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CURING CONDITIONS AND DIELECTRIC OBSERVATION OF AN EPOXY SYSTEM BASED ON EPIDIAN 6

In this work the dielectric properties and curing conditions of a selected epoxy resin are presented. The curing system consists of Epidian 6 with DDM amine. In the first step, optimal curing conditions were determined for different amine concentrations in the mixture. It is shown on a diagram, how the properties of the cured matrix depend on the percentage concentration of the curing agent. Dielectric measurements were carried out for two concentrations – 10% and 16% – both in the course of curing and for the final product. Significant differences in the dielectric responses were observed as a result of different conversion levels in the obtained resins.

Keywords: epoxy network, curing conditions, dielectric properties.

1. INTRODUCTION

Epidian 6 belongs to epoxy resins – a group of materials which are widely used nowadays in many branches of the industry [1,2]. Studying the process of curing a selected material with certain curing agents and determining the curing conditions and properties of the final product are essential steps needed for successful application of that material. A series of papers [3-5] dedicated to the process of curing Epidian 6 with triethylenetetramine may serve as an example. Those papers presented diagrams describing changes in the physical properties of the mixture with respect to the curing conditions i.e. time and temperature. Our paper shows the results of curing Epidian 6 with the DDM amine. Depending on the amount of the used curing agent, different properties of the cured product were obtained. For amine concentration of 10% and 16% dielectric studies were carried out. Changes in the dielectric response clearly reflect different levels of chemical conversion in both the products.

2. MATERIALS

Mixtures prepared for the dielectric measurements where made of commercially available basic components: epoxy monomer Epidian 6 and DDM amine. The mixtures were prepared with different mass ratios of DDM amine: 8%, 10%, 12%, 14% and 16%. Observations of the mixture behaviour were conducted during slow heating up to the temperature of 160°C. For further analysis, mixtures with 10% and 16% amine concentrations were selected. The chosen samples were cured for 5 hours at the temperature of 70°C and post-cured at 160°C (for 10% amine concentration) or 120°C (for 16% concentration). In situ monitoring of the dielectric response was carried out during the process of curing.

3. EXPERIMENTAL

The optical observations of the mixtures were done using a microscope at a magnification of 80×. The material was deposited on plain glass plates.

Dielectric monitoring of curing was performed for samples with thickness of 50 μm, placed between metal discs. The dielectric response was recorded using Solartron 1260 Impedance Analyser with Chelsea Dielectric Interface 1295. The real and imaginary components of capacitance were evaluated in the frequency range from 10^{-2} to 10^{5} Hz. The temperature of the samples was stabilized with the accuracy of 0.2 K using Unipan 620 temperature controller. Dielectric analysis of the final products was performed in a wide range of frequency (10^{6}-10^{-1} Hz) in the cooling route, using the Alpha high-resolution dielectric analyzer manufactured by Novocontrol. Temperature was controlled by a Quatro cryosystem (Novocontrol) and data was collected after reaching thermal stabilization (with accuracy of 0.1 K).

4. RESULTS AND DISCUSSION

In the first step, a series of mixtures of Epidian 6 with DDM amine in different concentrations were monitored during heating up to the temperature of 120°C. Changes in physical properties were observed in the mixtures with 8%, 10%, 12%, 14% and 16% contents of the amine. After annealing the samples at 120°C all the mixtures were further heated up to the temperature of 160°C and changes occurring in the already reacted samples were observed.

The conclusions from the observations are shown on the diagram (Fig. 1). At 8% concentration of the amine, a viscous plastic mass was obtained, which completely melted after being heated up.

