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Effect of the epoxyurethane modifier on the physicomechanical and electret properties of epoxy-based chemoelectrets cured in an electric field

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Abstract. This study investigates the influence of the epoxyurethane oligomer PEF-3A as a modifier on the crosslinking degree, physicomechanical properties, and electret characteristics of epoxy-based materials synthesized under simultaneous curing and polarization in a constant electric field. Unpolarized samples and chemoelectrets with varying PEF-3A content (2.5–10.0 wt. %) were prepared using the DER-331 epoxy oligomer and the polyaminoamide hardener L-20. Results reveal that increasing PEF-3A content decreases crosslink density, tensile strength, and Shore D hardness due to steric hindrance and reduced network frequency. Electret properties such as surface potential and charge density display modest dependence on modifier concentration and stabilize during storage. Simultaneous curing and polarization enhance molecular dipole orientation, improving strength in chemoelectrets relative to unpolarized analogs.

Keywords: epoxy oligomer, polyaminoamide, epoxyurethane modifier, gel fraction, crosslinking degree, polarization, chemoelectret, tensile strength, Shore D hardness

Introduction

Epoxy polymer materials are thermosetting polymers that form a three-dimensional mesh as a result of the reaction of epoxy resins with hardeners. Epoxy oligomers are widely used to produce industrial materials, serving as a base for compounds, adhesives, varnishes, and binders for laminated plastics due to their high strength and chemical resistance (Petrie 2006). Since various products experience different loads (in magnitude and direction), they are subject to different requirements in terms of their properties — in particular, rigidity or flexibility and hardness. Therefore, epoxy materials with different properties are needed. The properties of epoxy polymer materials depend both on the structure and characteristics of the hardeners and oligomers, and on polymerization conditions (Dallaev et al. 2023; Petrie 2006).

The structure of epoxy oligomers, their molecular weight, and the presence of functional groups affect the crosslinking density, degree of conversion, and morphology of the polymer network (Liubimova et al. 2024). For example, the use of the diglycidyl ether of bisphenol A and its modifications makes high strength and flexibility possible. Modifying additives, such as thermoplastic oligosulfones with different molecular weights and terminal reaction groups, contribute to an increase in glass transition temperature and heat resistance due to the formation of a denser and more stable structure with additional hydrogen bonds (Kochergin et al. 2018).

The nature of the hardener determines the curing rate and the degree of conversion of the epoxy groups. Amine hardeners, such as 4,4'-methylene bis-(3-chloro-2,6-diethylaniline), are widely used to obtain compositions with the desired mechanical and chemical properties. The polymerization rate and curing conditions — temperature and holding time — significantly affect the morphology of the material and its final properties: at high curing temperatures, impact strength can decline, and under optimal conditions, high strength and elasticity are achieved (Incerti et al. 2018; Kochergin et al. 2018; Lubimova et al. 2024).

Chemical modification of epoxy resins with the addition of various oligomers and copolymers makes it possible to control the frequency of crosslinking, flexibility of chains, and adhesion, expanding the scope of the material. The modification improves chemical, crack, and heat resistance, as well as reducing internal stresses caused by polymerization (Stroganov et al. 2018; Zagora et al. 2021).

Modern research also considers the use of biobasing epoxy resins with controlled rigidity of structural units to create more environmentally friendly materials with programmable properties. This area is actively developing due to sustainable development and environmental safety requirements (Zhou et al. 2023).

Thus, it is possible to identify the key factors influencing the properties of epoxy polymer materials:
— molecular weight and structure of epoxy oligomers, presence of functional groups;
— chemical composition and type of the hardener;
— polymerization conditions: temperature, time, and curing rate;
— the use of modifying additives to improve mechanical and thermal characteristics.

