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Chemistry

# EPOXY COMPOSITES FILLED WITH NATURAL CALCIUM CARBONATE. 1. EPOXY COMPOSITES OBTAINED IN THE PRESENCE OF MONOPEROXY DERIVATIVE OF EPIDIAN-6 EPOXY RESIN

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**Abstract.** Physico-mechanical properties of the products based on filled epoxy-oligomeric mixtures composed of Epidian-5 epoxy resin, oligoesteracrylate TGM-3 and monoperoxide derivative of Epidian-6 epoxy resin (PO) have been investigated. $CaCO_3$ was used as a filler and polyethylene polyamine was a curing agent. The effect of PO and $CaCO_3$ on the gel-fraction content and physico-mechanical properties was examined. Using a scanning electron microscopy (SEM) the morphology of the samples has been studied.

**Keywords**: epoxy resin, oligoesteracrylate, peroxide, $CaCO_3$, gel-fraction, physico-mechanical properties, SEM.

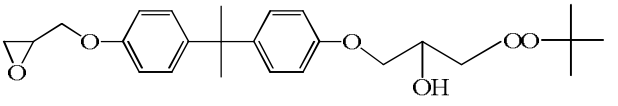
## 1. Introduction

One of the main tasks of modern material science is to obtain composition polymer materials with predefined operational characteristics [1]. This is achieved by the directed control of polymer matrix structural network formation, as well as thermodynamic, kinetic and mechanical compatibility of the system components [2]. The choice of polymer component is important too. To date the composites based on epoxy resin are of great scientific and practical interest [3]. Epoxy resins provide high adhesion on the boundary polymer-filler and possess necessary technological properties during products formation. Moreover, they are compatible with other polymer materials and improve the properties of the resulting products [4].

Previously we showed the possibility of obtaining polymer materials based on Epidian-5 with functional derivatives of epoxy resins as a polymer additive [5]. These derivatives contain, apart from epoxy group, unsaturated methacrylate fragment [5], free carboxy group [6], primary hydroxy group [7] or fluorine atoms [8]. The introduction of epoxy resin functional derivative into the polymer mixture based on Epidian-5 resin and TGM-3 oligoesteracrylate improves the operational characteristics of the products due to the binding of all components [5-8].

On the other hand, the simultaneous improvement of operational characteristics and the reduction of products price are achieved by the introduction of mineral fillers into the polymer mixture [9]. The used fillers are $TiO_2$ [10, 11], silver [12], nano $Si_3N_4$ [13], graphite oxide [14], carbon black [15], natural zeolite [16], $CaCO_3$ [17-21] and others [22, 23]. $CaCO_3$ is the most available, and thus the most often used filler. Apart from its using for the production of epoxy resins based materials, it is applied to produce composites on the basis of polyvinyl chloride, polypropylene and polyesters [17-24].

The aim of this work was to study Epidian-5 based polymer mixture filled with calcium carbonate. The mixture contains TGM-3 oligoesteracrylate as a plasticizer, polyethylene polyamine as a curing agent and monoperoxy derivative of Epidian-6 resin (PO) of the formula:



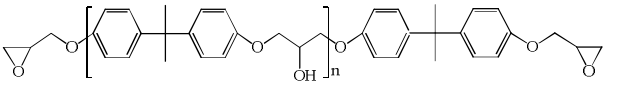
PO has a free epoxy group allowing to a introduce it into the polymer matrix which is formed by hardener. The peroxy group of PO contributes to the formation of free radicals during heating. Free radicals of the formed polymer matrix allows to graft TGM-3 molecules.

## 2. Experimental

### 2.1. Materials

The materials used for the experiments were:

Epidian-5 epoxy resin (Sarzyna-Ciech, Poland) of the formula, where n = 0–2:



with a molecular weight of 390 g/mol and epoxy groups content (e.n.) of 20.0 %.

