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The impact of crosslinking monomers concentration on the properties of unsaturated polyester resins

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The article illustrates the preparation of unsaturated polyester as well as the mechanical and thermal properties of his copolymers with crosslinking monomers (styrene and diethylene glycol dimethacrylate). The starting polyester was obtained from maleic anhydride, propylene glycol and isobutanol. The prepared series of unsaturated polyester resins were subjected to different studies concerning evaluation of their viscosity, mechanical and thermal properties and also dynamic mechanical behaviour (DMA).

Keywords: unsaturated polyester resin, styrene, DMA analysis.

1. INTRODUCTION

Unsaturated polyester resins are the solutions obtained by dissolving the unsaturated polyesters in vinyl, allyl or acrylic monomers. These unsaturated polyesters exist as a liquid of high viscosity or solid (at room temperature). Thanks to the presence of unsaturated bonds in the monomers structure, they can perform the function of crosslinking monomers during the curing of the resin. The unsaturated polyesters are obtained in the polycondensation reaction of two groups of compounds: dicarboxylic acids (saturated and unsaturated) or their anhydrides and glycols. Maleic anhydride, fumaric acid, phthalic acid isomers, ethylene

glycol and propane-1,2-diol, thanks to their low costs and widespread availability, are conventional substrates used in the preparation of the unsaturated polyesters. One of the above components used in the synthesis should have a double bond. The most often used is maleic anhydride. The degree of unsaturation of the polyester chain (the number of double bonds in the molecule) has a significant effect on the properties of unsaturated polyester.

The process of the polyesters synthesis is conducted in an inert gas atmosphere (N_2 , CO_2) or in solvents forming azeotropic mixtures with water that is produced during the reaction. In the first step, the monoesters of dicarboxylic acids and glycols are formed. Next, at temperature of approx. $200^\circ C$ longer polyester chains are created. In this temperature isomerization of maleic to fumaric residues takes place. The presence of fumarates in the polyesters molecules increases their reactivity in copolymerization with crosslinking monomers and improves the mechanical and thermal properties of the final product. The increase of reactivity can also be obtained by applying a molar excess of acids in relation to glycols in the synthesis. The polyesters obtained in this way were characterized by a high acid number. In consequence, the obtained resins are less stable during the storage and they cause the corrosion of packaging.

In industry, styrene is the most frequently used cross-linking monomer. Its general use is caused by several advantages such as: low price, good solubility of polyesters in it, the low viscosity of the solutions and the good quality of the cured products. That's why, its presence in resins is usually high – it is 30-50% of the total composition [1, 2]. One can keep in mind that styrene is a volatile organic compound. Because of its toxicity and suspicion of cancerogenic properties, the regulation limiting the concentration of styrene in the workplace has been introduced [3, 4]. The limitation of styrene concentration was achieved by the introduction of such compounds as paraffin or waxes. During the cross-linking these compounds exude from the resin, forming a protective layer on the resin surface, and protect styrene emission. However, a drawback of this solution is that such layer has antiadhesive properties [5–7]. Introduction of the compounds of the general formula of $[RCOOCH_2CH(OH)CH_2O]_n-A$, which are soluble in polyester resins was proposed in USA patent [8]. These compounds hinder the formation of the partition layer and decrease the evaporation of the monomer. The reduction of the emission of styrene is also achieved by manufacturing the resins in which styrene is partially or completely replaced by the less

volatile and less harmful monomers, e.g. methyl methacrylate or ethyl acrylate. They react only in a limited extent with maleic and fumaric double bonds and should be used in a mixture with styrene. Much less volatile compounds are methacrylate oligoesters. The most popular is triethylene glycol dimethacrylate having low toxicity but comparing with styrene it copolymerizes with polyesters much slower and the process is less exothermic.

Allyl monomers, for example diallyl phthalate are characterized by a lower volatility than methacrylic acid oligoesters. Additionally, resin solutions based on these monomers show better stability in comparison with those with styrene.

