NEW FINDINGS IN RESEARCH OF EPOXIDES WITH NANO FILLERS EXPOSED TO AGEING

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Abstract: During the past 4 years I have managed to acquire a huge amount of data, pointing to changes in properties of epoxides with nanofillers. These differences were mostly caused by thermal ageing, but also by natural ageing and manufacturing processes of epoxides with nanofillers. Changes were reflected on dielectric attributes of epoxy materials with nanofillers and were subjected to various examination methods. The core method is dielectric relaxation spectroscopy (DRS), which can detect changes not only on physical, but also chemical level. Differential Scanning Calorimetric (DSC) and Thermo Gravimetric Analysis (TGA) were used. These methods helped with better understanding of internal chemical changes in chains.

Keywords: DRS, DSC, TGA, ageing, epoxy, pure, nanofillers

1. INTRODUCTION

The revolutionary idea, that nanofillers prevent breakdowns, was discovered in 1990's, but there are still problems with uniform nanofiller distribution in epoxy. Nanofillers have a great potential, mostly thanks to their low price and beneficial attributes. Scientists have been trying to estimate, whether their characteristics would degrade over time and if the nanocomposite advanced material would deteriorate. Evaluation of changes in epoxy matrices had been a subject of research of many scientists around the globe for a long time.

Thermal ageing method was selected due to its simplicity, availability and accuracy. This method puts material into similar conditions as during natural ageing. Basically, thermal ageing is an accelerated process of natural ageing – after 10 hours we can achieve a state like after 10 years of natural ageing, provided some basic assumptions are met.

2. PRESENT STATE AND BACKGROUND

The most advanced research in this field is being carried out probably in Japan, the greatest contribution being the ability to manufacture samples having thickness of only a few nanometres, by which very high capacitances during dielectric relaxing spectroscopy can be reached. Another important research group is in Germany, where they were able to measure epoxy materials in very wide frequency and temperature range [1]. Also researchers from the Canadian "Institut de recherche d'Hydro-Québec" (IREQ) have managed to acquire interesting results – they manufactured samples only 150 μm thick, which is 6-times thinner than our manufacturing capabilities [4].

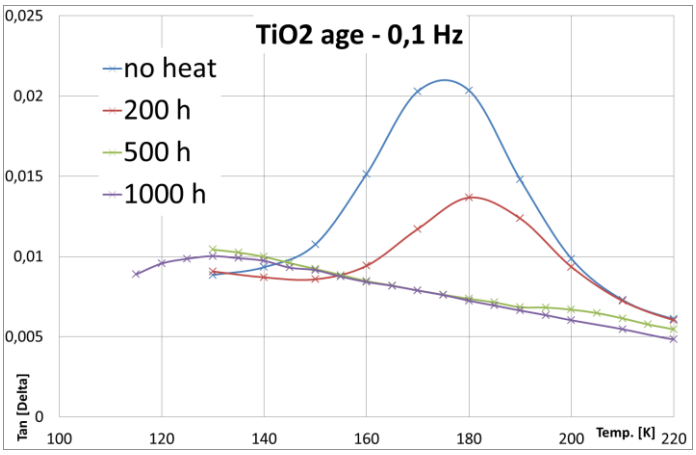
3. EXPERIMENT AND RESULTS

The goal of the experiment is to evaluate attributes of epoxies with nanofillers, as accurately as possible, during their ageing process. In order to achieve it, we used the most modern techniques and measurement instruments – like dielectric relaxation spectroscopy carried out on Novocontrol Alfa A analyser with QUATRO cryosystem, WinData collecting software a WinFit fitting program.

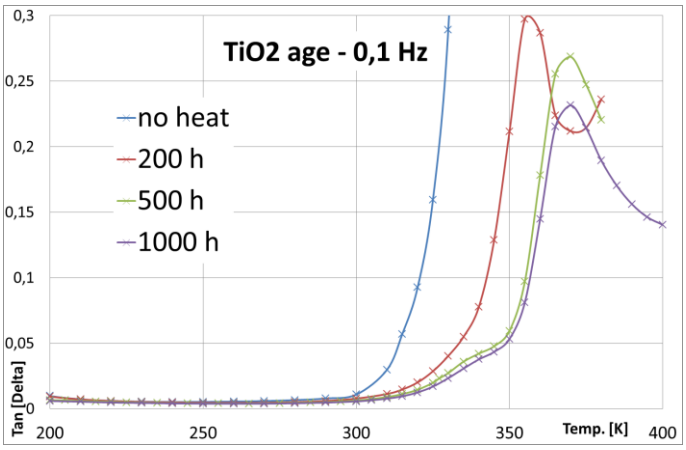
Two other very useful devices were the Differential Scanning Calorimeter, model DRS Q2000, from TA Instruments, which can measure and store 50 samples in a stacker, and Thermogravimetric Analyzer TGA Q500 from the same manufacturer.

