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Epoxy resins modified with palm oil derivatives — preparation and properties

RAPID COMMUNICATION

Summary — The epoxidized palm oil was synthesized and prepolymerized in a reaction with isophorone diamine. The resulting palm oil derivatives were used as modifiers (in the amount 10 wt. %) of a bisphenol A-based low molecular weight epoxy resin. The prepared compositions and the pure unmodified epoxy resin were cured with isophorone diamine, and then their mechanical properties (*i.e.*, tensile, flexural and compressive strengths, hardness and impact strength), thermal properties (using DMA) and morphology (by SEM) were examined. It was found that on one hand the palm oil derivatives led to a decrease in mechanical strength of the resin, but on the other hand, they contributed to an increase in relative elongation at break and significant improvement (even twice) in impact strength of the crosslinked products. A two-phase structure of the compositions studied, responsible for the increase of their impact strength was observed.

Keywords: epoxy resin, palm oil, composition, mechanical properties, thermal properties, morphology.

ŻYWICE EPOKSYDOWE MODYFIKOWANE POCHODNYMI OLEJU PALMOWEGO — OTRZYMYWANIE I WŁAŚCIWOŚCI

Streszczenie — Przeprowadzono syntezę epoksydowanego oleju palmowego, który następnie poddano prepolimeryzacji w reakcji z izoforonodiaminą (Schemat A). Oleju palmowego i jego pochodnych użyto jako modyfikatorów (w ilości 10 % mas.) małocząsteczkowej żywicy epoksydowej na bazie bisfenolu A. Przygotowane kompozycje i czystą niemodyfikowaną żywicę epoksydową utwardzono izoforonodiaminą, a następnie zbadano właściwości mechaniczne (wytrzymałość na zginanie, ściskanie i rozciąganie oraz twardość i udarność), właściwości termiczne (metodą DMA) i morfologię (za pomocą SEM) otrzymanych materiałów. Stwierdzono, że modyfikacja pochodnymi oleju palmowego powoduje pogorszenie wytrzymałości mechanicznej żywic (tabela 2), ale z drugiej strony przyczynia się do zwiększenia wydłużenia względnego przy zerwaniu i znacznej poprawy udarności (nawet dwukrotnie). Zaobserwowano, że kompozycje z pochodnymi oleju palmowego miały strukturę dwufazową (rys. 1), która odpowiada za zwiększenie udarności modyfikowanej żywicy (rys. 2).

Słowa kluczowe: żywica epoksydowa, olej palmowy, kompozycja, właściwości mechaniczne, właściwości termiczne, morfologia.

Continuously growing trend in the use of vegetable oils as additives for modification of polymer and raw materials for the synthesis of different polymeric materials has been observed in recent years [1, 2]. This is understandable if we consider that vegetable oils are non-toxic, cheap, and come not only from natural, but also from renewable sources. Moreover, while all vegetable oils are triglycerides of higher fatty acids, they are chemically diversified materials. The basic difference is in the content and type of fatty acid residues present in the oil molecules. These differences result in variation of the content and type of functional groups present in the fatty acid chains of the triglycerides. Usually, there are a number of unsaturated bonds in the fatty acid fragments, but hydroxyl groups (in castor oil and *lesquerella palmeri* oil) and epoxy groups (in vernonia oil) can also occur naturally.

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Due to the presence of functional groups, vegetable oils can be relatively easily converted into a number of useful derivatives. This is why vegetable oils are increasingly used not only as additives (mainly plasticizers) but also as raw materials for the synthesis of various polymers [3, 4]. For this application a range of different oils are most often utilized, such as: soybean, castor, linseed, rapeseed, cottonseed, peanut and palm oil. Palm oil is one of the most important oils produced worldwide, and its production is about one third of the global production of vegetable oils. Moreover, the price of palm oil remains at the lowest level among major industrial fats. Palm oil is used mainly in the food and cosmetic industries, but there are also proposals for the use of chemically modified palm oil as a plasticizer for poly(vinyl chloride) [5], a polyol for the synthesis of polyurethane materials [6, 7], a raw material for the preparation of UV-curable polyacrylates [8], and as a component of the composition of cycloaliphatic epoxy resins [9]. There are only few reports on the use of palm oil to modify the largest group of epoxy resins, which are resins based on bisphenols [10, 11].