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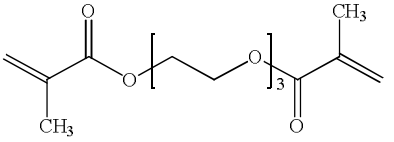
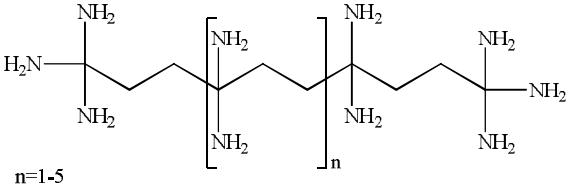
Monoperoxy derivative of Epidian-6 epoxy resin (PO) was synthesized according to the procedure described in [25]. It was found for PO: molecular weight of 430 g/mol; active oxygen content of 2.8 % and e.n. of 9.5 %.

TGM-3 oligoesteracrylate is an esterification product of methacrylic acid and triethylene glycol in the solvent medium with $M_n$ 286 g/mol. Its formula:



Polyethylenepolyamine (PEPA, Ukraine) of the formula



was the curing agent and was used as received without additional purification.

Calcium carbonate ($CaCO_3$, Sigma Aldrich) is a white odorless powder or colorless crystals.

## 2.2. Preparation of filled epoxy-oligomeric mixtures

Epidian-5, TGM-3, PO and $CaCO_3$ were mixed till the homogeneous mixture was obtained. Then it was degassed under vacuum to eliminate air bubbles. After PEPA addition the mixture was again mixed and degassed.

**Fig. 1.** General view of the moulds.
Sizes (mm) for dumbbell-shaped samples: length 165, width 10 and thickness 4.5; for bar: length 8, width 10 and thickness 4.5

To determine the film hardness and gel-fraction content the samples were poured over the standard glass plates. To determine physico-mechanical properties the samples were poured into special moulds in the form of dumbbell-shaped samples and bars (Fig. 1).

The dumbbell-shaped samples and bars were formed stepwise: first at room temperature for 24 h and then when heated to 423 K for 75 min.

## 2.3. Investigation Methods

Films hardness (*H*, rel.units) was determined according to the standard procedure [26] using M-3 pendulum device at room temperature. Gel-fraction content (*G*, %) was determined after extraction of grinded samples with acetone in Soxhlet apparatus for 12 h [26].

Tensile properties (ISO 527-21A), Charpy impact strength (ISO 179-1:2010), flexural properties (ISO 178:2010) and Shore D hardness (ISO 868) were determined with a Zwick/Roell device (Germany) in Gdansk University of Technology (Poland). Tensile tests were performed with a Zwick type Z020 tensile tester equipped with a 20 kN load cell. The tests were performed on molded samples having the dimensions of 75×4×2 mm. A grip-to-grip separation of 50 mm was used. The samples were pre-stressed to 3 N, then loaded with a constant cross-head speed of 50 mm/min. The average values reported were derived from at least five specimens.

SEM analysis of the freeze fractured samples was performed using HITACHI SU8010 apparatus equipped with a cold cathode field-emission source. The samples were sputter coated using Cressington Sputter Coater 108Auto with Au.

# 3. Results and Discussion

The described in the literature [17-21] epoxy resin based compositions with $CaCO_3$ do not contain monoperoxy derivative of Epidian-6 (PO). Therefore the plasticizer TGM-3 does not enter the three-dimensional cross-linked structure of the resulting product. This leads to the partial "sweating" of oligoesteracrylate during operational process and deterioration of the product properties. So, in this work it was important to determine the effect of PO and its amount on gel-fraction content and physico-mechanical properties of the product. The effect of $CaCO_3$ amount on the above mentioned characteristics should be determined as well.

The composition of the investigated mixtures is given in Table 1.

Mixture I is a standard mixture without mineral filler and PO. Mixture II additionally contains the mineral filler $CaCO_3$. In mixtures III-VIII the part of Epidian-5 resin is substituted for PO. $CaCO_3$ is absent in mixture III. For mixtures with PO the amount of filler varies from 10 to 60 mass parts.

## 3.1. Gel-Fraction Content and Hardness of Polymer Films

Gel-fraction content and hardness of polymer films were determined according to the procedures described in subsection 2.3. The experimental results are represented in Table 2.