The other solution is to use more than one crosslinking monomer. Noteworthy is vinyl ester of branched monocarboxylic acid of the general formula $R-COOCH=CH_2$ (wherein R is a branched alkyl group containing 8–11 carbon atoms) of low volatility which can be used with methacrylic esters [9]. The resins synthesized on the basis of such monomers can be used when the operating conditions favor the emission of monomer to the environment, for example by spraying the resin on a large open surface of the mold or the hand lay-up.

The other way to reduce the emissions of styrene is the modification of the polyester chain. Introduction of dicyclopentadiene to the ends of the chain enables the reduction of the polarity of the molecules. This improves their solubility in a monomer and it makes possible the reduction of its concentration [10–12].

In this work the synthesis of unsaturated polyester resins with reduced styrene content and a viscosity similar to popular commercial resins is presented. These properties allow for their wide application without the need for adjustment of processing conditions.

2. MATERIALS AND METHODS

2.1. *Materials*

- maleic anhydride (Erg Pustków),
- 1,2-propylene glycol (Erg Pustków),
- isobutanol (Erg Pustków),
- styrene (POCh Gliwice),
- diethylene glycol dimethacrylate – DEGDMA (Department of Polymer Chemistry, M.C.S University)
- hydroxides monobutyltin – Fascat 4100 (Arkema Canada),

- tert-butylhydroquinone – TBHQ (Eastman Chemical B.V.)
- Luperox DHD-9 (Aldrich Chemistry)
- *N,N*-dimethyl-*p*-toluidine, 10% solution in styrene (Pergan GmbH)
- cobalt(II) octoate, solution in styrene containing 1% Co(II) (Pergan GmbH).

2.2. *Methods*

The viscosities of the resins were measured using a digital viscometer (Brookfield DV-III). Thermomechanical properties of the samples were obtained by dynamic mechanical analyser (TA Instruments Q800). Thermal resistance was evaluated using apparatus HDT 3 VICAT. Mechanical studies were carried out using a strength machine (Zwick Roell Z010), and hardness was determined by means of a hardness tester HPK – according to Brinell scale.

2.3. *Synthesis of unsaturated polyesters*

Maleic anhydride (686.4g) was put into a 2000 cm³ flask equipped with a stirrer, a dropping funnel, a reflux condenser, thermometer, and a nitrogen inlet capillary and heated in order to melt it. After that, the content was heated to a temperature of 95°C and then isobutanol (233.5 g) was added drop-wise. The mixture was then kept at 90–100°C for 2 h.

To the obtained acidic ester, 1,2-propylene glycol (479.4 g), Fascat 4100 (0.98 g), and tert-butylhydroquinone (0.098 g) were added and nitrogen was introduced by capillary. Next, polycondensation was continued at 220°C. The process was interrupted when the acid number of the polyester was less than 10 mg KOH/g.

2.4. *Preparation of unsaturated polyester resins*

The synthesized polyester was used for the preparation of unsaturated polyester resins. They are obtained by dissolving him in crosslinking monomers (DEGDMA, Styrene) at room temperature. Five solutions of resins were prepared. Composition of unsaturated polyester resins are shown in Table 1.

Table 1. The composition of unsaturated polyester resins.

Resin	Components (%)		
	Polyester	DEGDMA	Styrene
IZO – GP1	70	–	30
IZO – GP2	70	20	10
IZO – GP3	60	30	10
IZO – GP4	70	30	–
IZO – GP5	60	40	–

2.5. Curing procedure

The obtained composition were cured with a typical system (initiator/accelerator) consisting of 3 parts of Luperox DHD-9 mass, 0.9 part of cobalt(II) octoate mass containing 1% metal and 1.2 part of 10% solution of *N,N*-Dimethyl-*p*-toluidine mass. The castings were cured in two stages: first at room temperatures for 24 h, and then at 90°C for 10 h.

3. RESULTS AND DISCUSSION

3.1. The viscosity of the resins

For the studies 5 unsaturated polyester resins were used. They were obtained by dissolving polyester in crosslinking monomers. Thus, the impact on the viscosity of the resin was associated with the type and concentration of crosslinking monomer. Figure 1 shows the differences in the viscosity of unsaturated polyester resins obtained according to the proportions shown in Table 1. Among them, is a resin IZO – GP4, which contains only DEGDMA as crosslinking monomer and 70 % of polyester. This composition have the largest viscosities exceeding 1000 mPa·s. The lowest viscosity indicates the resin containing only styrene (IZO – GP1). Similar values are observed for the mixture containing 30 % DEGDMA and 10% of styrene as crosslinker and 60 % of polyester.