This paper is a continuation of earlier research conducted by us on the use of modified vegetable oils in the technology of epoxy resins [12—14]. Therefore, the aim of this study was to examine the possibility of using for that purpose also palm oil. Due to its low viscosity, epoxidized vegetable oils can be used as reactive diluents for epoxy resins. However, palm oil, and epoxidized palm oil, are solid at room temperature and melt in the temperature range 33—39 °C. Nevertheless, the epoxidized palm oil could be applied as an additive, improving impact resistance and increasing flexibility of epoxy resins. Moreover, the epoxidized palm oil could at least partly replace petroleum derived epoxy resins.

In the course of this work we have prepared epoxidized palm oil and prepolymerized palm oil, and we used them to prepare compositions with bisphenol A-based low molecular weight epoxy resin. Then the compositions were cured using isophorone diamine and finally the structural, mechanical and thermal properties of the polymeric materials were determined.

EXPERIMENTAL

Materials

Commercial grade refined palm oil (PO) was obtained from PPH MEKPOL (Poland). A commercial liquid epoxy resin based on diglycidyl ether of bisphenol A (EPR 162, characterized by epoxy value 0.582 mol/100 g, was purchased from Hexion Specialty Chemicals, Inc., USA). The curing agent Aradur 46 (isophorone diamine, with amine value 320 mg KOH/g) was supplied by Huntsman Advanced Materials GmbH (Germany). Acetic acid (99.5 %; POCh, Poland), sulphuric acid (96 %; POCh, Poland), hydrogen peroxide (30 %; POCh, Poland) and toluene (POCh, Poland) were used as received.

Oil modification and preparation of compositions

Epoxidation of the palm oil was carried out by well known method using hydrogen peroxide/acetic acid (0.5 mol of acid and 1.5 mol of H_2O_2 per 1 mol of unsaturated bonds in the oil) as an oxidant, concentrated sulphuric acid (1.6 wt. % of H_2SO_4 relative to the total weight of acetic acid and hydrogen peroxide) as a catalyst and toluene as a solvent. The reaction mixture was heated up to 47—50 °C while stirring and H_2O_2 was added dropwise within 1 hour. Next, the stirring was continued for 6 hours at 60—65 °C.

The prepolymerized palm oil (PEPO) was obtained by reacting the epoxidized palm oil (EPO) with isophorone diamine (0.5 mol of diamine per 1 mol of epoxy groups in the oil), for 4 h at 70 °C. The composition containing epoxidized palm oil was prepared by direct mixing (one-step method) of the oil with the epoxy resin at 40 °C for 20 min, followed by heating at 60 °C for 10 min. In the case of two-step method, the palm oil-based prepolymer was synthesized first and then it was mixed with the resin under the same conditions as those used for the epoxidized palm oil.

Curing conditions

The freshly prepared compositions and the pure unmodified resin were mixed in stoichiometric amounts with isophorone diamine and the mixture was poured into a Teflon mold. The samples were cured for 24 hours at the room temperature and next post-cured for 24 hours at 80 °C. A silicon-based defoamer (BYK A530 from Chemie GmbH, Germany) was applied in amount of 1 % relative to the mass of the composition to facilitate proper degassing of the compositions before cure.