*Table 1*

**Composition of the mixtures**

| Component | Components content, mass parts | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | I | II | III | IV | V | VI | VII | VIII |
| Epidian-5 | 100 | 100 | 90 | 90 | 80 | 70 | 90 | 90 |
| PO | 0 | 0 | 10 | 10 | 20 | 30 | 10 | 10 |
| TGM-3 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| PEPA | 14 | 14 | 13.2 | 13.2 | 12.5 | 11.7 | 13.2 | 13.2 |
| $CaCO_3$ | 0 | 30 | 0 | 30 | 30 | 30 | 10 | 60 |

*Table 2*

**Gel-fraction content and hardness of polymer films**

| Mixture number according to Table 1 | Gel-fraction content, % | Hardness, rel.units |
|---|---|---|
| I | 93.6 | 0.57 |
| II | 94.1 | 0.72 |
| III | 93.2 | 0.74 |
| IV | 96.0 | 0.80 |
| V | 94.7 | 0.74 |
| VI | 93.5 | 0.72 |
| VII | 93.7 | 0.67 |
| VIII | 95.9 | 0.80 |

The least hardness is observed for the films without $CaCO_3$ and PO (mixture I). The introduction of $CaCO_3$ (mixture II) allows to considerably increase the films hardness with a slight increase in gel-fraction content. The partial substitution of Epidian-5 for PO also increases hardness (0.57 rel.units for mixture I *vs.* 0.74 rel.units for mixture III). This phenomenon may be explained by PO participation in the formation of film structure due to the binding of TGM-3 molecules. In the presence of PEPA, at room temperature, PO with epoxy group and labile peroxy bond in its structure enters the cross-linked matrix based on Epidian-5; –O–O– bonds are preserved. When heated, labile –O–O– bonds decompose and form free radicals which cause grafted polymerization of TGM-3 molecules to already cross-linked structure formed by Epidian-5 and PO molecules. The additional introduction of mineral filler to the mixture contributes to the increase in gel-fraction content and hardness of the films (mixture IV).

The decrease in $CaCO_3$ amount to 10 mass parts when PO amount is constant (mixture VII), decreases both gel-fraction and hardness. If we compare mixtures VIII and IV ($CaCO_3$ amount is 60 and 30 mass parts, respectively), we do not observe essential changes in the mentioned values.

The increase in PO amount from 10 to 20 and 30 mass parts (mixtures IV, V and VI, respectively) decreases gel-fraction content and hardness. The reason is possible reactions between PO molecules (at constant amount of TGM-3) leading to the formation not cross-linked structures but linear ones, which are soluble in organic solvents.

Thus, the introduction of $CaCO_3$ into the structure of polymer mixture considerably increases hardness of polymer films. The same results may be achieved by partial substitution of Epidian-5 for PO molecules. The simultaneous introduction of $CaCO_3$ in the amount of 30-60 mass parts abd PO in the amount of 10 mass parts (mixtures IV and VIII) increases both gel-fraction content and hardness of the films if compared with standard mixture I.

## 3.2. Physico-Mechanical Properties

Physico-mechanical properties of the mixtures were studied according to the procedure described in subsection 2.3. The experimental results are given in Table 3.

The comparison of mixtures without PO (mixtures I and II) shows that the introduction of mineral filler in the amount of 30 mass parts decreases the values of maximum tensile strength ($TS_b$), elongation at break ($E_b$), Charpy impact strength, maximum flexural strength ($F_{max}$) and break deformation (e-break) but increases Young's modulus ($E_{Mod}$) and Shore D hardness. It means that $CaCO_3$ increases hardness of the product but makes it brittle. Virtually the same results are obtained when 10 mass parts of PO were introduced (mixture III). The results are in agreement with those of Table 2 and once again indicate the participation of PO molecules in the formation of three-dimensional cross-linked structure based on Epidian-5 and TGM-3. The resulting product becomes hardener and less flexible. Simultaneous introduction of PO and $CaCO_3$ (mixture IV) decreases break deformation and impact strength by three times.