Taking into account that typical resins that are offered by industry are characterized by the viscosity in range 300–2000 mPa·s, all the obtained

resins can be useful. Convenient processing is guaranteed when DEGDMA with a small amount of styrene were used as crosslinking agent.

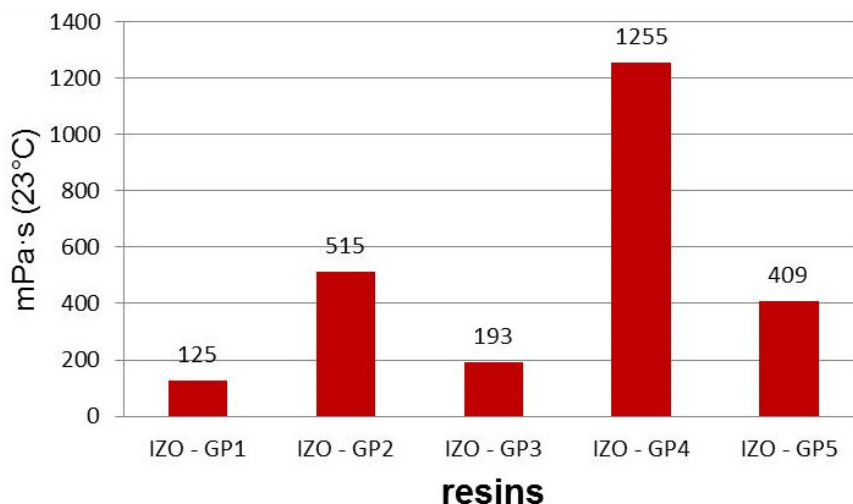


Fig. 1. The viscosity of the resins.

3.2 Viscoelastic properties of the resins

Tests of dynamic mechanical analysis (DMA) were conducted with a double cantilever device with a support span of 35 mm, calibrated according to the producer's recommendation. Resins were measured from 0 to 200°C with a constant heating 3°C/min. Dimensions of the samples were 35×10×4mm. Viscoelastic properties of the cured resins were evaluated from the changes of storage modulus (E') and tangent delta in the function of temperature. DMA curves are shown in Figures 2 and 3.

Post-cured resins were subjected to mechanical and thermal studies. The DMA results along with other thermal and strength properties are presented in Table 2.

At room temperature, resins are characterized by the largest values of storage modulus which decreases with the increasing temperature. Figure 2 presents change in the temperature function.

With the decrease of the amount of the DEGDMA in resin, the value of storage modulus is higher in the glassy state and the slower transition to the highly elastic state was proceeded at higher temperatures. From the tangent delta (Figure 3) it can be observed their glass transition temperatures. Also, the heterogeneity of resins was evaluated by

examining the full width at half maximum (FWHM) of tangent delta peak. The results indicate that FWHM values decreases with styrene content increases.

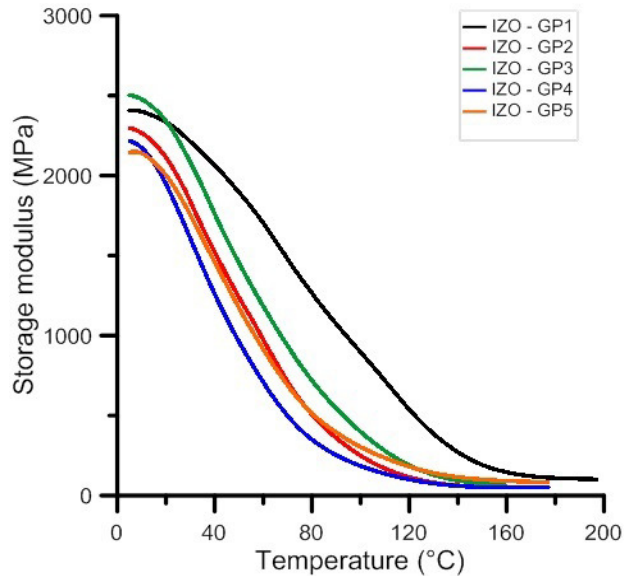


Fig. 2. Storage modulus versus temperature.