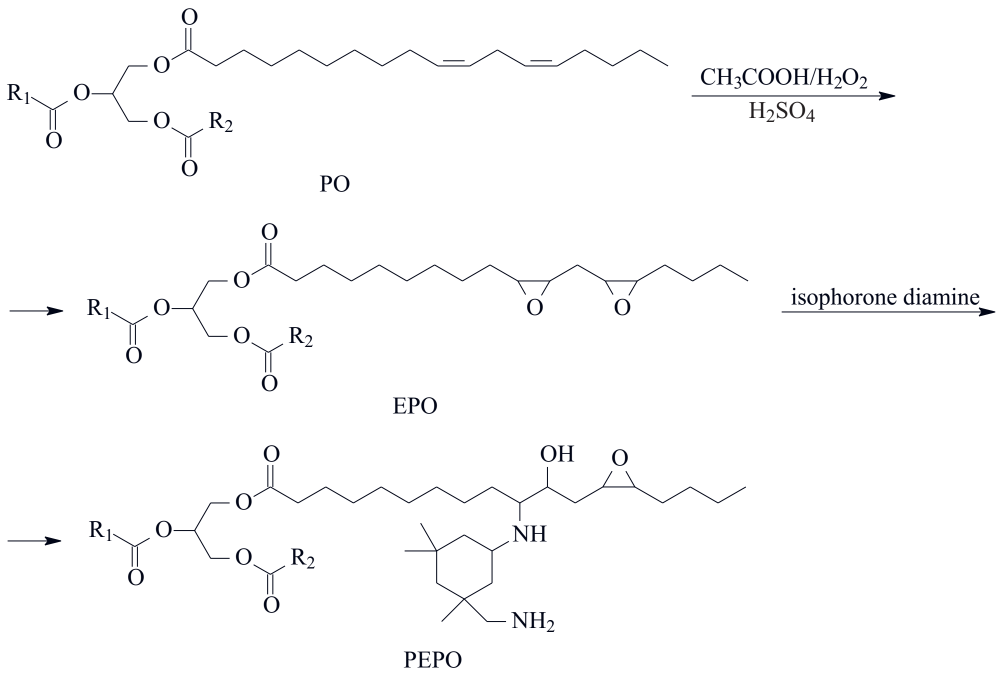
Methods of testing

Palm oil was characterized by iodine value determined with Hanus method according to PN-EN ISO 3961:2011 standard. Epoxy values of palm oil derivatives were determined according to PN-87/C-89085/13 standard.

The number-average molecular weight ($\overline{M}_n$), weight-average molecular weight ($\overline{M}_w$), and dispersity (*Đ*) of obtained resins were determined by Knauer gel-permeation chromatography with two PL-gel columns (300 × 7.5 mm) with grain size 3 μm and MIXED-E pore. Tetrahydrofuran dried over metallic sodium and distilled was used as eluent.

FT-IR spectroscopic measurements were performed on a BIO-RAD model FTS 165 spectrometer by casting thin liquid samples onto a KBr plate.

Tensile strength (according to PN-EN ISO 527:1 2012 standard), flexural strength (according to PN-EN ISO 178:2011 standard) and compressive strength (according to PN-EN ISO 604:2006 standard) were determined with Zwick 1445 testing machine. Hardness was established



Scheme A. Synthesis of the epoxidized palm oil and the prepolymerized palm oil

by the ball indentation method according to ISO 2039-1:2004 standard with Zwick 3106 equipment. The Charpy impact strength was measured according to ISO 179-2:2001 standard, using ZORN PSW 4 J Digital testing machine.

Dynamic mechanical analysis (DMA) was carried out with Netzsch DMA 242C instrument operating in the three-point bending mode at the oscillation frequency 1.0 Hz. Samples were in the form of bars of nominal 50 × 10 × 4 mm. Data were collected from -100 °C to 200 °C, at the scanning rate of 2 °C/min. The glass transition temperature (T_g) was assigned when the loss factor reached its maximum.

The fracture surfaces of materials studied were examined using Hitachi S-4700 Scanning Electron Microscope (SEM) at 10 and 20 kV accelerating voltage, after the surfaces of Charpy impact specimens were coated with Au thin film.

RESULTS AND DISCUSSION

The chemical structure of commercial palm oil and prepared palm oil derivatives were studied using FT-IR spectroscopy and GPC analysis as well by determination of the epoxy value. Characteristics of PO, EPO and PEPO are presented in Table 1. The epoxidized palm oil with the epoxy value of 0.173 mol/100 g was obtained successfully. The data presented in Table 1 show that almost all unsaturated bonds were oxidized and most of them (86.1 %) were converted into epoxy groups. However, this is a relatively low epoxy value in comparison to other epoxidized natural oils, which usually reach more than 0.200 mol/100 g that confirms the low functionality of palm oil. Such low functionality of the oil in combination with relatively low reactivity of epoxy groups centrally located in triglyceride chains may hinder achieving fully crosslinked compositions with epoxy resins. Therefore, the epoxidized palm oil was prepolymerized in the reaction with isophorone diamine used in stoichiometric ratio relative to the epoxy groups content presented in Scheme A.

A one-step and a two-step technique were used to prepare compositions of low molecular weight bisphenol A-based resin with the palm oil derivatives. Both, EPO and PEPO are solid materials. Nevertheless, they are very well miscible with the resin and therefore there was no problem with preparation of uniform oil-resin compositions. However, the compositions prepared using the

Table 1. Characteristics of the palm oil derivatives used in the research

Oil	$\overline{M}_n$	$\overline{M}_w$	Đ	Iodine value I_2 g/100 g	Unsaturated bond content mol/100 g	Epoxy value mol/100 g	FT-IR absorption bands, cm^{-1}		
							unsaturated bonds	epoxy groups	amine and hydroxyl groups
PO	745	819	1.1	51.0 ± 0.3	0.201 ± 0.001	0	3008	—	—
EPO	782	994	1.3	0	0	0.173 ± 0.001	—	841	—
PEPO	1071	1545	1.4	0	0	0.140 ± 0.002	—	841	3100—3650

one-step and the two-step techniques remained opaque both before and after crosslinking. This may indicate the formation of a heterogeneous system in both cases.

