STUDY OF SELF-HEALING ABILITY OF THERMOSETTING POLYMER COMPOSITES, CONTAINING HOLLOW GLASS FIBERS AND MICROCAPSULES USING ULTRASONIC NON-DESTRUCTIVE TESTING

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Received 16 March 2022
Accepted 12 July 2023

ABSTRACT

This study presents a comparison of the self-healing ability of two types of thermosetting polymer composites based on unsaturated polyester resin as a matrix. The first type contains hollow glass-fiber fabric as a healing agent carrier. In the second type, microcapsules made of urea-formaldehyde condensation, containing a healing agent were introduced. In both cases butanediol diglycidyl ether was used as a healing agent. The kinetics of the healing process of studied polymer composites was estimated via alteration of Young and shear moduli (G') during a time, using ultrasonic defectoscopy. It was found that the healing process of the micro-cracks made in the volume of composites was complete in 5 hours.

Keywords: self-healing, composites, kinetics, hollow fibers, microcapsules.

INTRODUCTION

For the last decade, smart materials have marked an increased development in the industry. They have the ability to react to different external stimuli through a specific change of their properties. Typical representatives of these materials are the so-called "self-healing" polymer composites [1]. The development of these synthetic organic materials is based on the analogy with the living matter being able to heal itself from external or internal damages. Self-healing polymers and the composites based on them have the capability for repairing the mechanical demolition in their structure [2].

There are three different mechanisms involved in the self-healing of the composite materials by now: healing based on capsules, capillary self-healing systems, and internal healing process. In general, most of the polymers including thermoplastics, thermoset materials, and rubbers have a potential for self-healing. Most investigations and studies are focused on the restoration of mechanical entirety, followed by quasistatic cracking. There are also some examining processes of self-healing of materials by fatigue wearing out, the destruction caused by impact, drilling, and corrosion [3].

The concepts focused on self-healing polymer materials propose a new trend for the development of more durable, more stable, and resistant to damages products for a wide range of the industry including coatings, electronics, transport, and energetics.

The damage and destroying are natural consequences of the application of materials. Engineering research is focused mostly on the development of more stable and advantageous materials [4].

Approaches of self-healing

Self-healing polymers can be classified into three groups: capsule-based, capillary systems, and materials with internal healing. Each of these types differs according to the mechanism used - i.e. isolation and detention of healing agent to the moment of demolition [4].

In the capsule-based self-healing composites, a healing agent is separated from the polymer matrix via microcapsules. When the capsules rupture, their content outpours into the matrix a healing mechanism starts: the healing agent penetrates the cracks where it reacts and polymerizes. Thus, a local healing process occurs [5, 6].

In the case of capillary self-healing composites, a healing agent is placed in a network of fine capillaries.

They can be connected to each other in one dimension mode, as well as in two or three dimensions. Once the network is broken, a healing agent is released in the area of cracking.

There is a great variety of encapsulation methods. They can be classified as interfacial, in-situ prepared, coalescence of droplets, melt dispersion, as well as physical, based on the mechanical formation of the shell.

In the case of self-healing polymer materials, the most common methods are: in-situ methods of capsule preparation but interfacial reactions and melt dispersion are very popular too. In-situ and interfacial capsulation methods are carried out through a reaction between urea-formaldehyde, melamine-formaldehyde, polyurethanes, and acrylates. The formed shell covers and separates the droplets in a water-oil emulsion [7, 8].

The first challenge is to determine the most appropriate method for capsulation as well as the polymer for the capsule preparation. The main factors of importance are: solubility, reaction ability, volatility, and pH of the agent inserted into the capsules [8, 9].

Once prepared, the capsules should be integrated with the matrix polymer. Shear stresses occur in the process of mixing the matrix with all the fillers and additives. The processing temperature can vary as well as the sizes of the capsules. The capsules based on urea-formaldehyde, melamine-formaldehyde, polyurethanes, used for the preparation of self-healing polymer composites are stable enough during the manufacturing of the composites [10, 11].

The aim of this article is the study of the self-healing ability of two kinds polymer composites (capillary and microcapsule based), by ultrasonic defectoscopy.

EXPERIMENTAL

Materials and methods

For the preparation of fiberglass-fabric laminate composites, a hollow glass fiber fabric was used and supplied from Faserverbundwerkstofe GmbH.

For the synthesis of urea-formaldehyde microcapsules the following reagents were used: Resorcine - Sigma-Aldrich; Urea - Sigma-Aldrich; Formaline (37 %) - Sigma-Aldrich; Epoxy resin DER 331 - Dow Chemical with epoxy number 480; Unsaturated polyester resin Viapal U - Hoechst; Methylethylketonhydroperoxide - Hoechst; Poly (ethylene - alt maleic anhydride) copolymer CAS : 9006-26-2 (EMA).