At the constant value of $CaCO_3$ amount in the mixture the PO increase from 10 to 20 and 30 mass parts (mixtures IV, V and VI, respectively) results in the

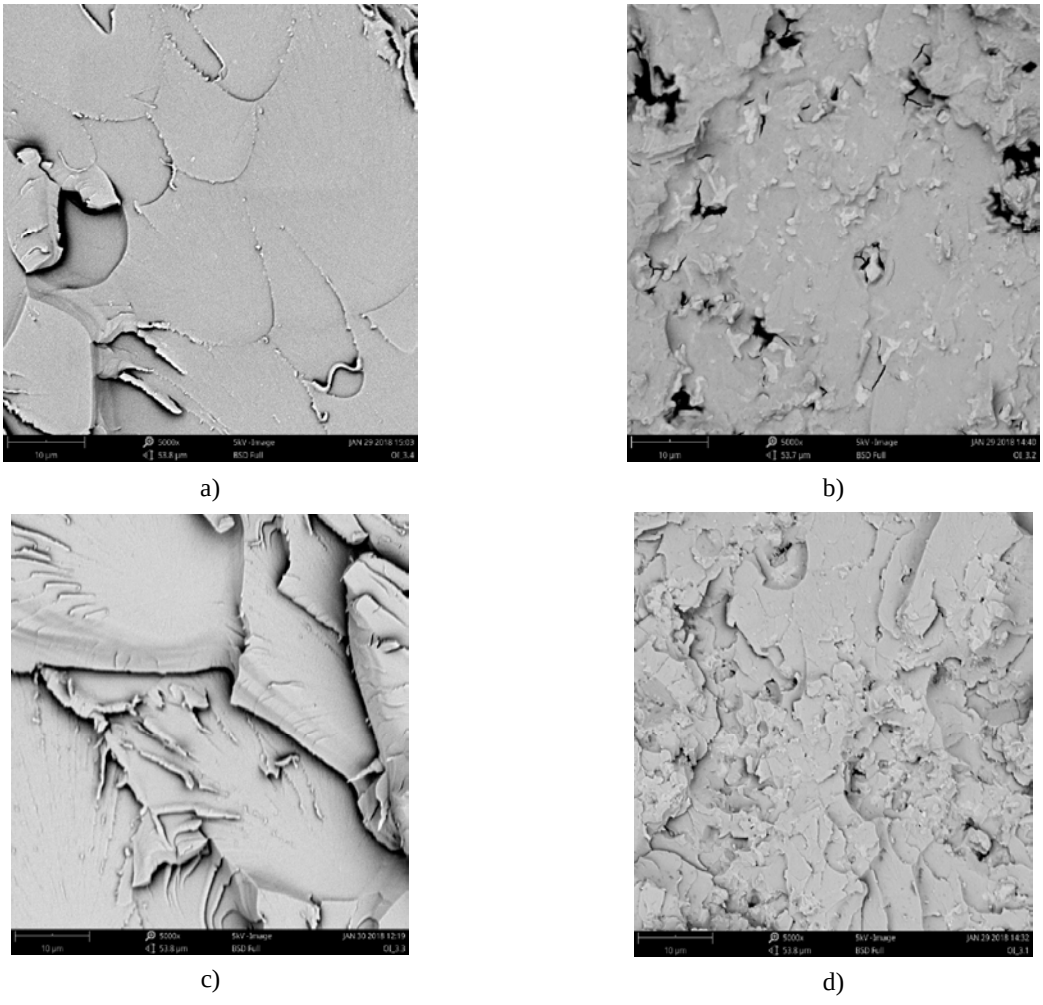
decrease of hardness and impact strength but increases the product flexibility. These data are also in agreement with the results from Table 2 and confirm the assumption that a great amount of PO leads to the less cross-link density of the mixture components.

The increase in $CaCO_3$ amount (mixtures VII, IV and VIII) increases hardness, Young's modulus, tensile strength and flexural strength but decreases impact strength.

Fig. 2 represents SEM images of some investigated mixtures.