Once prepared, the compositions were mixed with isophorone diamine, chosen as a curing agent, in stoichiometric ratio relative to the epoxy group content in each formulation. Addition of a small amount of the silicone polymer additive BYK-A 530 facilitated the air-releasing and defoaming of the compositions, for obvious reasons, kept at elevated temperature shortly to avoid premature gelling of the material before filling the forms.

Mechanical tests of the crosslinked samples were performed to determine the effect of the addition of palm oil derivatives on the static tensile, flexural and compressive strengths as well as hardness and impact strength of the epoxy resins. The results are collected in Table 2. It can be concluded, that tensile, compression and flexural strengths of the epoxy resins were decreased due to modification with EPO and PEPO. A decrease in hardness of the composition was also observed. However, relative elongation at break increased. Moreover, Charpy impact strength was also significantly improved.

The fracture surfaces of the studied compositions were observed with SEM, and the microphotographs are presented in Figure 1. The compositions containing EPO and PEPO exhibit a rough surface and a two-phase microstructure of oil domains dispersed within the epoxy resin matrix (Fig. 1a and 1b). The formation of a two phase system is a result of the difference between reactivity of terminal epoxy groups in the resin and epoxy groups located centrally in the modified oil in relation to the amine curing agent. The SEM micrograph (Fig. 1b) of the composition obtained with the two-step method displayed smaller amount of spherical oil domains dispersed within the resin matrix. This confirms that using this technique more homogeneous compositions can be obtained. In addition, the composition containing PEPO is characterized by smaller hardness, better flexibility and higher impact strength than the composition obtained with the one-step technique.

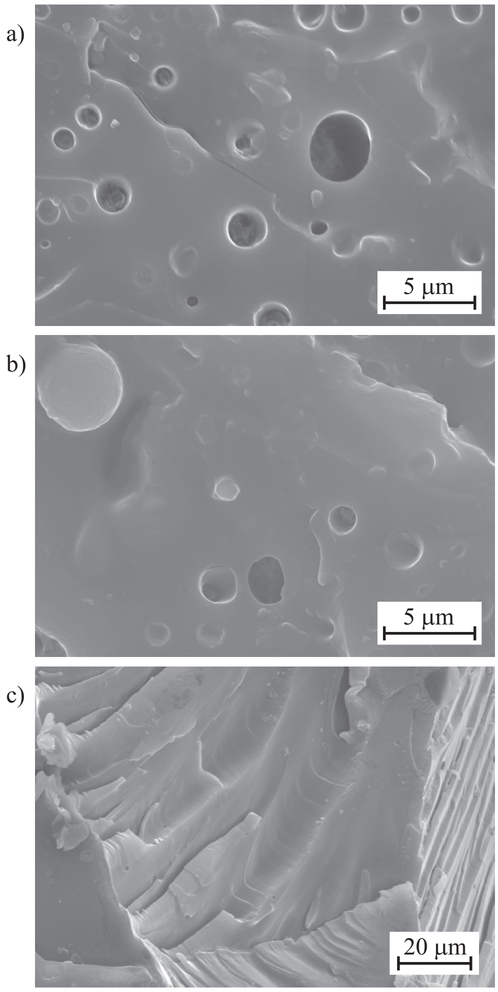


Fig. 1. SEM micrographs of the impact fracture surface of: a) epoxy resin composition containing 10 wt. % of EPO, b) epoxy resin composition containing 10 wt. % of PEPO, c) pure EPR 162 resin

In contrast, the unmodified epoxy resin sample revealed a number of brittle fractures (Fig. 1c), without any phase separation. Such a difference in the microstructure of the tested compositions is observed because the oil domains acted as centers of dissipation of mechanical energy that led to improvement in the impact strength of the compositions containing the palm oil derivatives in comparison to the pure epoxy resin. This observation,