The ability of electret materials to create an electric field in the surrounding space serves as a means of increasing the life of many parts and assemblies of modern technology, providing an anti-fungal and anti-corrosion effect. Several methods are used to lend electret properties to polymers. These are the treatment of polymer films in a permanent corona discharge, thermal electretation, friction, irradiation, etc. When chemical reactions occur in polymers during electretation, it is a case of chemopolarization. Conducted in an electric field, the curing process produces unique structural features and a set of material properties, which are associated with the creation of a three-dimensional polymer matrix network under physical modification (Balakina et al. 2007; Burganov et al. 2017; Galikhanov et al. 2019; 2024; Haque, Park 2022; Nazmieva et al. 2015; Studentsov et al. 2014; Vakhonina et al. 2011). Electrets based on an epoxy oligomer, an epoxyurethane modifier, and a polyaminoamide have good and stable properties sufficient for their practical use.

The purpose of this paper is to prepare unpolarized samples and chemoelectrets with the same composition under identical conditions and to investigate how varying the content of the PEF-3A modifier affects the crosslinking degree, physicomechanical properties (including tensile strength and Shore hardness), and electret characteristics of the resulting epoxy-modified materials, such as surface potential V_s, effective surface charge density σ_{eff}, and electric field intensity E.

Materials and methods

The epoxy oligomer DER-331 (The Dow Chemical Company), the epoxyurethane oligomer PEF-3A, and the polyaminoamide-based hardener L-20 were chosen as study materials (Galikhanov et al. 2024).

For the experiments, both unpolarized samples and chemoelectrets were prepared by curing a mixture of the original epoxy (DER-331) with varying amounts of the epoxyurethane oligomer PEF-3A (ranging from 2.5 to 10.0 wt. %) and the polyamide hardener L-20, mixed in a stoichiometric ratio relative to the main oligomer and modifier. This polymer synthesis was combined with a polarization step conducted at 120 °C under a constant electric field, followed by cooling for 30 minutes while maintaining the polarization. The gel fraction content for the prepared polarized and unpolarized ground samples was determined by the extraction with a boiling acetone for 24 hours in a Soxhlet apparatus.

Temperature transitions were recorded using the differential scanning calorimeter DSC Q200TA instruments by heating the sample in the calorimeter up to 300°C at the rate of 2 degrees per minute.

The surface potential V_s, effective surface charge density σ_{eff}, and electric field intensity of the electret E were performed by the method of periodic shielding of a reception electrode with an IPEP-1 device. The tensile strength (modulus of rupture) σ_t was determined for the hardened samples on a Test P108 tensile testing machine in accordance with GOST 11262-2017. The Shore D hardness (HD) of the cured samples was measured using a Shore D durometer (HGIB) according to the GOST 24621-2015 standard, with a testing speed of 100 mm/min.

Each measurement was repeated at least five times. The error in determining the strength and electret properties of the samples was within 5%.

Results and discussion

It is known that the characteristics of cross-linked polymers are substantially dependent on the temperature of the curing reaction. By varying the curing temperature, a change in the properties of cross-linked polymers is associated with different topologies of the resulting three-dimensional polymer structure. Lower curing temperatures contribute to the formation of a heterogeneous (defective) structure of the polymer matrix; with an increase in the reaction temperature, a polymer matrix with a more uniform structure is formed and the strength characteristics for such samples are ameliorated (Galikhanov et al. 2019; 2024). Synthesis of the polymer simultaneously with the polarization process in a constant electric field with a temperature increase up to 120 °C leads to a rise in the spatial grid frequency of the three-dimensional polymer matrix. Previous studies have shown that the maximum values of the electret and physicomechanical characteristics correspond to the stoichiometric content of the hardener in the composition. With a deficiency and excess of the hardener, the values of electret and physicomechanical characteristics decrease (Burganov et al. 2017; Galikhanov et al. 2024). Consequently, all further studies were carried out with a stoichiometric content of the hardener in relation to the main oligomer and modifier.