3.1. DIELECTRIC RELAXATION SPECTROSCOPY

Relaxation maxima, like α, β, etc., can be observed in dielectric materials using DRS. During our observations of epoxy samples subjected to ageing of different ageing times, we registered shifts in these spikes. As can be seen in fig. 1 and 2, the shift of α and β relaxation is huge. While new samples have α relaxation maximum at around 330 to 230K, samples subjected to 500 h ageing have this maximum measured at constant frequency shifted to 400 – 300 K. Similar observation was made in β relaxation – new samples have this spike at 130 to 80 K compared to aged samples, where this maximum ranges from 220K to 140K. This spike was later evaluated as water.



Obrázek 1: β relaxation of aged samples, ageing time is parameter (shown top left)

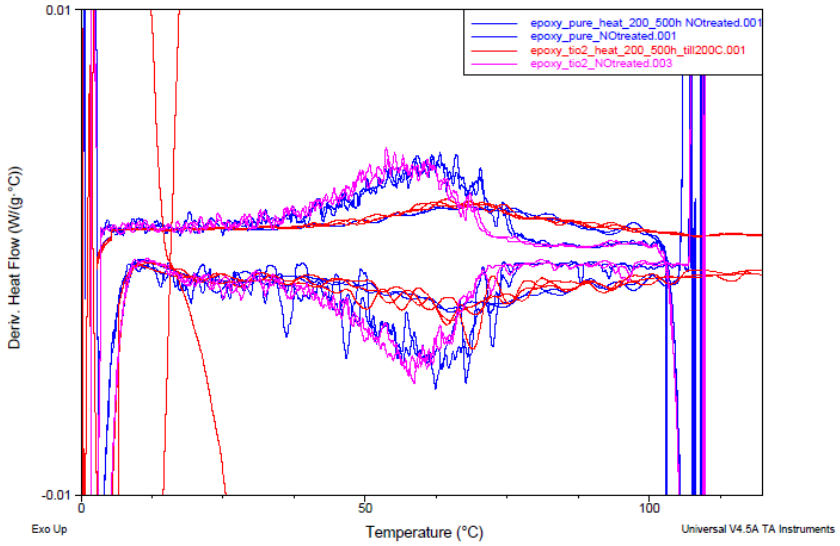


Obrázek 2: α relaxation of aged samples, ageing time is parameter (shown top left)

Figures 1 and 2 show several plots; the most interesting curve is the plot of loss factor vs. temperature after 1000 h of ageing, becasue alpha shifted along with conductivity during the ageing process. Sample subjected to 200h of ageing shows only marginal shift, which could have been caused by several factors. For examples, measurement was, compared to other samples, carried out after some time from ageing, so the sample was exposed to external conditions over long time, which caused water absorbtion of the samples. Water peek can be seen in Fig. 1 at temperature of 180K.

3.2. DIFFERENTIAL SCANNING CALORIMETRY

In order to properly determine changes in dielectric materials after ageing, DSC method is used, which also allows to see the process of the sample being heated up and subsequently being cooled down. During the cooling process we measure the amount of heat the sample emits without heat source. This measurement is used to find glass transition temperature, as seen in fig. 3.

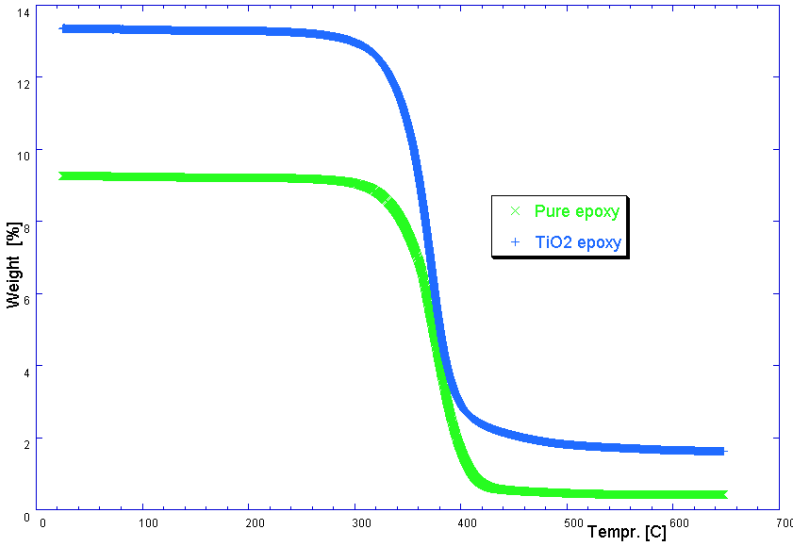


Obrázek 3: DSC of original samples and samples subjected to 500 h of ageing

Figure 3 shows glass transition temperature of a sample before ageing, which is about 60 °C. After 500 h ageing, this temperature is raised to 65°C. This shift in temperature is related to observation in the α relaxation.