The composition of obtained polymer microcapsules was studied using FTIR Spectrometer Varian. The surface morphology of the capsules was observed with SEM - LIRA Scan, UK. The dynamic elastic moduli were determined based on the relationship between the propagation velocities of ultrasonic waves and elastic moduli of studied material according to equations (1) and (2):

$$E = \frac{\rho C_t^2 (4C_l^2 - 3C_t^2)}{C_t^2 - C_l^2} \quad (1)$$

$$G = \rho C_{t^2} \quad (2)$$

where ρ is a density of the medium, C_l, C_t are velocities of propagation, respectively longitude and transversal velocity of ultrasonic waves, E - Young's modulus, G - shear modulus. The ultrasonic study was performed through a transition of ultrasonic waves in a longitudinal and transverse direction. For the aims of the experiment an ultrasonic equipment OLYMPUS EPOCH 600 was used. The frequency of the ultrasonic was 4 MHz.

Synthesis of microcapsules

Microcapsules were prepared by *in situ* polymerization in oil to water emulsion. At temperature 20°C - 24°C, in a 1000 mL flask, 200 mL deionized water and 50 mL 1 wt. % aqueous solution of EMA copolymer were mixed, which acted as a surfactant. Then, the flask was kept at a water bath equipped with a temperature controller. The solution was well stirred. Then, 5.00 g urea, 0.50 g ammonium chloride, and 0.5 g resorcine were added to the solution. The stirring was kept till the components become fully dissolved. The hydrochloric acid was added dropwise till the pH solution reached a value of 3.5.

For elimination of the surface bubbles, 1 - 2 drops of butanol were added. Then 60 mL of epoxy resin was added, forming a stable emulsion for 10 minutes (at least). To the stabilized emulsion was added 12.67 g formalin to obtain 1:1.9 molar ratio from formaldehyde to urea. The final emulsion was heat-treated at 60°C for 4 hours. Then the mixture was stirred well and cooled to 20°C. The average size of the produced microcapsules was approximately between 10 to 20 μm.

The obtained microcapsules were washed with deionized water and then filtered. Further, the obtained microcapsules were mixed with unsaturated polyester resin and methaphenilene diamine, which was used as a latent hardener for the epoxy resin.

The separated layers of micro-hollow glassfiber fabric were filled with epoxy resin and hardener by vacuum technique.

The mechanism of synthesis of ureaformaldehyde microcapsules is shown in Fig.1.

RESULTS AND DISCUSSION

Capsule based composites preparation and their healing ability kinetics

Once urea-formaldehyde capsules were prepared, they were introduced into the polymer matrix based on unsaturated polyester resin (Fig. 2). The SEM images clearly showed the formation of microcapsules containing epoxies with an average diameter in the range of 10 to 20 μm.

The total matrix mixture was stirred to a homogeneous consistency. Diaminodyphenylmethane was introduced in the system as a latent hardener for encapsulated epoxy

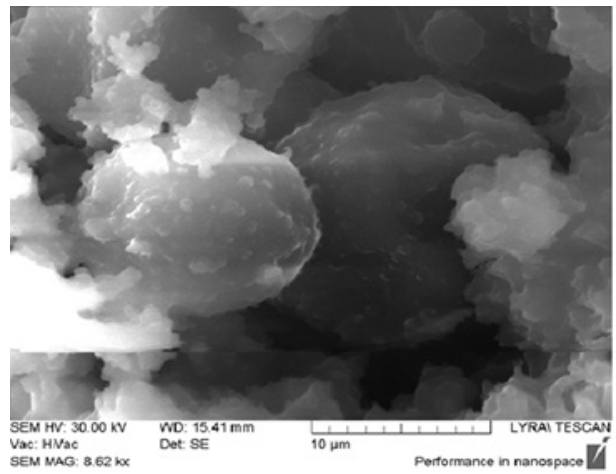

Fig. 2. SEM image of urea-formaldehyde microcapsules, containing epoxies.