Fig. 1 shows a DSC curve for the unpolarized sample based on the DER-331 oligomer after curing with the stoichiometric amount of L-20 at the temperature of 120 °C for 2 hours. As it is known, when the curing process is carried out at high temperatures, this leads to the formation of a polymer matrix that is more homogeneous in structure. The glass transition temperature of the resulting spatial polymer network, meanwhile, has higher values (Tc ≈ 88 °C) compared to the glass transition temperature of systems (obtained at room temperature), for which the curing reaction does not proceed completely. This is hindered by the transition of the cured polymer to the glassy state (Petrie 2006). As the temperature rises above T_c, there is practically no exothermic peak on the DSC curve, which characterizes the process of additional curing of the epoxy system as the topological structure of a three-dimensional polymer matrix for this system is determined by a sufficiently high conversion rate (the value of the gel fraction is about 99%). The gel fraction value is 98.07% for the studied unpolarized epoxy compositions and 98.73% for the chemoelectrets based on them.

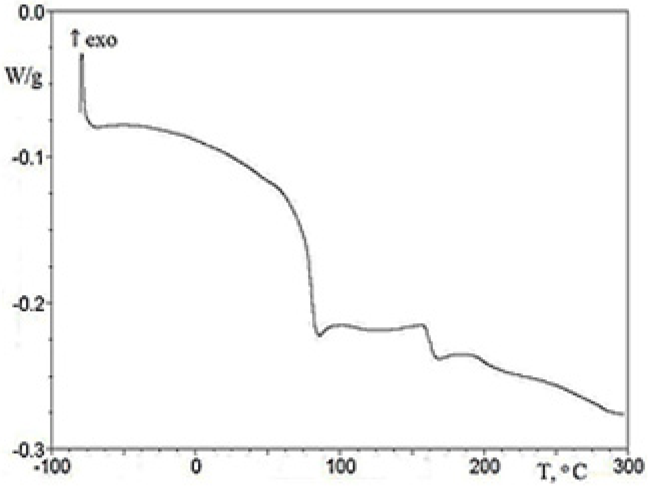
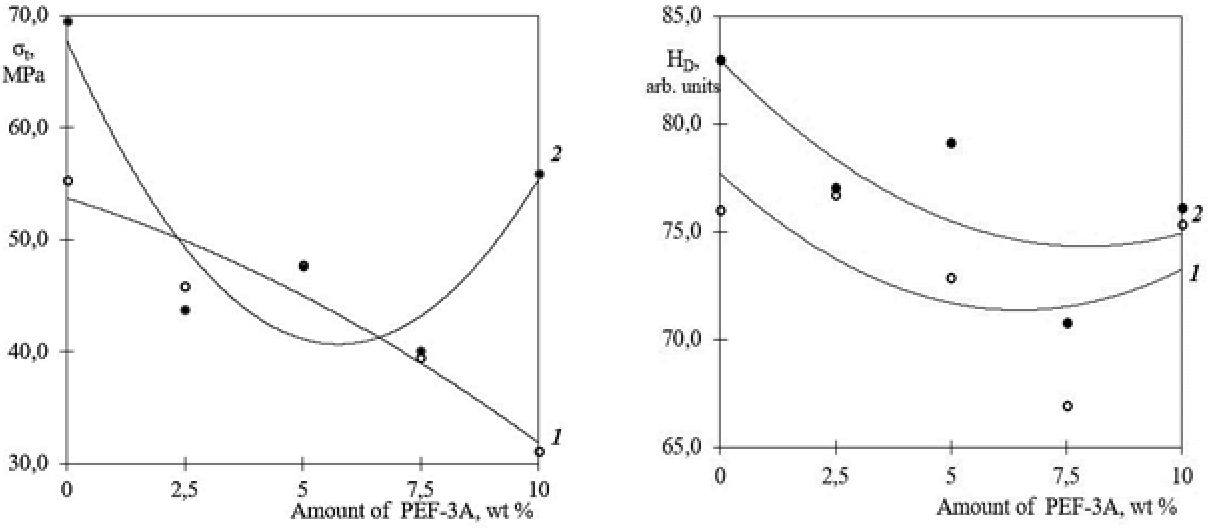