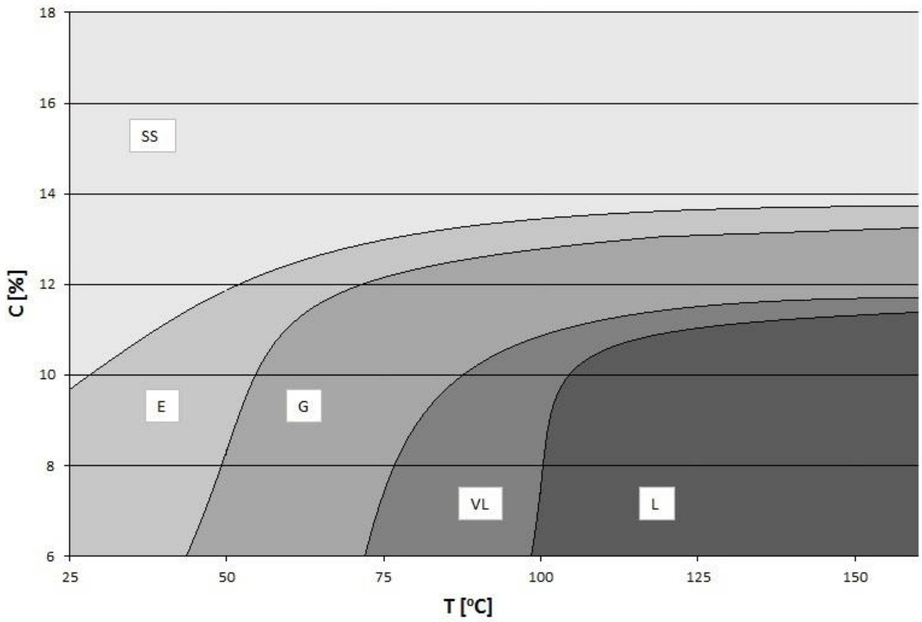


Fig. 1. Diagram showing varying degree of curing Epidian 6 with DDM amine, depending on the percentage concentration of the curing agent. Regions corresponding to different physical properties of the obtained product are indicated with different grey levels: SS – solid state, E – elastic, G – gel, VL – viscous liquid, L – liquid

For 10% and 12% mixtures, the curing product was solid at room temperature but became plastic after being heated up. Only for concentrations above 14% the obtained product was solid and non-plastic even at elevated temperatures.

For further dielectric measurements, the mixtures with 10% and 16% amine concentration were selected. The previously observed changes of the physical properties of the cured products at varying temperatures are also confirmed in the dielectric response (Figs. 2, 3 and 4). Differences in the progress of the curing process were clearly seen already during dielectric monitoring of that process (Fig. 2).

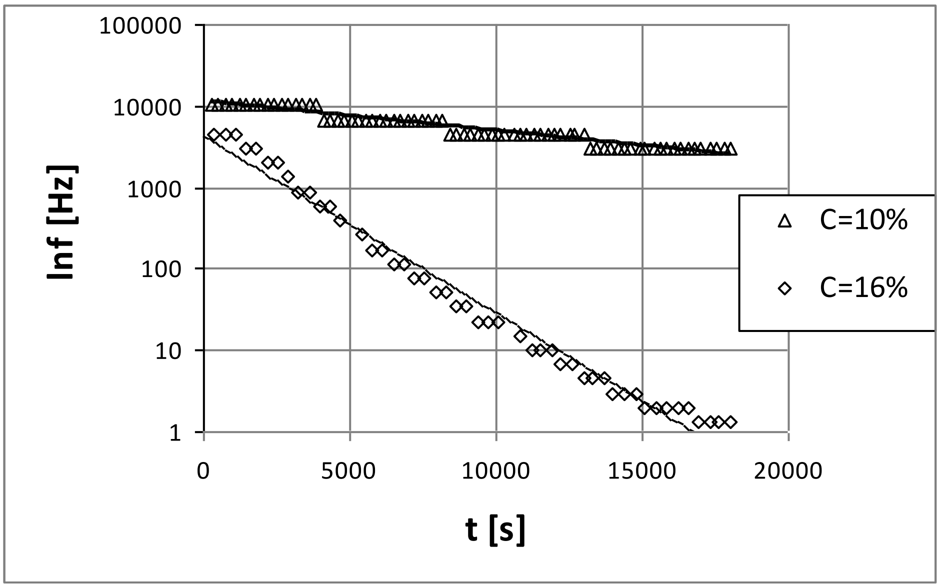
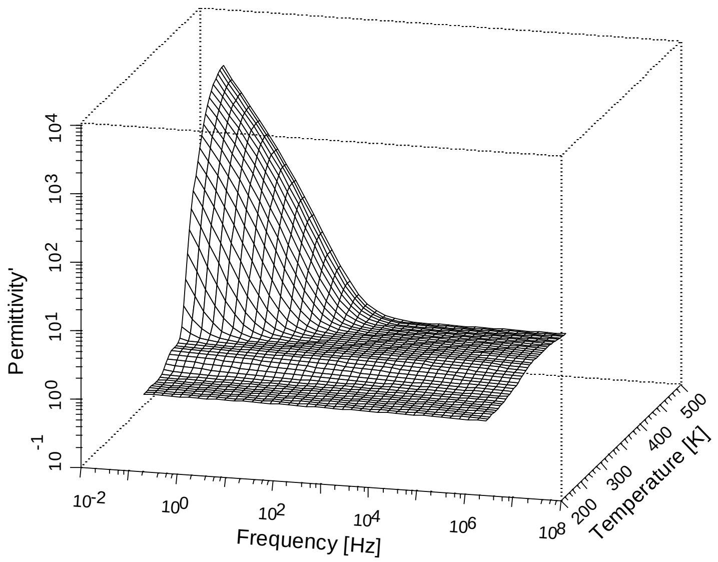


