HYDROPHILIZATION OF UNSATURATED POLYESTER RESIN WITH SULFUR, SODIUM HYDROXIDE AND WATER WITH A POSSIBILITY FOR ITS CURING IN THE PRESENCE OF WATER AS A SOLVENT

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Abstract

This work is a continuation of previous research in formation of hydrophilized unsaturated polyester resin (HUPR). In that specific work, HUPR was produced by using sulfur (0.08 – 0.32 %), in the form of powder or dissolved in ethyl alcohol; combination of sodium hydroxide and sulfur; with or without solvent water. Kinetic dependencies of cross-linking with the content of the hydrophilizer sulfur were studied. IR spectroscopy analysis were conducted. The so-obtained cross-linking multicomponent system is a base for new materials with various applications.

Key words: *unsaturated polyester resin, hydrophilization*

1. INTRODUCTION

Unsaturated polyester resins (UPR) are relatively cheap raw materials for the production of products of strong composites. Among them, the polymer concrete[1,2] draws attention, as it is a potentially useful material in construction due to its strength, water and chemical resistance. Currently, its application is limited by several disadvantages: lack of adhesion to silicate concretes and other mineral materials, and styrene emissions during product manufacturing, which cause environmental pollution.

One solution of these problems is the use of hydrophilized unsaturated polyester resin.[3] It forms composites that provide excellent adhesion to silicate concretes and other hydrophilic mineral materials.[4] In the process of curing, the resin and styrene are 'capsulated' in the nanoparticles of water emulsion. Thereby, at the first stages of curing, the emission of styrene fumes is suppressed and subsequently, when the greatest part of the monomer is exhausted in terms of polymerization, an inversion of phases and formation of a composite product occurs.

Different sources in literature describe the possibilities for modification. The improvement in thermal and mechanical properties of nanocomposites prepared with unsaturated polyester as polymer matrix and various loadings of amino-modified nano kaolinite clay as filler has been studied.[5] Influences of the vinyl modified nanosilica Aerosil® 380, i.e., vinyl and methacryloyl silane coupling agent and linseed oil fatty acids reactive residues, on the mechanical properties of the unsaturated polyester resins based nanocomposites, was studied.[6] Composites of untreated and 6% sodium hydroxide treated kenaf fiber mat and unsaturated polyester resin matrix were manufactured via a resin transfer molding (RTM) technique.[7] The transformation of solvent soluble UPR into resins able to form stable water dispersion is presented.[8] To make the hard fiber reinforced polyester composites more competitive with commercial products, a chain extender was developed. The extender has been tested with the composition of the general purpose unsaturated polyester resin filled with low cost conventional fillers and hard fibers such as jute (in form of jute cloth).[9]

There are no sources to report the use of hydrophilizers on already synthesized UPR. Therefore, it is necessary to develop the hydrophilization process, as various resin alkalizing reagents are discovered in the process of work with not only theoretical but also practical application. This work demonstrates possibilities for hydrophilization of UPER with elementary sulfur in a combination with NaOH and water.

2. MATERIALS AND METHODS

2.1. Materials

Resin of type Vinalkyd 550 PE-R (Orgachim – Ruse) was used, containing 35% styrene and 65% unsaturated polyesters, which is a condensation product of propylene glycol and maleic anhydride. 50% solution of cyclohexanone perodxide (CHP) in dibutylphthalate was used as a curing initiator, and 10% solution of cobalt naphthenate (CN) in styrene was used as an accelerator.

2.2. Methods

A methodology for obtaining HUPER based on sulfur in different amounts was developed. The formulation sequence of adding the respective components to the resultant compound is as follows: resin (UPER), sulfur, accelerator (CN) and initiator (CHP). Also, a methodology for obtaining HUPER in the presence of sulfur and water that is added immediately after sulfur was developed. A methodology was developed according to which sodium hydroxide is added in the presence of sulfur with strict observance of a specified sequence of the formulation composition: resin (UPER), sodium hydroxide, sulfur, accelerator (CN) and initiator (CHP). Also, a methodology for obtaining HUPER in the presence of sulfur, sodium hydroxide and water in the following sequence was developed: resin (UPER), sodium hydroxide, sulfur, water, accelerator (CN) and initiator (CHP). In the given sequence of adding each of the components, it is stirred very intensively before adding the next component.