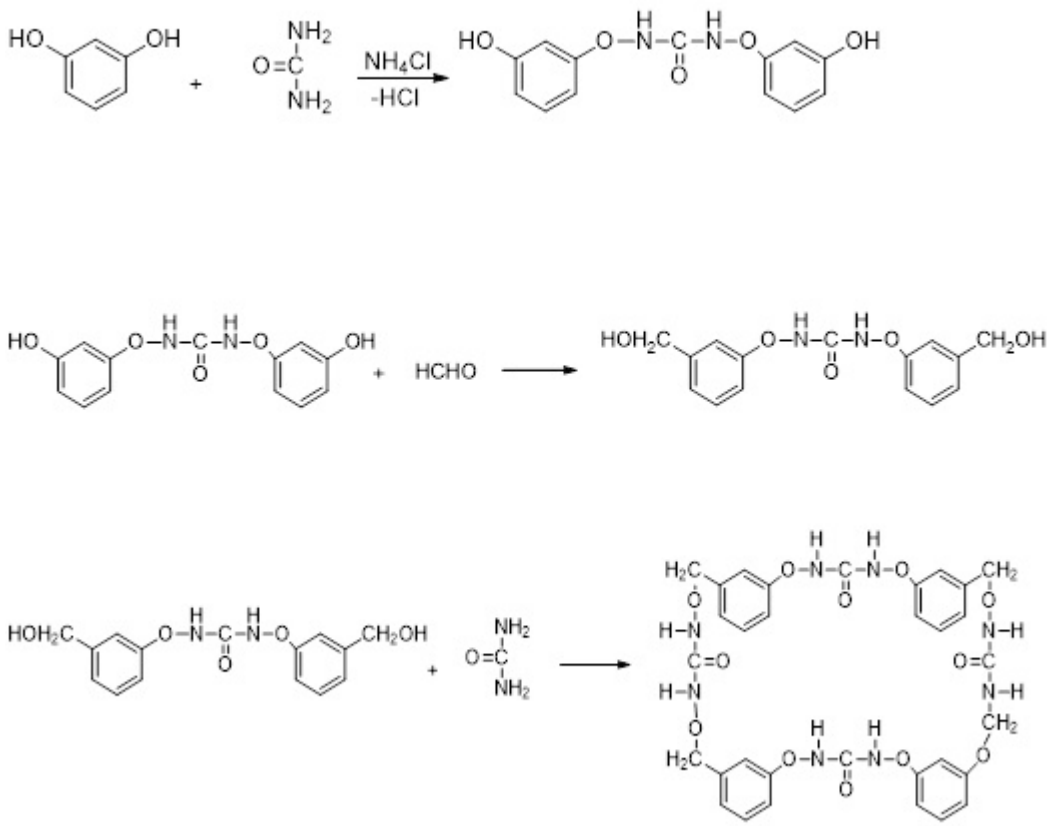

Fig.1. Synthesis of urea-formaldehyde microcapsules.

resin abiding by the equimolar ratio to epoxy amount, which will react with encapsulated epoxy at elevated temperature. After arising of cracks and other structural damages into the test specimens the last were heated to the 80°C. After the appearance of discoloration in the point of cracking the samples were subjected to ultrasonic investigation.

The microcapsules were characterized using FTIR spectroscopy. FTIR spectrum of the microcapsules is presented in Fig. 3.

In the FT-IR spectrum, the NH-deformation band for ureaformaldehyde oligomer appeared in the range 3430 cm^{-1} - 3050 cm^{-1}, while the absorbance band for the urea coupling CO-NH could be seen at 1649 cm^{-1}. The deformation band for the C-O-C association was observed at 1027 cm^{-1}. The vibration bands at 915 cm^{-1} and 830 cm^{-1}, corresponded to the oxirane group and 1,4-substituted aromatic rings of the epoxy resin, respectively. The spectral data proved that the encapsulation process of epoxy oligomer into urea-formaldehyde resin was successful.

Further, it was interesting to inspect the reaction ability of the prepared microcapsule. This can be seen in Fig. 4, which presents the reaction of epoxy resin with the amine curing agent.

The reaction between encapsulated epoxies with a curing agent was characterized by full disappearance of the epoxy absorbance band at 915cm^{-1} as well as with a significant decrease of the intensity of amine group band at 3430 cm^{-1}.