*Table 2*

| Mixture number according to Table 1 | Tensile tests | | | Charpy impact strength, kJ/m$^2$ | Flexural properties | | Shore D hardness |
|---|---|---|---|---|---|---|---|
| | $TS_b$, mPa | $E_b$, % | $E_{Mod}$, GPa | | $F_{max}$, MPa | e-break, % | |
| I | 58.3 | 1.74 | 3.02 | 14.75 | 119.6 | 4.29 | 82.6 |
| II | 28.1 | 0.82 | 3.77 | 3.45 | 41.7 | 1.20 | 85.2 |
| III | 21.3 | 0.62 | 1.67 | 9.71 | 39.2 | 1.86 | 84.5 |
| IV | 21.2 | 0.61 | 3.79 | 3.31 | 39.2 | 1.13 | 85.0 |
| V | 29.3 | 0.90 | 3.16 | 3.01 | 49.2 | 1.48 | 84.0 |
| VI | 37.9 | 1.03 | 3.84 | 2.18 | 64.1 | 1.88 | 83.3 |
| VII | 24.6 | 0.88 | 2.99 | 5.15 | 47.1 | 1.36 | 85.7 |
| VIII | 34.8 | 0.77 | 4.70 | 2.80 | 53.5 | 1.21 | 86.6 |



a) b) c) d)

**Fig. 2.** SEM images of mixture I (a), mixture II (b), mixture III (c) and mixture IV (d)

The introduction of PO into the mixture virtually does not affect the morphology of the samples (Figs. 2a and 2c). Large pores are not observed when PO and $CaCO_3$ are introduced simultaneously (cf. mixture IV, Fig. 2d and mixture II, Fig. 2b). It means that PO acts as a compatibilizer and binds all components of the mixture into unified three-dimensional cross-linked structure. This assumption correlates with the results represented in Tables 2 and 3.

## 4. Conclusions

Physico-mechanical properties of the samples formed on the basis of epoxy-oligoesteric mixtures have been investigated. The mixtures composed of Epidian-5 epoxy resin, TGM-3 oligoesteracrylate, monoperoxy derivative of Epidian-6 resin and calcium carbonate were cross-linked by polyethylene polyamine. The introduction of $CaCO_3$ considerably increases the films hardness. Similar results were obtained when Epidian-5 molecules were partially substituted for PO. Simultaneous introduction of $CaCO_3$ in the amount of 30–60 mass parts and PO (10 mass parts) increases both gel-fraction content and hardness if compared with mixtures without these components.

Mixtures without PO and with 30 mass parts of $CaCO_3$ are characterized by less values of maximum tensile strength, elongation at break, Charpy impact strength, maximum flexural strength and maximum deflection but higher values of Young's modulus and Shore D hardness. The analogous results are obtained when 10 mass parts of PO were introduced. The results indicate the participation of PO molecules in the formation of three-dimensional cross-linked structure. The resulting product becomes hardener and less flexible.

The increase in PO amount from 10 to 30 mass parts results in the decrease of hardness and increase in product flexibility. These data are also in agreement with the results from Table 2 and confirm the assumption that a great amount of PO leads to the less cross-link density of the mixture components. The increase in $CaCO_3$ amount increases hardness, tensile strength and flexural strength but decreases maximum deflection and impact strength.

SEM analysis confirms the improvement of product structure due to the simultaneous introduction of PO and $CaCO_3$.

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**ЕПОКСИДНІ КОМПОЗИТИ З НАТУРАЛЬНИМ НАПОВНЮВАЧЕМ КАРБОНАТОМ КАЛЬЦІЮ. 1. ОДЕРЖАННЯ ЕПОКСИДНИХ КОМПОЗИТІВ У ПРИСУТНОСТІ МОНОПЕРОКСИДНОЇ ПОХІДНОЇ ЕПОКСИДНОЇ СМОЛИ EPIDIAN-6**

***Анотація.*** *Вивчені фізико-механічні властивості зразків на основі наповнених епокси-олігоестерних сумішей, що складаються із промислової епоксидної смоли Epidian-5 та олігоестеракрилату TGM-3 і містять монопероксидну похідну епоксидної смоли Epidian-6 (PO. Як мінеральний наповнювач використано $CaCO_3$, затвердни ком сумішей слугував поліетиленполіамін. Встановлено вплив PO і $CaCO_3$ на вміст гель-фракцій та фізико-механічні властивості виробу. З використанням скануючої електронної мікроскопії показана морфологія отриманих зразків.*

***Ключові слова:*** *епоксидна смола, олігоестеракрилат, пероксид, $CaCO_3$, гель-фракція, фізико-механічні властивості, СЕМ.*