

CLASS H ELECTROINSULATING VARNISHES BASED ON UNSATURATED POLYESTERS

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Lucrarea prezintă sinteza unei serii de poliesteri nesaturați obținuți pornind de la anhidrida maleică (MA) și un diol aromatic (BFPOX); produsul linear a fost amestecat cu diverși monomeri vinilici și lăsat să reacționeze la cald. S-au stabilit condițiile experimentale optime în vederea obținerii unui produs care să poată fi folosit ca lac electroizolator de tip H. S-au obținut mai multe compoziții care inițial prezintă vâscozitate redusă și timp scurt de gelificare și care conduc în final la straturi solide sticloase, stabile la 180-200°C.

The present paper reports on the synthesis of a series of unsaturated polyesters obtained from maleic anhydride (MA) and an aromatic diol (BFPOX); the linear product was mixed with various vinyl monomers and temperature-cured. Optimal experimental conditions have been established, in order to obtain a product that can be used as a class H electroinsulating varnish. Several formulations have been obtained, with a low viscosity in the initial state, short gelification time and that lead to glassy final layers after hardening, with negligible mass loss at 180-200°C.

Keywords: unsaturated POLYESTER, class H electroinsulating varnish, kinetics, thermal resistance

1. Introduction

Polymers and oligomers with internal ester functions and containing vinyl groups able to promote cross-linking via free radical polymerization or copolymerization are well known and interesting because of the wide variety of compositions and structures that may be used to obtain final products with properties varying between large limits. Practical applications of these products

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are known since 1920, when they were first obtained at industrial scale. Basically, unsaturated polyesters belong to one of the following main categories:

- a. polyesters with unsaturated side chains, obtained from natural aliphatic monocarboxylic acids with long chains;
- b. polyesters containing the unsaturation in the main chain, obtained from: (b1) unsaturated dicarboxylic acids or (b2) unsaturated dihydroxilic alcohols;
- c. terminal unsaturated polyesters, obtained from synthetic short chain unsaturated monocarboxylic acids.

Strictly speaking, the term unsaturated polyesters refers only to type (b1) products; more than 90% of the world production consists in esters of maleic and fumaric acids [1-8]. The history of unsaturated polyesters has started with the definition of the main structure and has continued with the synthesis and application principles for these compounds, as stated by the first patents recorded between 1933 and 1934 [4]. After 1940, industrial production of unsaturated polyesters has known an extensive development due to their applications especially for manufacturing glass fibers reinforced laminates. During the last 20 years the production capacities have grown up and the diversity of the chemical composition has widened. The main applications of the unsaturated polyesters are as binders for composites, as adhesives, putties and film-forming materials or for manufacturing profiles or other objects using conventional techniques for processing thermo-setting resins (casting, transfer moulding, centrifugation etc.).

The special capacity of the cross-linked products based on unsaturated polyesters to maintain their physico-mechanical properties at high temperature is due to two distinct mechanisms:

A. Increase of the intrinsic strength of the polyester chain by using a higher proportion of aromatic or cycloaliphatic divalent hydrocarbon fragments in the main chain. In order to preserve the unsaturated character requested for cross-linking, the ratio of fumaric/maleic units can not be reduced under a specific threshold; thus, the maleic anhydride is only exceptionally missing among the polycondensation monomers. However, the other dicarboxylic component should be completely substituted with isophthalic, terephthalic or other aromatic dicarboxylic acid (respectively anhydride).

B. Styrene's substitution with less volatile monomers such as vinyl toluene, α -methyl styrene and divinyl benzene and/or with other monomers more appropriate to form denser and stiffer three-dimensional networks (diallylphtalate, triallylcyanurate etc.).

The present paper presents the synthesis and the characterization of cross-linked unsaturated polyester-based products with improved thermal resistance, suitable for use as thermoinsulating varnishes.