FT-IR spectroscopy. The spectra were registered on FT-IR Tensor 27 spectrophotometer in the 3996 - 399 cm^{-1} range and resolution 2. The spectra were registered in the form of tablet with KBr.

3. RESULTS AND DISCUSSION

A new HUPER was developed, in which the previously used nitrogen-containing hydrophilizers were substituted by sulfur in the form of powder or dispersed in ethyl alcohol. It was a possibility to enrich the concept of hydrophilization with entirely new reagents, as the main essence of that idea again is the solvent water. It is important to be successful (the largest possible amount) when including it in the multicomponent system without hindering the cross-linking process. It is supposed that it would change the microstructure of materials. The sole fact of reaching to that new type of modification passed through different stages of technological realization but we reached the conclusion that the minimum content of sulfur is of key importance. Therefore, we left the idea of how to use the sulfur, in the form of powder or in a mixture with ethyl alcohol, for further development, and focused on determining the concentration limits of sulfur in relation to the other part of the polymer system. The results obtained showed that, at 0.16 ± 0.08%, it could participate as a presumable chemical modifier and thereby to represent a favorable environment for subsequent dilution with water. Above that limit, sulfur could play an entirely new role that is interesting due to its prospective different properties mostly related to the possibility of being an inactivator (inhibitor) in the curing process. Therefore, it is possible to develop materials in the future, whose gelation time is required to be very long.

Table 1 shows some of the formulation compositions for obtaining HUPER based on sulfur in different amounts.

Table 1. Influence of the amount of sulfur additive on polymerization activity of hydrophilized resin. Amounts: UPER – 30 g; CHP – 1.2 ml; CN– 0.6 ml.

Sample No.	Amount of sulfur, g	Time [τ , min]	Temperature [Tmax, ˚C]
1	0,025	15	137
2	0,05	36	95,5
3	0,1	10	39,5

Included in table 1 are data on the time to reach the maximum temperature (Tmax) for sample curing. Since that process is exothermal, it follows that the respective kinetic dependencies could be determined by the amount of heat released till gelation. Such kinetic dependencies are shown in Fig. 1 by temperature changes with time.