Fig. 1. DSC curve for a sample based on the DER-331 oligomer after curing with the stoichiometric content of L-20 at the temperature of 120 °C for 2 hours

When PEF-3A, an epoxyurethane, is used as a modifying agent, it introduces additional polar urethane groups into the polymer's three-dimensional network compared to the original DER-331 oligomer. In DER-331, positive charges are mainly carried by hydrogen atoms, while oxygen atoms primarily bear negative charges. Increasing the amount of the modifier in the mixture leads to a decrease in the density of the polymer's network due to the integration of the epoxyurethane oligomer, which also reduces the overall functionality of the system.

The slight changes observed in the electret properties of chemoelectrets with increasing PEF-3A content result from two competing factors: the decreased mobility of polar groups caused by strong physical intermolecular forces within the polymer's network, and the greater number of functional groups capable of participating in polarization through dipole-segment interactions. As the PEF-3A concentration rises, the availability of functional groups for polarization increases despite the diminishing mobility of polar groups.

In contrast to the electret characteristics, the change in the content of the PEF-3A modifier in the composition has a significant effect on the physicomechanical characteristics of the obtained unpolarized samples and chemoelectrets of a similar composition (Fig. 2).



a *b*

Fig. 2. Dependencies (*a*) of the strength at break and (*b*) the Shore D hardness for unpolarized samples (*1*) and chemoelectrets (*2*) based on the DER-331 oligomer on the content of the PEF-3A modifier

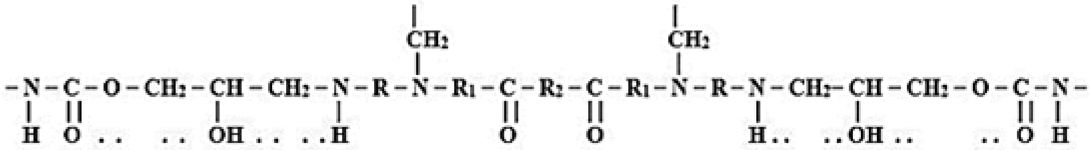
The dependences of the breaking stress at rupture σ_t of unpolarized samples (curve 1) on the content of the PEF-3A modifier shown in Fig. 2(*a*) demonstrated that an increase in the modifier content of the composition coincided with a decrease in σ_t compared to the unmodified sample (σ_t=55.3 MPa). The values of breaking stress at rupture σ_t with an increasing content in the PEF-3A modifier in the composition were: σ_t = 45.8 MPa for 2.5 wt. %, σ_t =39.5 MPa for 7.5 wt. %, and 31.15 MPa for 10 wt. %.

For chemoelectrets based on the DER-331 oligomer (Fig. 2(*a*), curve 2), the introduction of the PEF-3A modifier also results in a decrease in the rupture stress at break associated with a decrease in the spatial grid frequency. Minimal values of the rupture stress at break for the modifier PEF-3A in the composition correspond to the modifier content of 2.5–7.5 wt. %. The rupture stress at break is 43.8 MPa at the PEF-3A content of 2.5 wt. % and 40.1 MPa at 7.5 wt. %. The extreme character of dependencies is explained by the predominance of steric factors preventing the mobility of polar groups due to a strong intermolecular interaction dominating over a simultaneously increasing number of functional groups capable of polarization.