2. Experimental part

2.1. Materials

MA - maleic anhydride, purified by recrystallisation from chloroform, dried under vacuum and stored under anhydrous conditions and POXBFA - propoxilated bisphenol A - 2,2-bis[4(2-hydroxypropoxi)phenyl] (Aldrich) have been used as monomers for the synthesis of the linear unsaturated polyester. S - styrene, purified by rectification under vacuum (70°C/60 torr), NVC - N-vinyl-carbazole, recrystallized from methanol and dried under vacuum, TAC - tri-allyl-cyanurate - 2,4,6 tris(allyloxi)1,3,5-triazine (Merk) and DAF - di-allylphthalate (Fluka) have been used as vinyl monomers for the cross-linking. Radical copolymerisation was initiated with t-butyl-perbenzoate (Chimopar) (TBP). Other materials used were T - toluene (purified by rectification, 110°C/760 torr) as diluent and agent for the azeotropic polycondensation, D- dioxane (Merk) as solvent for the polyester, alcoholic KOH solution 0.1 n as reactive for measuring the acidity index.

2.2. Apparatus and reaction conditions

a. Polyester synthesis

Polyesters were synthesised in a thermostated reactor (heated in a silicone oil bath) provided with variable speed stirrer, system for maintaining the reaction mass under nitrogen atmosphere, reflux condenser with water separation elbow (ASTM), fitting for sample collection and coupling to a vacuum pump. The reactor was insulated from the environment by a system of silicone oil traps.

The succession of operations involved in the polyester synthesis was the following:

1. Pre-heating the reactor (50-100°C).
2. Feeding the reagents under nitrogen atmosphere.
3. Sealing the reactor and maintaining the temperature at 100-150°C for a first synthesis stage, in molten state.
4. Feeding toluene in the reactor (2-5% with regard to the reaction mass) and gradually raising the temperature to 220°C.
5. Azeotropic polycondensation at 220°C, at atmospheric pressure and under nitrogen atmosphere.
6. Distillation of the toluene until the complete elimination from the molten polymer.
7. Applying vacuum, simultaneously with cooling the reactor (100-150°C) to eliminate last traces of low-molecular compounds from the molten polyester.
8. Pouring the reactor content in a metallic tank, where the polyester is left to cool until becoming a glassy amorphous mass.

b. Preparing the polyester-vinyl monomer homogeneous mixture

Weighted amounts of polyester were preheated at 80-90°C to become fluid and measured volumes of vinyl monomers (previously inhibited with hydroquinone, 100 ppm) were added gradually, under intermittent stirring, to give a homogeneous mass. Since NVC and TAC are solids at room temperature, they were used only in combination with S in order to obtain liquid polyester solutions with a low enough viscosity to be acceptable for the use as a varnish.

c. Curing process

Copolymerisation of the vinyl monomers with the unsaturated polyester was performed in presence of TBP (1-2%) as an initiator for free-radical polymerisation at 110-140°C in a reaction vial provided with interior thermometer and heated in a silicone thermostated bath. During the curing, internal temperature of the sample was measured together with the temperature of a reference (a polyester-vinyl monomer sample with no initiator added); comparison between the two temperatures gave the cross-linking exothermicity curve. Curing was considered completed when the sample's temperature exceeded with 10°C the temperature of the reference.

d. Products characterisation

d1. The acidity index of the unsaturated polyester was measured by titration with alcoholic KOH solution 0.1 n, using phenolphthalein as pH-indicator.

d2. Viscosity of polyester solutions was measured according to ISO 2431 standard by measuring the time needed for the flow of 50 g polyester through the calibrated orifice of the Φ4'' cups.

d3. The gel time was measured for curing at 110°C; aspect and consistency of the resin were appreciated both after gelification and after completing the reaction in a heated oven, at 140°C.

d4. Thermal resistance of the cured polyester was measured by thermogravimetric analysis (TGA).

3. Results and discussion**3.1. Preliminary tests**

Preliminary tests have been performed to check the reactivity of the monomers in the polycondensation reaction and the characteristics of the polyester – vinyl monomer mixture (viscosity, curing time). Polycondensations using POXBFA/MA molar ratios between 1.1 and 1.2 have lead to polyesters with an average polycondensation degree of $X_n=10$ (as compared to the theoretical value of $X_n=11$) that mixed with vinyl monomers gave solutions with a too high viscosity to be suitable for use as a film-forming material. Gel times ranged between 15 and 35 minutes, depending on the nature of the vinyl monomer,

values considered too high from the point of view of the final intended application (obtaining an electroinsulating varnish with a curing time at 110°C of about 10 min).

