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Budapest University of Technology and Economics

Faculty of Mechanical Engineering

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PhD dissertation

**DEVELOPMENT OF EPOXY RESIN-BASED SHAPE
MEMORY POLYMER COMPOSITES**

Thesis booklet

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The referees' opinion and the minutes of the PhD examination can be inspected at the Dean's Office of the Faculty of Mechanical Engineering of the Budapest University of Technology and Economics

1. Introduction

In materials science researchers have been investigating smart materials since the middle of 20th century. Smart materials are such functional (i.e. primarily not structural) materials, which give a prompt, explicit and reversible answer on certain change of its own environment by changing its own material properties. Shape memory materials are such smart materials, which can change its own shape upon a certain change in its own environment (external stimulus). The external stimulus could be the change in temperature, magnetic field, electric current rate, light intensity, moisture content or acidity. The shape memory effect has been described for numerous materials (metal alloys, polymers, ceramics, gels). Among them shape memory alloys and shape memory polymers are of greatest importance.

Deformability of shape memory polymers, which can reach even 800%, exceed that of shape memory alloys, which is typically 1-8%. Because of their low prize shape memory polymers are urged to replace shape memory alloys, but their low recovery force present a problem for the most application.

Epoxy resin (EP) is included among the most excellent heat-responsive shape memory polymers because of chemical net-points and tailorable glass transition temperature (T_g). Shape memory epoxy has lower deformability (<80%) than that of other shape memory polymers, but it is more suitable for structural material because its higher elastic modulus. Moreover epoxy resin is traditionally a good matrix material, since it has good adhesion to the most reinforcing agent, such glass fibre, carbon fibre.

As a consequent shape memory epoxy is the most promising candidate to replace shape memory alloys in such fields (e.g. automotive-, aerospace-, robotic application), where the shape memory part should recover against some kind of mechanical load (activators, deployment mechanisms).

2. Overview of related literature and aims of the work

Epoxy can fix a temporary shape, which is different from the original one, if it is deformed at higher temperature than its T_g , so in its rubbery state, and cooled down below T_g maintaining the external constraint. It will recover its original shape without external force, if it is heated up above its T_g . Epoxy resins have shape fixity and shape recovery abilities of at least 95% both. Other shape memory polymers have mostly lower shape memory abilities than that of epoxy resins.

Epoxy resins can be reinforced successfully with multifarious reinforcing fibres, such as glass fibre, carbon fibre, natural plant fibre etc. Shape memory epoxy composites can be used for example as the frame of large aerospace structures (reflectors, antennas, solar arrays etc.), because they can be folded into a smaller temporary shape before shipping. At the destination they can unfold automatically upon some kind of external stimulus, which is mainly the heat induced by electric current or by solar radiation. This application of shape memory epoxy composites can make the transportation of extended structures more economical.

There are commercially available carbon fibre fabric reinforced shape memory epoxy composites (*viz.* elastic memory composites) for preparation of deployable structures, but the studies on the effect of reinforcement on the property of shape memory epoxy matrix are missing in the literature. Next to carbon fibre fabric the effect of glass fibre fabric has not been studied yet, in spite of the fact that glass fibre has higher elongation at break than that of the most carbon fibres. Therefore I have appointed to supply these missing information as a main goal of this work.

Next to traditional reinforcements it is worth to investigate the effect of natural plant fibres on epoxy resin's shape memory properties, because plant fibres have higher or at least same elongation at break compared to that of traditional fibres. Natural plant fibres, which are renewable, should be embedded in such epoxy resin, which is derived also from renewable resources joining the development of biopolymers, which is nowadays a prominently favoured research area thank to its willing on environmental protection.

Publications dealing with shape memory epoxy composites originated from renewable resources can not be found in the literature. Bio-epoxy resin can be made by anhydride curing of epoxidized vegetable oils such as soybean oil or linseed oil, which are the most popular raw materials for this purpose. Natural reinforcements can be made from different plant fibres such as flax, hemp, jute, kenaf, sisal, bamboo etc.

Unreinforced shape memory epoxy is normally tested in tension mode, while with textile reinforced shape memory epoxy composites are measured in flexure. However bending is a complex deformation, two main bearing stresses awake locally in the test specimen: from the neutral axis to the curves with smaller radius there are compression stresses, and from the neutral axis to the curves with larger radius there are tension stresses. The reinforcing fibre affect the epoxy composite's shape memory properties depending on its localization; it can be positioned either on the compression side or on the tension side. This can be practically examined on asymmetrically reinforced shape memory epoxy composites.