Fig. 2. Logarithmic plot of the electric modulus' imaginary component's peak frequency against time for two different mixtures with 10% and 16% concentration of the DDM amine

Fig. 2 presents changes in the peak frequency of the imaginary component of the electric modulus with time. That peak is directly related to the DC conductivity of given material. Therefore, changes observed in Fig. 2 reflect the nature and rate of conductivity changes in the dielectric material. The plot clearly shows that the reaction runs slower in the mixture with 10% amine concentration and the conductivity of that material does not reach the same value as in the other mixture – even though the initial values of the conductivity are similar and curing takes place at the same temperature of 70°C. As a result, both materials have quite different physical properties after being heated up which is a confirmation of the earlier observations. The material with 16% amine concentration did not reach a stable, constant final value before the end of the measurements. This leads to a conclusion that the curing time was too short for achieving full conversion of the mixture. Consequently, additional annealing at a higher temperature was done in the second phase of the investigations to let the reaction run to completion. The annealing was applied to both the mixtures and full stabilization was observed after some time in both the cases. In the next step, dielectric response was recorded for both the cured products in a wide range of frequency and temperature (Figs. 3 and 4).



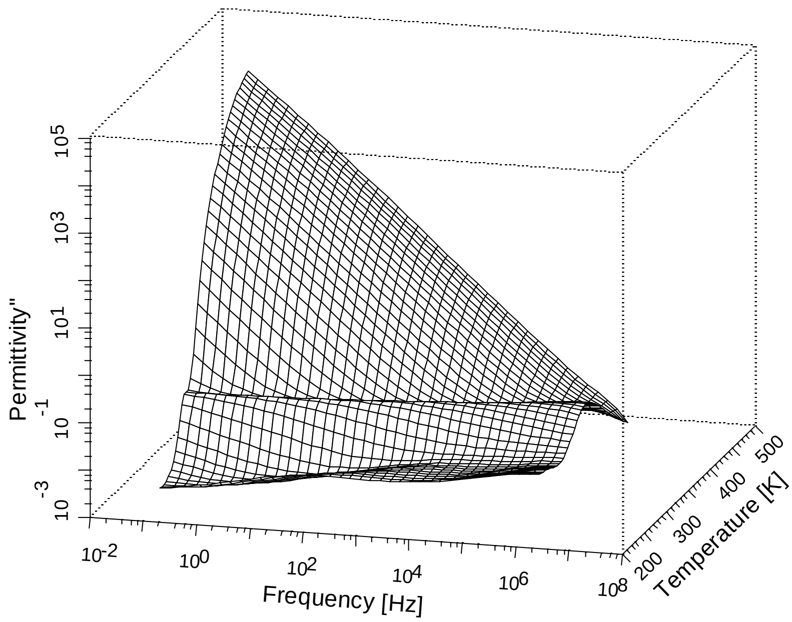


Fig. 3. Dependency of the real (a) and imaginary (b) component of the electric permittivity on frequency in a broad range of temperature, for a cured mixture with 10% concentration of DDM amine