Table 2. Mechanical properties of crosslinked epoxy compositions

	EPR 162	EPR 162 + 10 wt. % of EPO	EPR 162 + 10 wt. % of PEPO
Tensile strength, MPa	50.7 ± 1.3	47.9 ± 0.4	45.5 ± 1.5
Tensile modulus, MPa	2177 ± 174	1720 ± 139	2319 ± 438
Relative elongation at break, %	2.6 ± 0.4	3.3 ± 0.3	2.9 ± 0.4
Flexural strength, MPa	67.4 ± 3.0	64.1 ± 2.9	66.2 ± 2.2
Flexural modulus, MPa	1996 ± 94	1742 ± 17	1924 ± 70
Compression strength, MPa	67.1 ± 0.9	65.8 ± 1.1	65.7 ± 0.9
Hardness, MPa	131.2 ± 3.7	108.0 ± 2.4	100.0 ± 2.3
Charpy impact strength, kJ/m^2	8.8 ± 1.9	17.4 ± 4.1	19.8 ± 2.4
Glass transition temperature, °C	87.3	86.8	79.8

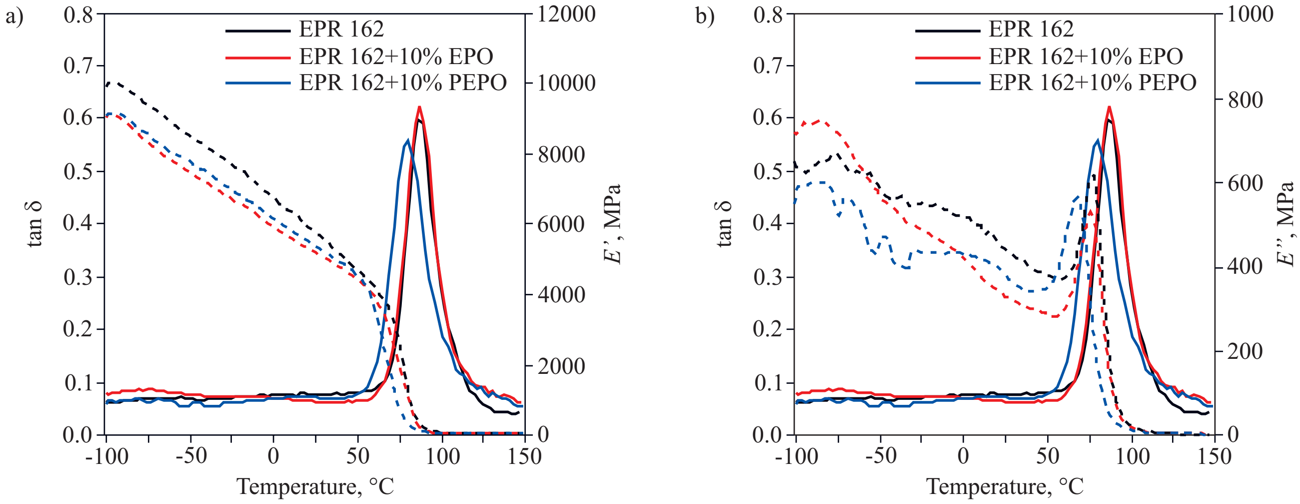


Fig. 2. Effects of EPO and PEPO addition to EPR 162 resin on tan δ and: a) storage modulus (E'), b) loss modulus (E'')

well consistent with the DMA results, was presented in Figure 2. It was found that the storage modulus (*E'*) versus the temperature curve for compositions with the modified palm oil shifted down. The observed reduction in *E'* and the glass transition temperature (Fig. 2, Table 2) occurs due to the decrease in stiffness of the epoxy resin as a result of the oil addition. *E'* in the rubbery phase is almost constantly falling down for both compositions studied. However, a small thermal effect is visible in loss modulus (*E''*) and tan δ at low temperature between -100 and -25 °C, that may confirm existence of the second phase in compositions containing 10 wt. % of EPO and PEPO. This effect is clearly greater for composition with epoxidized palm oil.

CONCLUSIONS

The results presented in this paper show that the modified palm oil can be successfully applied as an additive for modification of mechanical and thermal properties of bisphenol A-based low molecular weight epoxy resins. Addition of 10 wt. % of both: the epoxidized palm oil or its prepolymer decreases stiffness and brittleness of the modified epoxy resin, resulting in significant improvement in the impact strength of the resin. This is the effect of reducing of crosslink density of the modified resin as well as effect of formation of the two-phase structure composed of the oil microdomains dispersed in the epoxy resin matrix. The palm oil derivatives act as plasticizers, while causing reduction in the mechanical strength of the modified resin. However, the palm oil-modified epoxy resin compositions still preserve relatively high tensile, compression and flexural strengths.

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