Shape memory epoxies bear one-way shape memory effect. However researchers have not produced shape memory epoxy resin with two-way shape memory effect yet, but shape memory epoxy resin with triple shape (two temporary and one original shape in the same shape memory cycle) already exists. Shape memory polymer with triple shape is also called triple-shape memory polymers, however they memorize and recover only two shapes: the firstly programmed temporary shape and the original one. Till now only two different methods have been investigated for making triple-shape memory epoxy. The simplest one is when two different epoxy resins with different T_g -s are layered on one another. The shape memory properties (shape fixity and shape recovery ratios) can be easily optimized by making epoxy bilayers with different layer's thickness ratios. Disadvantage of this method that the heterogeneous and asymmetric structure affect the shape memory phenomenon, which makes the evaluation of test results more difficult. On the contrary the other method is more complicated, and results heterogeneous (macroscopically homogeneous), practically symmetric triple-shape memory epoxy based polymer alloy. Here an electrospun thermoplastic (namely polycaprolactone *viz.* PCL) web is embedded in epoxy resin, where melting temperature (T_m) of the thermoplastic is higher than the T_g of epoxy

resin. In this case optimization of shape memory ratios is a more challenging task than in case of epoxy bilayers. These optimization opportunities have not been investigated yet. Increasing the elastic modulus of the thermoplastic web with nanoparticles such as carbon nanotubes or graphene nanoplatelets could be a feasible route for increasing the otherwise low shape fixity ratio of the first temporary shape fixed by crystallisation of the thermoplastic web.

If the thermoplastic resin can be dissolved in epoxy component, it can open the door to a new *in-situ* preparation method of triple-shape memory epoxy based polymeric alloys. For this purpose PCL is a proper thermoplastic, since epoxy resin and PCL have similar solubility parameters.

On the basis of the studied literature, the aims of the work are summarized as follows:

- Reinforcing shape memory epoxy resins with textiles made of different fibres such as glass fibre, carbon fibre, natural plant fibres, and examination of their effect on dynamic mechanical, mechanical and shape memory properties in flexure, and analysis of the relationships between these properties.
- Investigation of the effect of asymmetric reinforcing on shape memory properties (shape fixity and shape recovery ability, recovery stress) and deformability of shape memory epoxy composites, and analysis of the relationships between these properties.
- Modification of triple shape memory EP/PCL web polymer alloy with graphene nanoplatelets. Examination of the effect of graphene nanoplatelets on the morphology and shape memory properties (shape fixity and shape recovery ability).
- *In-situ* preparation of triple shape memory EP/PCL polymer alloy, and comparison with EP/PCL web (PCL web embedded in EP) especially regarding to the shape memory properties (shape fixity and shape recovery ability).

3. Materials and methods

Glass fibre fabric-, carbon fibre fabric- and unidirectional carbon fibre textile reinforced epoxy resin based composites were prepared by hand lamination technique and hot pressing. In these cases commercially available amine-cured epoxy resins were used. Asymmetrically reinforced carbon fibre fabric/epoxy composites were prepared by pouring epoxy resin on the top of a partially cured laminate in a glass mould (two glass sheet in standing position with silicone strips between them). Plant fibre reinforced biocomposites were produced using hot pressing technique. Differently textured (plain, twill, quasi-unidirectional) flax-, jute- and hemp fibre fabrics were after drying at 80°C for 2 hours immediately impregnated with bioepoxy resin. In these cases two kind of bioepoxy resins were used. One of them was epoxidized linseed oil cured by an anhydride, and the other sorbitol polyglycidyle ether cured by a glycerol-based triamine.

PCL nonwoven fibrous mat (PCL web) was made from solution with PCL concentration of 3.5 w%, where the solvent was the mixture of dichloromethane and ethanol. The PCL solution was formed by electrospinning into PCL web. With graphene modified PCL web was produced in similar way. In this case graphene was added to the solution and dispersed by an ultrasonic stirrer during cooling. Graphene content was 3,5 w% relative to the PCL content. PCL webs were impregnated with epoxy resin by vacuum infusion resin transfer moulding. Impregnated PCL webs were cured for 48 hours at room temperature and post cured for 2 hours at 80°C. During post curing PCL fibres melted and after curing they recrystallized, which finalized their microstructure.

In-situ EP/PCL sample with 23 w% PCL content was prepared without fibre formation. PCL granule were solved in epoxy component by mixing for one hour at 100°C. Next to continuously mixing the sol was cooled down to 70°C and amine type curing agent was added. After two minutes mixing it was poured into an open mould and cured at room temperature for 48 hours. Post curing was also applied: 80°C for two hours.