Preliminary tests have also shown that using DAF or TAC as unique vinyl monomers led to mixtures that hardened only partially, while using an S excess gave the mixture a sufficient fluidity to allow application on support's surfaces.

In order to reduce the viscosity, two measures have been applied in subsequent experiments: synthesising the polyester in presence of a higher hydroxyl group excess (in order to diminish the polycondensation degree) and using an S excess both to give supplementary fluidity to the polyester-vinyl monomer mixture and improve the properties of the cured resin.

3.2. Synthesis and characterisation of the unsaturated polyester

All synthesis were performed using a wt. ratio POXBFA/MA = 1.5, varying the duration of the various stages of the synthesis, as presented in Table 1. Phases 1 and 2 correspond to the semiesterification stage; stage 3 is the azeotropic polycondensation of the semiester, indicated by the water elimination (in presence of toluene as agent for azeotropic distillation).

Table 1

**Reaction conditions for the synthesis of the unsaturated polyester
for a wt. ratio POXBFA/MA =1.5.**

Code	Phase 1		Phase 2		Phase 3		Phase 4	
	τ	T	τ	T	τ	T	p	T _c
A	2	125	2	140	5	205	150	150
B	2	125	4	170	6	205	150	150

(τ - stage duration, hours, T – reaction temperature, °C, p – depression in the vacuum stage, torr, T_c – cooling temperature, °C)

Samples from the reaction mass were extracted during the synthesis and the acidity index of the reaction mass was measures. The data thus obtained was used to compute the reaction extent and the polymerisation degree as functions of time, for the two stages of the polycondensation process (semiesterification and polyesterification), according to the following relations:

$$\bar{p}' = 2 \left(1 - \frac{n_{COOH}}{n'_{COOH}} \right) / (1 + r) \quad (1)$$

$$\bar{X}'_{n,abs} = 1 / (1 - p') \quad (2)$$

$$\bar{p} = \frac{1}{1 + R} \left(1 - \frac{n_{COOH}}{n_{COOH,0}} \right) \quad (3)$$

$$\bar{X}_{n,rel} = 1 / (1 - p) \quad (4)$$

where r is the initial BFPOX/MA ratio, $R = r - 1$ is the molar ratio between the functional groups in the polycondensation stage, p and p' are the reaction extents, X_n and X'_n are the polymerisation degrees, n_{COOH} is the concentration of the carboxyl groups and $n_{\text{COOH},0}$ is the initial concentration of the carboxyl groups. (X'_n, p') denote the semiesterification stage and (X_n, p) the polycondensation.

Theoretical values obtained for BFPOX/MA = 1.5 are $X'_{n,\text{abs}} = 3$ and $X_{n,\text{rel}} = 5$. Figs. 1-4 give the time dependency of the reaction extents and polycondensation degree for the two syntheses (code A and B in table 1).

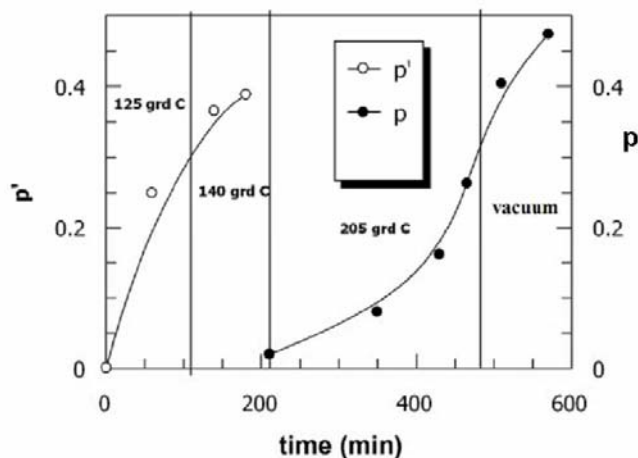


Fig 1. Time dependency of the reaction extents for the code A synthesis of the unsaturated polyester

