions able to improve the electrical conductivity.

In this regard all the materials have to be studied by SEM and XR means to point out eventual structural changes. Also mechanical properties of materials have to be studied being useless to improve other properties if the mechanical ones are damaged. All the analysis have to be repeated for each material formed with dispersant starch or functionalized starch because even a concentration of 10% will be used it is possible that active fillers' particles to change the properties due to their presence or equally it is possible that complex combinations used to functionalize the starch to chemically interact with the polymer components.

Using filled matrix it is possible to design and form reinforced materials with certain properties only by means of type and amount of the filler. Also using the lay-up method of forming with pre-polymer or filled pre-polymer mixture it is possible to obtain materials with certain properties at different depths inside the material (high electric conductivity at external layers, high magnetic properties in the core etc) but having the same type of polymer chains in all the volume and ensuring by this a right transfer of efforts inside the material.

Using fabrics to reinforce such composites (instead of pre-pregs) it is also possible to obtain polymer bridges through reinforcement layers and not only between them as in the case of laminates.

The presented results are encouraging the continuation of the studies not only in the two above mentioned directions but also in using starch filled epoxy to form laminae and stratified materials to point out also the changes induced in electromagnetic, thermal, mechanical and tribological properties in the case of reinforced materials

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