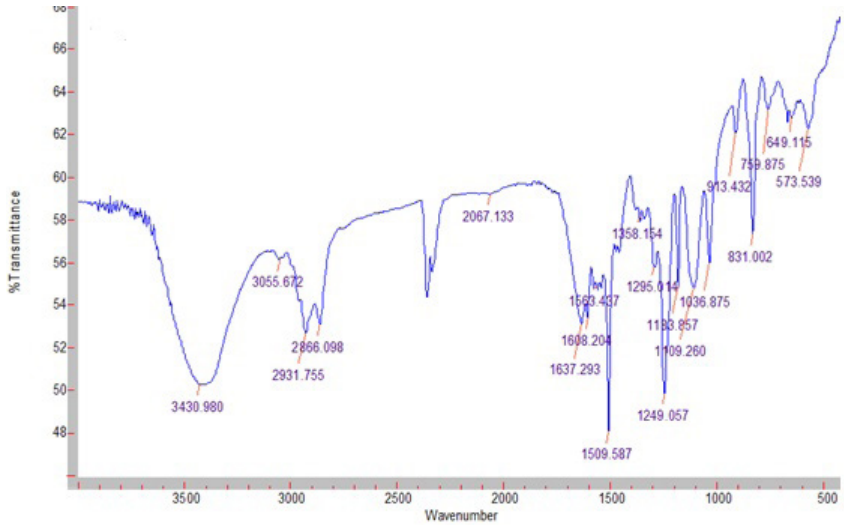

Fig. 3. FTIR spectrum of urea-formaldehyde microcapsules.

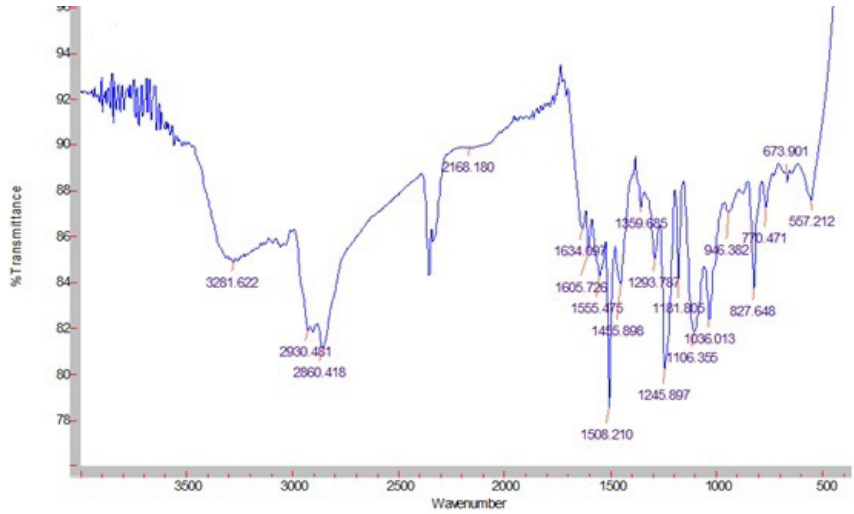

Fig. 4. FTIR spectrum of cured epoxy-containing microcapsules.

Microcapsules have to respond to several requirements: they must be stable for a long period, keeping the healing agents unaffected; they must be stable enough in structural relation, and to have a modulus of elasticity smaller than those of the material in which they are incorporated. At the same time, they must be insoluble in the polymer matrix.

Therefore, the influence of microcapsules and especially their content on the self-healing capabilities of the composites was investigated.

The kinetics of self-healing process is presented in Fig. 5. It shows the dynamic modulus as a function of the concentration of polymer microcapsules. According to the data, the highest level of healing activity is reached with the composite, containing 50 % microcapsules. The maximum degree of healing is gained after the fourth hour. The process of healing of mechanical integrity of these thermosetting composites containing microcapsules can be explained by the fact that, after the beginning of cracking in the area of the fracture, epoxy component (healing agent) penetrates through the matrix and mixes with amine hardener.

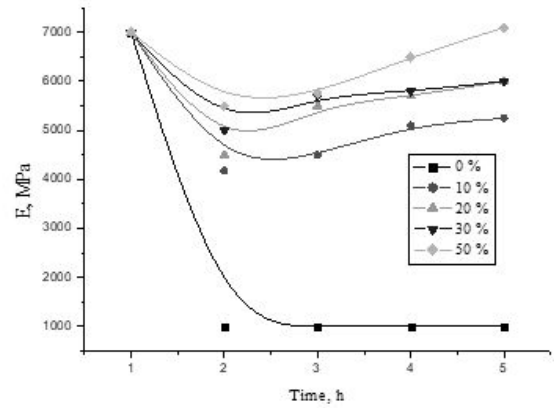

Fig. 5. Kinetics of the healing process of mechanical properties (Elastic Modulus) for composites containing microcapsules.

Preparation of hollow glass fiber polymer composites and their healing ability

These types of composites were prepared using the layer by layer technique. The reinforcement of the polyester resin composites has dimensions 100 x 10 mm. They comprise 4 layers of hollow glass fiber fabrics. Every one of these layers was glued with unsaturated polyester resin. After curing of the polymer matrix, the specimens were filled with a healing system, comprising of buthanedioldiclycidil ether and diethylene triamine, as a hardener under vacuum. For visualization of the filling process into the epoxy resin, the methylene red was used as a coloring agent.