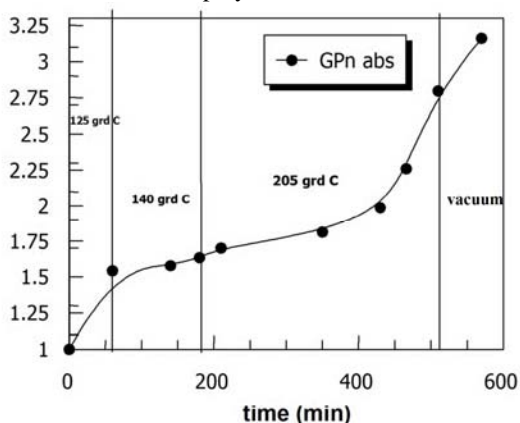


Fig 2. Time dependency of the polymerisation degree for the code A synthesis of the unsaturated polyester

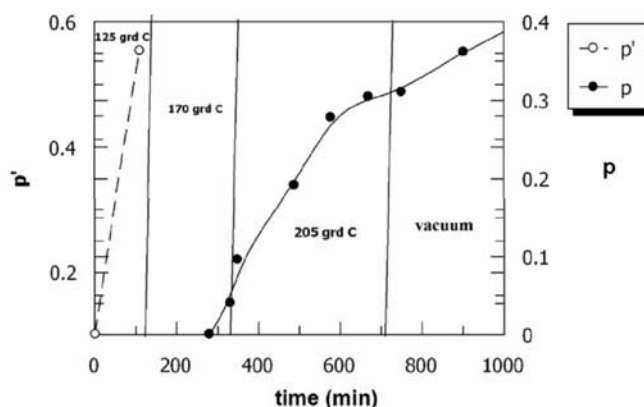


Fig 3. Time dependency of the reaction extents for the code B synthesis of the unsaturated polyester

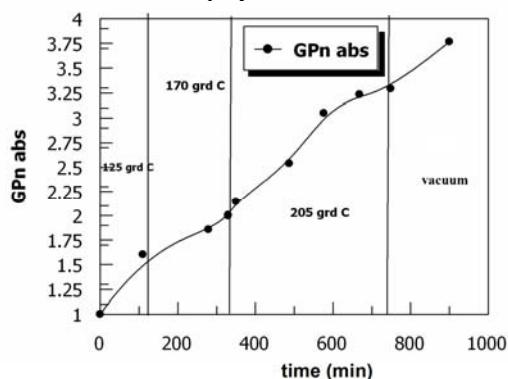


Fig. 4. Time dependency of the polymerisation degree for the code B synthesis of the unsaturated polyester

Experimental data have shown that synthesis of the unsaturated polyester starting from MA and an aromatic di-hydroxyl compound (BFPOX) are significantly slower as compared to the usual rates obtained by using aliphatic diols, which justify increasing the duration and/or temperature of each stage of the synthesis process. The products obtained, even at modest polymerisation degree, were glassy at room temperature that could be stored indefinitely before mixing with vinyl monomers.

3.3. Curing of the polyester-vinyl monomers mixtures

Various formulations, different by the vinyl monomer /polyester mass ratio type of vinyl monomer/monomers used and initiator concentration have been prepared. All solutions have been homogeneous, with no particles in suspension. For each formulation, several tests have been performed.

a. Study of the heat evolved during curing. An example of the cross-linking exothermicity graph is presented in Fig. 5. Results for various formulations are given in table 2.

Table 2

Gelification times as resulted from the cross-linking eothermals (UP – unsaturated polyester)

Code	Composition (mass ratios)	Initiator Concentration (mass %)	τ_{gel} (min.)	τ_{ret} (min.)	T_{max} ($^{\circ}C$)	Remarks
1C	UP:S:DAF 50:40:10	1,5%	9	11	137	non-sticky surface
2C	UP:S:TAC 50:30:20	1,5%	7	9	120	Incomplete hardening
3C	UP:S:TAC 50:40:10	1,5%	10	5	139	Very hard surface, almost glassy
		3%	5	4,5	150	
4C	UP:S:NVC 50:40:10	1,5%	13	10	135	Sticking surface
		2%	8	4,2	141	
5C	UP:S 50:50	1%	9	4	154	Glassy aspect, non-sticking surface
		1,5%	5	3,5	166	
		2%	4	2,5	190	