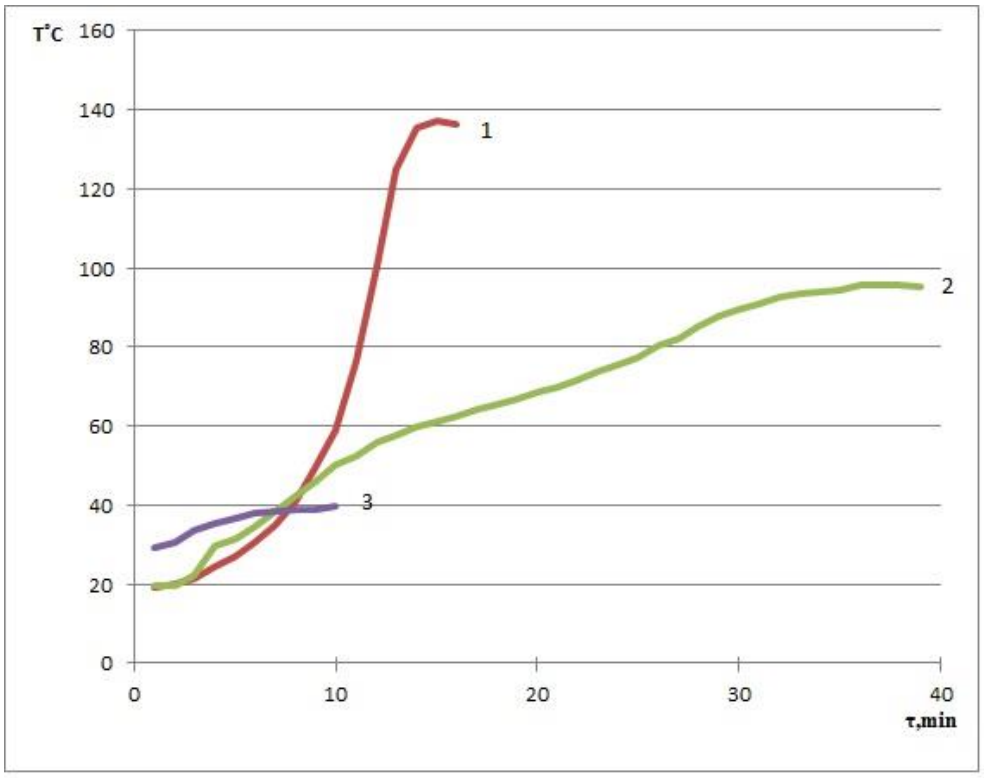


Fig. 1. Kinetics of polymerization process, where: curve 1 – 0.025 g S; curve 2 – 0.05 g S; curve 3 – 0.1 g S.

As table 1 and figure 1 show, hydrophilization of UPER requires minimum amount of sulfur. Its increase delays the polymerization process and even inhibits it to a significant degree.

An important stage of experimental work is the monitoring of the influence of the amount of water on the process of sample curing. For that purpose, different compositions have been produced at the same amount of resin and sulfur with gradual increase of amount of water. The results are presented in table 2.

Table 2. Influence of the amount of water on polymerization activity of hydrophilized resin. Amounts: UPER – 30 g; CN– 0.6 ml; sulfur – 0.05 g

Sample No.	Amount of water, g	Time [τ , min]	Temperature [Tmax, ˚C]
1	-	29	71.5
2	0.25	21	94.5
3	0.5	52	91
4	0.75	154	95.5
5	1	293	65.5

Fig. 2 shows the kinetics of polymerization process depending on the addition of different amounts of water.

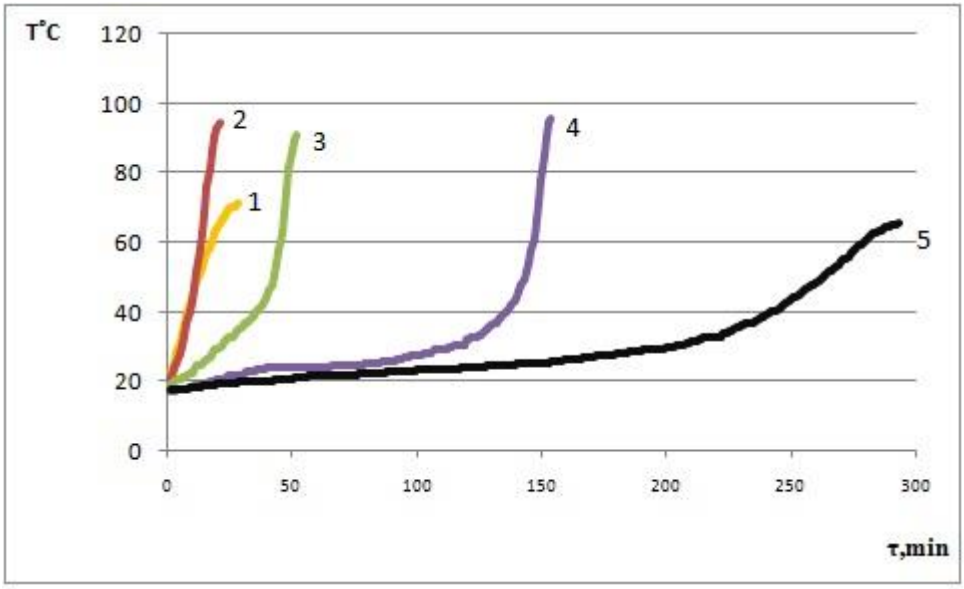


Fig. 2. Kinetics of polymerization process, where: curve 1 – addition of 0.05 g S; curve 2 – 0.25 ml water; curve 3 – 0.5 ml water; curve 4 – 0.75 ml water; curve 5 – 1 ml water.