After introducing of crack into the volume of test specimens, a discoloration of the place of cracking was observed. This is due to the reaction of the acidic resin with the alkaline amine hardener (Fig. 6).

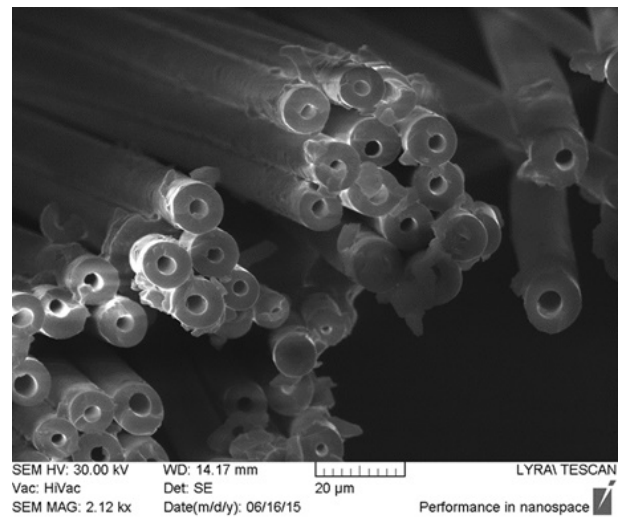

Fig. 6. SEM image of hollow glass fiber fabric.

Fig. 7 shows that composites, which contained an empty capillary system, did not exhibit self-healing properties. This was proved by the lack of alteration of the elastic moduli, after the crack propagation. It is also seen that after the damage, a serious decrease in the values of the dynamic moduli can be observed, due to the absence of chemical agents, capable to impart healing of

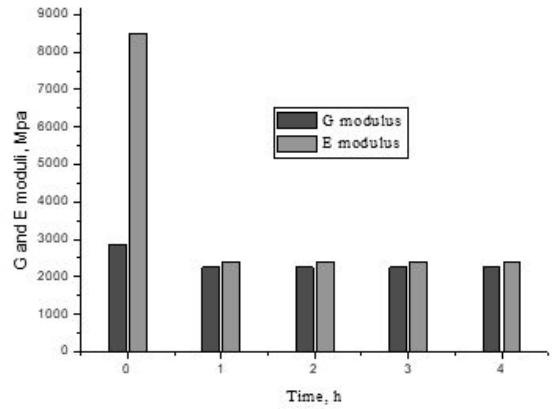

Fig. 7. Kinetics for the fiber-reinforced thermosetting composite, which does not contain healing agents.

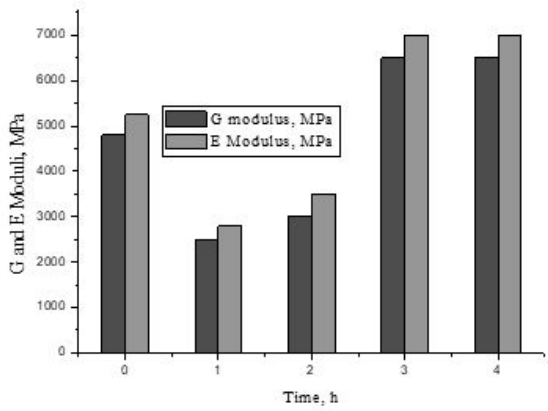

Fig. 8. Kinetics for the fiber-reinforced thermosetting composite, which does not contain healing agents in hollow fibers.

the structural disturbance into the volume of material. Fig. 8 shows the appearance of alteration in dynamic moduli for the thermosetting systems containing in their capillaries healing agents (epoxides and diamines), proving the healing process of physicomechanical properties. As it can be seen from the figure, dynamic moduli start to grow up one hour after crack propagation through the volume of composites as they have maximal values after the third hour.

It can be mentioned, that for reaching the healing effect of the initial material structure it is necessary a period of approximately two hours. During this period, the healing agents penetrate the damage area, mixing and polymerizing each other. For the healing process, the active agents must have a good wetting ability to the carrier (in our case microcapillaries), and at the same time a low viscosity to ensure fast diffusion ability into the damage zone.

CONCLUSIONS

In this study, polymer microcapsules were successfully prepared, which shell was built up from urearesorcinolformaldehyd polymer through inter-phase emulsion polymerization. The experiments proved that this method was suitable for encapsulation of epoxy oligomers. The healing ability of polymer systems was characterized for the first time with ultrasonic defectoscopy, used as an indicator of the alteration of the dynamic moduli. It was proved, that the duration of the healing process of the tested composites is 4 hours.

The studied self-healing composites systems can found different applications according to their behavior: a capsule-based composite system can be used for paint formulation, while capillary based can find applications in the structural and aerospace engineering.

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