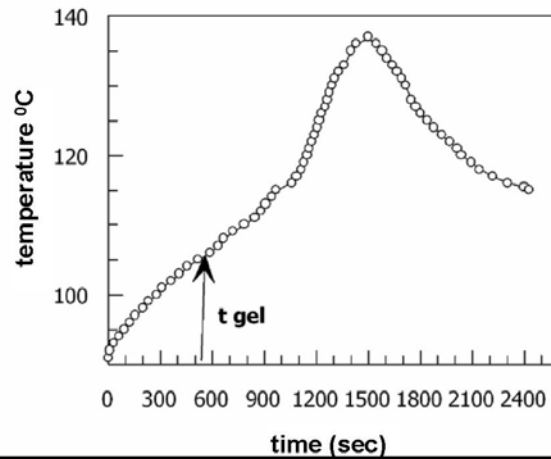


Fig 5. Cross-linking exothermal line for sample 1C.

The data show a strong dependency between the gelification time and the maximum temperature on the cross-linking exothermal line. A short gelification time is associated with a strongly exothermal reaction, with a step increase of the temperature inside the reaction mass. Formulations that did not harden until reaching a glassy consistency have been submitted to a supplementary post-curing stage, in ovens heated at 130-140°C for 20 minutes, but in most cases in which the setting was not completed as a result of its own evolved reaction heat, supplementary thermal treatment did not improve the quality of the hardened product.

b. Standard testing of the fluidity in the non-cured state and of the gelification time.

Table 3 gives the flow time from the ISO 2431 $\Phi 4''$ cup for the uncured mixtures, standard gelification times and the aspect of the hardened product after post-curing. Results show that the products analysed have a viscosity suitable for their purpose; however, increasing either the polymerisation degree of the unsaturated polyester or its concentration in the mixture should lead to a rapid decrease of the fluidity of the uncured product. At least part of the formulations is acceptable from all the point of view of the exploitation conditions (high fluidity in the non-cured stage, short setting time and toughness of the final, hardened layer).

Table 3.

Results of the standard tests for various formulations of unsaturated polyester/vinyl monomers mixtures. (UP – unsaturated polyester)

Code	Formulation	τ_{flow} (s), $\Phi 5''$ cup	τ_{gel} (min) for curing at T = 110°C	Aspect after 20 min conditionning at T=140°C
1C	UP:S:DAF 50:40:10	20	6-7	Glassy
2C	UP:S:TAC 50:30:20	32	6-7	Rubbery
3C	UP:S:TAC 50:40:10	22	6-7	Glassy (after 18 min)
4C	UP:S:NVC 50:40:10	Insufficient amount to perform the test	6-7	Rubbery
5C	UP:S 50:50	20	6	Intermediate
6C	UP:S:TAC 50:45.5	21	7	Glassy (after 15 min)

3.4. Characterisation of the thermal resistance.

Samples 1C, 2C, 3C and 4C have been submitted to thermogravimetric analysis. For all formulations, the mass loss is negligible at temperatures up to 200°C. The order of the thermal resistance is 2C > 1C > 3C > 4C. According to these results, all formulations above should be class H thermoresistant products (negligible losses at 180°C) since the mass loss at 180°C was in all cases under 2%. Specimens show mass losses at 300, 350 and 400°C, that probably correspond to the breaking of the ester bonds (at lower temperature) and then of the carbon-carbon bonds.

4. Conclusions

A series of unsaturated polyesters obtained from MA and an aromatic diol (BFPOX) has been obtained; the linear product was mixed with various vinyl monomers and cured at 110°C. Experimental conditions for all the stages have been established, in order to obtain a product that can be used as a class H electroinsulating varnish. At least 4 different formulations have been obtained that have low viscosity in the initial state, short gelification time and give glassy hardened final layers, with negligible mass losses at 180-200°C.

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