3.3. THERMOGRAVIMETRIC ANALYZER

Using thermogravimetric analyzer we can observe carbonization and vaporization temperatures of a sample. This analysis is used to determine the amount of nanofiller in sample.

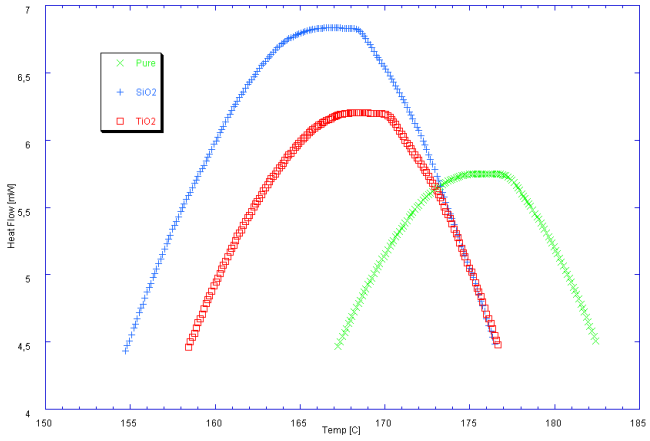


Obrázek 4: TGA of an epoxy with nanofiller

Figure 4 shows epoxy with nanofiller, which was heated to 1000 °C. It completely burned down at 400 – 450 °C. By using thermogravimetric analyzer we estimated the per cent amount of nanofiller in sample to 1.5 % and also heating temperature to max 350 °C, so the sample would not evaporate.

3.4. POLYMERIZATION

In order to specify polymerization of the epoxy with nanofiller, we used the above mentioned Q2000 analyzer, which allowed the precise determination of the time and duration of the change from liquid to solid state. This will help us with sample manufacturing, which is very important, because measurements are difficult without properly made samples. The polymerization process can be seen in fig. 5. This graph also shows transition from liquid to solid state at approximately 130 °C after 60 minutes. At about 170 – 175 °C, the transition is almost instant and one can observe, how liquid epoxy turns into a solid matter.

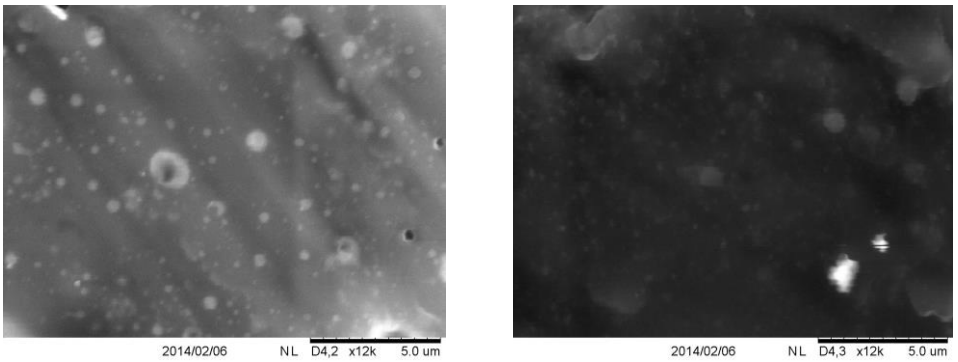


Obrázek 5: Polymerization of epoxy with nanofiller

The graph in fig. 5 shows the main peak, which determines transition temperature between liquid and solid state. All three curves represent three samples with different nanofillers (blue, red) or pure (green).

3.5. ELECTRON MICROSCOPY

Electron microscope emits electrons to material surface, where they attach on certain layers. Using their absorption we are able to visualize not only the surface of the material, but also its internal structure. The advantage over classic microscopy is that electron microscope can be used to observe dark samples.



Obrázek 6: Nanofiller distribution in samples. Left – epoxy with SiO_2, right – TiO_2.

View on two sampels can be seen in Figure 6 - left image shows nanofiller distribution in SiO2 sample and distances between nanoparticles between each other. It is also possible to observe clusters of particles; nanofiller is prone to clustering. Right part of the image also shows subtle cluster-

ing in TiO2 sample, but there are bright spots representing nanoparticles, as well as clusters of nanofiller.

4. CONCLUSION

Using above mentioned methods we were able to better examine epoxy materials with nanofillers, not only surface, but also their structure.

We have acquired vital information about each particular material and also how these materials react to temperature ageing. This knowledge will further help us with the direction of our research and with better understanding of epoxy materials.

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