The Shore D hardness values shown in Fig. 2(*b*) reflect the influence of the PEF-3A modifier content on both unpolarized samples (curve *1*) and chemoelectrets (curve *2*) based on the DER-331 oligomer cured with a stoichiometric amount of L-20. These samples were prepared by simultaneous curing and polarization at 120 °C under a 5 kV voltage applied to the electrodes. The data indicate a decline in physicomechanical properties (Shore D hardness) corresponding to a reduced frequency of the spatial network in the resulting three-dimensional structure. For unpolarized samples, Shore D hardness does not increase with more modifier present (76 arbitrary units for the unmodified sample compared to 75.35 units at 10 wt% modifier). Thus, even though the number of physical crosslinking points in the system grows — due to an increase in polar groups with a higher PEF-3A content in unpolarized samples and the additional alignment of polar groups during polarization in chemoelectrets — this does not result in an increase in Shore D hardness. For the chemoelectrets, Shore D hardness decreases from 83 conventional units in the unmodified state to 76.1 units when the modifier content reaches 10 wt% (Fig. *2*(*b*), curve *2*).

Polarizing the polymer network structures enhances their strength compared to unpolarized systems of similar composition, which is attributed to the orientation of polar groups encouraging the formation of a denser network of physical bonds.

When the PEF-3A modifier is incorporated into a three-dimensional polymer matrix, tightly crosslinked regions formed by the DER-331 oligomer alternate with more loosely crosslinked areas created by PEF-3A molecules. This is due both to the higher molecular weight of the modifier and to a reduced reactivity of the secondary amino groups formed, resulting in lower functionality of the polymer network units compared to unmodified epoxy materials, mainly due to strong hydrogen bonding effects (see Fig. 3).



$$-\underset{H}{N}-\underset{\underset{O\,..}{\|}}{C}-O-CH_2-\underset{..\,OH\,..}{CH}-CH_2-\underset{..\,H}{N}-R-\overset{\overset{|}{CH_2}}{N}-R_1-\underset{\underset{O}{\|}}{C}-R_2-\underset{\underset{O}{\|}}{C}-R_1-\overset{\overset{|}{CH_2}}{N}-R-\underset{H\,..}{N}-CH_2-\underset{..\,OH\,..}{CH}-CH_2-O-\underset{\underset{..\,O}{\|}}{C}-\underset{H}{N}-$$

Fig. 3. Schematic representation of the unit for samples based on the epoxy oligomer DER-331 when the PEF-3A modifier is embedded in the polymer matrix, hardener L-20

The investigation into how the PEF-3A modifier content affects chemoelectrets showed that increasing the modifier from 2.5 to 5.0 wt.% leads to a rise in the surface potential only during the early storage period of up to 10 days. On the 10th day, the surface potential values were 0.7 kV for the chemoelectret with 2.5 wt.% PEF-3A and 0.16 kV for the one with 5.0 wt.% PEF-3A. Increasing the modifier beyond 5 wt.% does not significantly improve the electret properties; for example, the surface potentials on the 10th day were 0.08 kV for the sample with 7.5 wt.% and 0.10 kV for the sample with 10 wt.% PEF-3A.

After more than 20 days of storage, the surface potential values of all samples tend to converge and show little dependence on the amount of the PEF-3A modifier in the composition. V_s for 60 days of storage was: 0.02 kV (for chemoelectrets containing 2.5 and 10 wt. %) and 0.04 kV (for chemoelectrets containing 5 and 7.5 wt. % PEF-3A). Similar results were obtained for other electret characteristics (σ_{eff} and E).

Conclusion

The electret state of the polymer matrix, developed under simultaneous curing and polarization, is stabilized by a three-dimensional network of chemical bonds, allowing the macromolecules to retain a free state. During this process, molecular dipoles align with the polarizing field, and the polymer's spatial structure becomes fixed by the chemical bond network. As a result, the charge carriers within the chemoelectret are held firmly in the network structure formed by curing. The structural characteristics and proportions of the system's initial components strongly influence the physicomechanical properties of the final polymer materials. Converting cross-linked polymer structures, including those modified, into a polarized state leads to improved strength properties compared to unpolarized samples of similar composition.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

All the authors contributed equally to this work.

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