Fibre reinforced composites and their reference samples were measured in three point bending arrangement with span length of 20, 40 and 50 mm. Determination of T_g was executed by dynamic mechanical analysis (DMA, Q800, TA Instruments) with heating rate of 3°C/min and oscillation frequency of 1 Hz. Deformability of samples was determined by quasi-static bending at elevated temperature (that is deformation temperature, $T_d > T_g$) in the Q800 DMA testing machine. Bending was conducted with force controlled mode and a loading rate of 3 N/min. Examination of shape memory properties were performed also in Q800 DMA testing machine. Shape fixity and shape recovery ratios were determined by unconstrained shape memory test, while recovery stresses were found out by fully constrained shape memory test. In case of biocomposites and their reference samples quasi-static bending was executed in GABO Eplexor DMA testing machine equipped with a 150 N load cell. In this case shape fixity and shape recovery ratios were determined from partially constrained shape memory test in the GABO Eplexor DMA machine.

Transition temperatures of triple-shape memory EP/PCL polymer alloys were firstly determined by differential scanning calorimetry (DSC, Q2000, TA Instruments) applying a heating and cooling rates of 10°C/min. After that transition temperatures and also temperature dependent dynamic mechanical properties were examined by DMA in the Q800 tester applying tension arrangement. For these tests heating rate, clamping distance and oscillation frequency were 3°C/min, 10 mm and 10 Hz, respectively. Deformability of triple-shape EP/PCL samples were examined by quasi-static tension test using the Q800 tester in force controlled mode. Loading rate was 3 N/min during quasi-static tension test. Shape fixity and shape recovery ratios of triple-shape memory samples were examined in tension using the DMA Q800 machine.

For the study of microstructure of the EP/PCL samples scanning electron microscopy (SEM, JEOL JSM-6380LA) was used. Test specimens for SEM measurements were prepared in two different way. One of them resulted in a cryofractured surface, and the other in cryocut surface. Cryocutting was performed at -80°C by a microtome (Leica EM UC6) equipped with a glass knife. Fractured and cut surfaces were covered with an Au/Pd alloy before SEM imaging.

4. Results

This work deals with development of shape memory epoxy in two main direction. One of them is aimed at increasing shape recovery stress by using textile reinforcements, the other tend towards to investigate triple shape memory epoxy based polymeric materials.

Textile reinforcements decrease the deformability of epoxy above its T_g , because the mobility of long fibres are not increasing with temperature, or rather the increase is negligible. Fibres decrease the shape fixity ratio caused by the big difference between moduli of fibres and matrix at the storage temperature (in the glassy state of the epoxy), and the shape memory epoxy matrix has not enough stiffness to fully counterweight the aim of fibres to go back in their original position after deloading. I studied the effect of long fibre reinforcing on the recovery stress and its undesirable side effects by examination of glass-, carbon- and natural fibre consisted textile reinforced epoxy composites in flexure and by comparison the properties of these composites to that of unreinforced epoxy. Glass fibre increases the recovery stress by two orders of magnitude, thus the recovery stress of glass fibre fabric reinforced composite could be up to 40-50 MPa. However this value means the third of that, which can be measured for shape memory alloys (150 MPa), it could be enough for certain technical application. Glass fibre fabric reinforced epoxy has a limited deformability of 1.2% at outer (tension side) axis and its shape fixity ratio decreased from 100% down to 80% compared to pure epoxy resin. Although the shape recovery ratio was not decreased, it stayed at 100%. These tendencies were similar for carbon fibre fabric- and unidirectional stitched carbon fibre textile reinforced epoxy composites.

Natural plant fibre fabric reinforced epoxy composites have lower shape fixity and shape recovery ratios than that of glass or carbon fibre reinforced ones. However the matrices were also biobased. In addition plant fibres decreases the T_g of epoxy to a great extent (by up to 30°C), which depend on the nature of curing agent (amine or anhydride), the fibre content and the residual water content of the fabric.

Carbon fibre fabric was chosen to investigate the influence of asymmetry on measurable shape memory properties of epoxy resin based composites. Measurements arranged in flexure revealed that composites, where carbon fibres located on the tension side, have higher shape fixity and shape recovery ratios than that of composites reinforced on the compressed side. Asymmetrically reinforced composite become deformed upon temperature change without shape memory programming, because there are difference between the thermal expansion coefficients of fibre rich side and matrix rich side. Since carbon fibre has negative thermal expansion coefficient, the effect causing by asymmetry is the most expressive. On the tension side reinforced carbon fibre fabric/epoxy composites have shape recovery stress of 3-10 MPa and shape fixity ratio of 100% at deformation level of 2,5%.