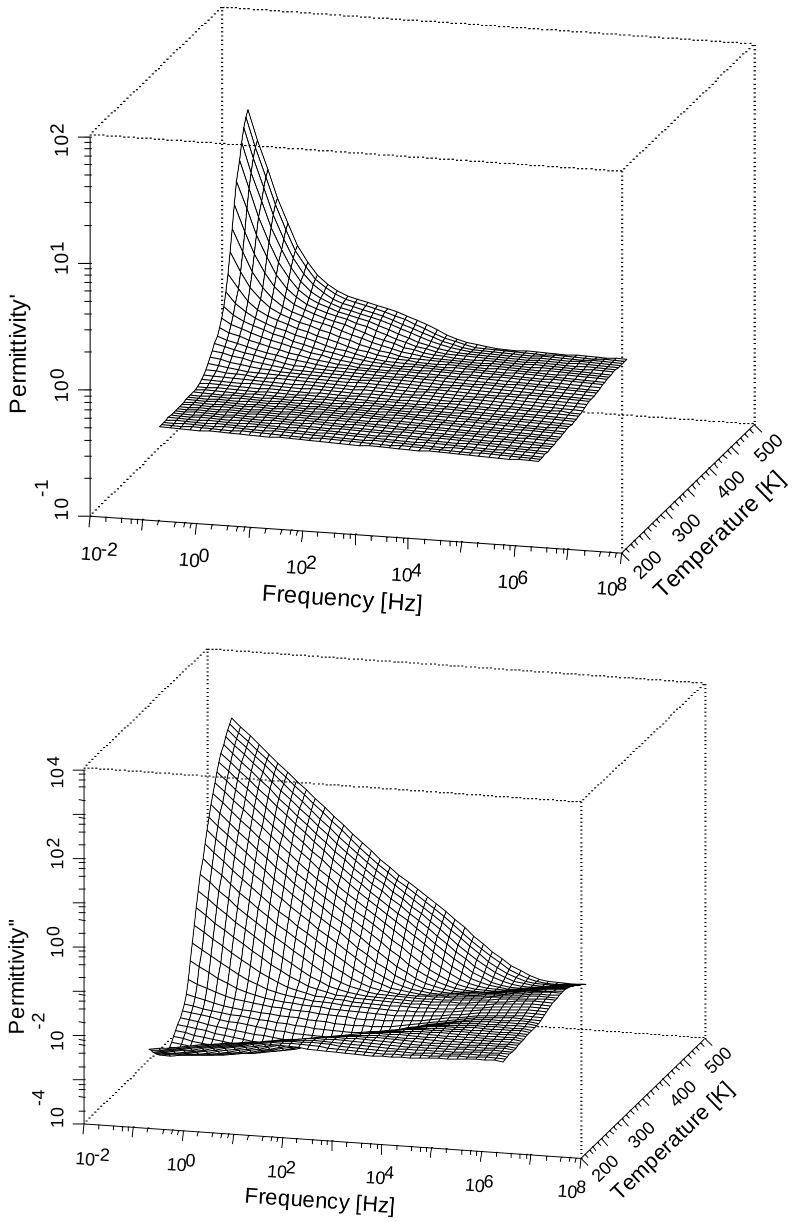


Fig. 4. Dependency of the real (a) and imaginary (b) component of the electric conductivity on frequency in a broad range of temperature, for a cured mixture with 16% concentration of DDM amine

Figs. 3 and 4 show 3D plots of the real and imaginary components of the electric permittivity, plotted against frequency and temperature. The same rapid growth of electric permittivity at low frequencies and elevated temperatures is present in both the figures. This growth is connected with similar electric conductivity of the two materials. Below the temperature of 400 K significant differences between the two materials can be noticed, particularly by comparing the plots of the imaginary component of the electric permittivity. In this case, an α-process related to molecular motions of whole polymeric structures clearly appears in the material with 10% amine concentration. This process becomes visible near the temperature of 353 K (~80°C) and its disappearance marks vitrification of the material which occurs at temperatures below 283 K (~10^{o}C). No analogous process can be seen in the material with 16% amine concentration (Fig. 3) which means that a glass transition does not occur in that material in the studied range of temperatures. Another relaxation process can be observed at low temperatures (below 300 K) in both the materials. This process can be attributed to molecular motions of local polar groups.

5. CONCLUSIONS

The performed observations enabled determination of the optimal curing conditions and percentage composition of the mixture of Epidian 6 with the DDM amine. The dielectric measurements revealed differences both in the curing process and in the physical properties of two different cured products. In both cases, a relaxation process connected with mobility of local polar groups was detected. An additional process related to a phase transition was found in the material with lower concentration of the amine. It was noted that dielectric studies can be applied in order to determine appropriate curing conditions as well as to perform in situ monitoring of the curing reaction.

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WARUNKI SIECIOWANIA I OBSERWACJE DIELEKTRYCZNE UKŁADU EPOKSYDOWEGO OPARTEGO NA EPIDIANIE 6

Streszczenie

W pracy przedstawiono właściwości dielektryczne oraz warunki sieciowania dla wybranej żywicy epoksydowej. Badany układ zawierał Epidian 6 oraz aminę DDM. W pierwszym kroku określono optymalne warunki sieciowania dla różnej procentowej zawartości aminy w mieszaninie. Na diagramie pokazano, jak właściwości usieciowanej matrycy zależą od procentowej zawartości utwardzacza. Pomiary dielektryczne wykonano dla dwóch mieszanin o zawartości 10% i 16% wagowych DDM podczas sieciowania, jak i po usieciowaniu. Zaobserwowano znaczące różnice w odpowiedzi dielektrycznej, co było wynikiem różnego stopnia utwardzenia badanej żywicy.