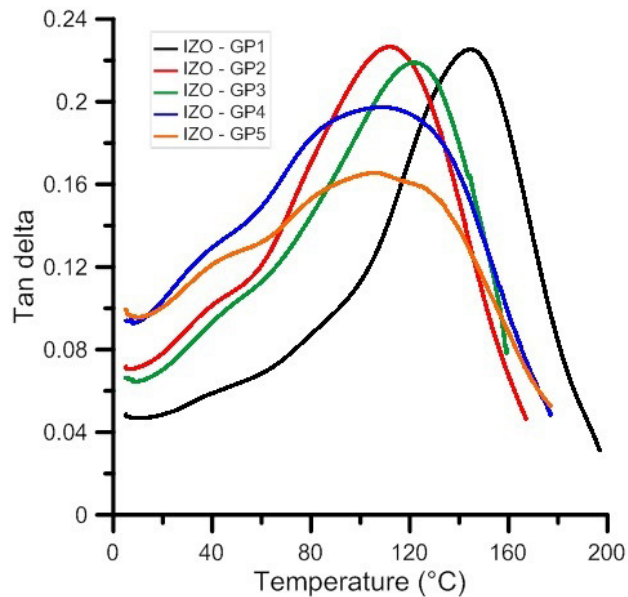


Fig. 3. Tangent delta versus temperature.

3.3 Flexural and thermal properties of cured resins

Resin with styrene (IZO – GP1) show greater resistance to temperature and exhibit better physicommechanical properties *i.e.* higher hardness and resistance to bending and larger flexural modulus. Properties of resins change with their composition. With the increase of DEGDMA and decrease of styrene content in the resin, flexural modulus, hardness, heat deflection temperatures as well as glass transition temperatures decrease. Strength and thermal properties of the resins are presented in Table 2.

Table 2. Thermomechanical properties of cured resin.

Properties	Resin				
	IZO – GP1	IZO – GP2	IZO – GP3	IZO – GP4	IZO – GP5
Storage modulus (MPa), (T=25°C)	2282	1992	2223	1785	1890
Glass transition temperature according to DMA (°C)	144	113	121.9	113.9	108.5
FWHM (°C)	62	72	66	96	95
Flexural modulus at bending (GPa)	2.54	1.44	1.84	0.93	1.33
Maximum force at bending (N)	127	99	113	74	85
Hardness, Brinell method (MPa)	108	95	92	67	82
Deflection temperature HDT (°C)	92	55	66	53	60

4. CONCLUSION

The presented studies show that the total replacement of styrene with diethylene glycol dimethacrylate significantly increases the viscosity of the composition. Use of DEGDMA with 10% addition of styrene provides

for obtaining a composition with optimum viscosity with simultaneously minimum concentration of styrene. Further, flexural, thermal and viscoelastic properties depended on styrene content. These studies confirmed that the resin with reduced content of styrene as crosslinker gives promising materials for practical application.

REFERENCES

- [1] W. Królikowski, Z. Kłosowska - Wołkowicz, P. Penczek, Żywiec i laminaty poliestrowe, WNT, Warszawa 1986.
- [2] J. Pielichowski, A. Puszyński, Technologia tworzyw sztucznych, WNT Warszawa 1998.
- [3] Offic. J. Europ. Commun: Directive 2004/42/CE.
- [4] Offic. J. Europ. Commun: Commission Decision L50/14/2000.
- [5] Patent No.: GB 713332.
- [6] Patent No.: GB 744468.
- [7] Patent No.: GB 774807.
- [8] Patent No.: US 4424299.
- [9] Patent No.: PL 197021.
- [10] Patent No.: US 3347806.
- [11] J. Księżopolski, T. Matynia, Przem. Chem. 2012, 91(7), 1396.
- [12] A. Chabros, B. Gawdzik, J. Osypiuk-Tomasik, Przem. Chem. 2016, 95(7), 1315.