Triple shape memory with epoxy resin impregnated PCL web was prepared using vacuum assisted resin transfer moulding. PCL content was 23 w%. The morphology was analysed on microtomed and also cryofractured surfaces by scanning electron microscopy. After impregnation and heat treatment (post curing of epoxy resin) PCL keeps its fibrous structure, but the diameter of fibres or rather bundles increased significantly. This EP/PCL web sample showed shape fixity for the first temporary shape fixed by crystallisation of PCL of about 70%. Other sample with graphene was prepared in similar way, only graphene was added to the electuspun solution. Graphene and PCL content were 0.8 w% and 23 w% in the EP/PCL web/graphene sample. Dynamic mechanical analysis showed, that graphene increased the flexural storage modulus. Morphology analysis revealed that graphene kept back the bundling of PCL fibres. However graphene decrease the shape fixity ability of PCL.

In-situ preparation method was developed for producing triple shape memory EP/PCL polymeric alloy. PCL content, which can be easily varied with this new *in-situ* method, was set to 23 w% in order to be comparable with EP/PCL web sample. The *in-situ* EP/PCL sample showed similar shape memory properties than that of with EP impregnated PCL web, except that shape fixity ratio of PCL phase increased slightly up to 80%.

5. Thesis points

The following thesis points summarise the results of the previously presented scientific experiments highlighting their novelty.

1. I demonstrated, that at the highest reachable maximum deformation (1-1,6%) the recovery bending stress of glass fibre fabric-, carbon fibre fabric- or unidirectional carbon fibre textile-reinforced shape memory epoxy composites are higher with one or two orders of magnitude than that of unreinforced epoxy resins, while their shape recovery ratio remain at high level: higher than 98%. The negligible decrease in shape recovery ratio is because the irreversible processes, which change the material structure and cause damage do not occur , if the deformation is in the linear viscoelastic region. In this case the shape recovery stress is almost equal to the loading stress [1, 5, 7, 8, 9].
2. I proved with dynamic mechanical analysis, that plant fibres can decrease the glass transition temperature (T_g) of epoxy resin with 6-12°C in case of amine curing and just like with 18-30°C in case of anhydride curing. Anhydride curing causes higher decrement than amine curing because anhydride function groups can react chemically with rest water (remained in the plant fibre after drying) and also with function groups of plant fibres. The fewer than required anhydride group causes imperfect curing, and therefore decreases the T_g . In case of amine curing only the rest water causes the observed decrement in the T_g , because of its physical softening effect [2, 6, 10].
3. I demonstrated, that in case of carbon fibre fabric reinforced shape memory epoxy composite the reinforcement arranged asymmetrically on the tension side during three-point bending can compensate the decrement of shape fixity ratio caused by reinforcing. I verified, that asymmetric reinforcing

causes deflection because of the different thermal expansion coefficients, which deflection is added to the shape memory effect, if the reinforcement is arranged on the tension side, and subtracted, if the reinforcement is arranged on the compressed side during flexural shape memory test [3, 9].

4. I proved with scanning electron microscopy, that graphene embedded in electrospun polycaprolactone (PCL) web, which has fibres with the diameter of 0.1-1 μm , can improve its impregnation with epoxy resin in case of using vacuum assisted resin transfer moulding technique. I demonstrated, that the graphene situated between the PCL fibres acts practically as a spacer, thus the epoxy resin can reach better the space between fibres [4, 10].

5. I proved, that epoxy (EP)/ polycaprolactone (PCL) polymer alloy can be produced also *in-situ* in such a way that epoxy component, in which PCL melt has been dissolved, cures with meanwhile added diamine, which results in phase separation. In this way produced *in-situ* EP/PCL containing 23 w% PCL has similar shape fixity (81-95%) and shape recovery (85-94%) ability compared to with epoxy resin impregnated electrospun PCL web containing the same quantity of PCL, which shape memory properties are 67-95% and 89-96%, respectively [4, 10].

6. List of own publications

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- [3] Fejős M., Karger-Kocsis J.: Shape memory performance of asymmetrically reinforced epoxy/carbon fibre fabric composites in flexure. *Express Polymer Letters*, 7, 528–534 (2013).
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- [10] Fejős M., Karger-Kocsis J.: The role of biobased polymers in shape memory epoxy composites. International conference on Bio-Friendly Polymers and polymer additives (BPPA14): from Scientific Aspects to Processing and Application, Budapest, P40 (2014).