As evident, if water is 95% vs. sulfur, i.e. 3% of the entire system, this will result in 40-fold increase of the curing time.

Table 3. Influence of sodium hydroxide on the activity of polymerization process of hydrophilized UPER in the presence of optimal amount of sulfur. Amounts: UPER – 30 g; CHP – 1.2 ml; CN – 0.6 ml; Sulfur – 0.05 g

Sample No.	Amount of 33% NaOH, ml	Time [τ , min]	Temperature [Tmax, ˚C]
1	0.1	14	113
2	0.2	17	105,5
3	0.4	31	89,5
4	0.6	32	94,5
5	0.8	38	91,5
6	1	48	82,5
7	1.2	44	82,5

Figure 3 shows the kinetic dependencies of curing time (gelation) up to the maximum temperature of the specified compositions. They show that, given the sodium hydroxide to sulfur ratio is in the range from 0.9 to 10.7, the time decreases inversely to the increase of 33% water solution of sodium hydroxide vs. constant (optimal) amount of sulfur (0.05 g).

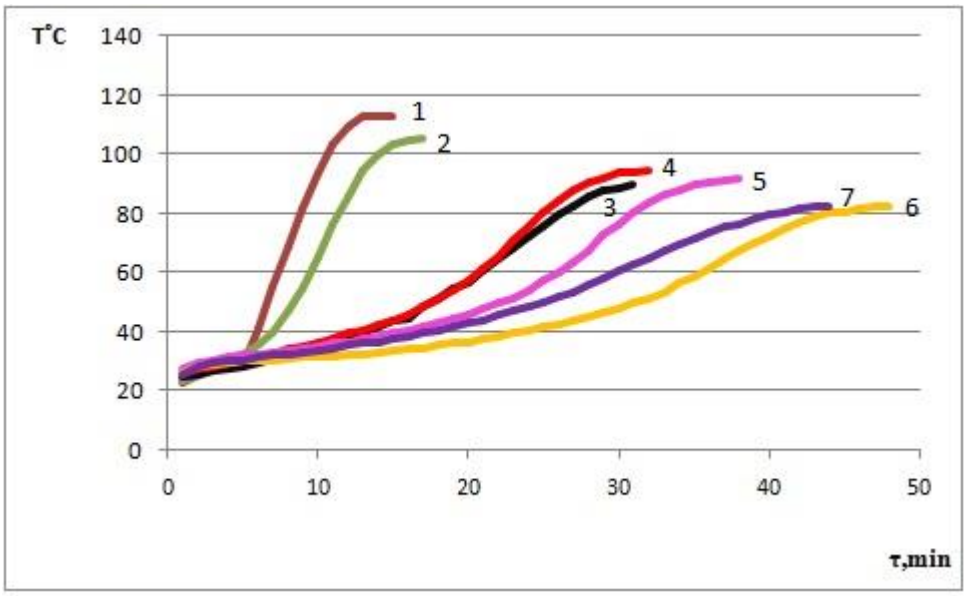


Fig. 3. Kinetics of polymerization process, where at 0.05 g sulfur curve 1 – 0.1 ml NaOH; curve 2 - 0.2 ml NaOH; curve 3 – 0.4 ml NaOH; curve 4 – 0.6 ml NaOH; curve 5 – 0.8 ml NaOH; curve 6 - 1 ml NaOH; curve 7 – 1.2 ml NaOH.

IR spectrum (fig.4) of one of the compositions specified in table 3 (sample 4).

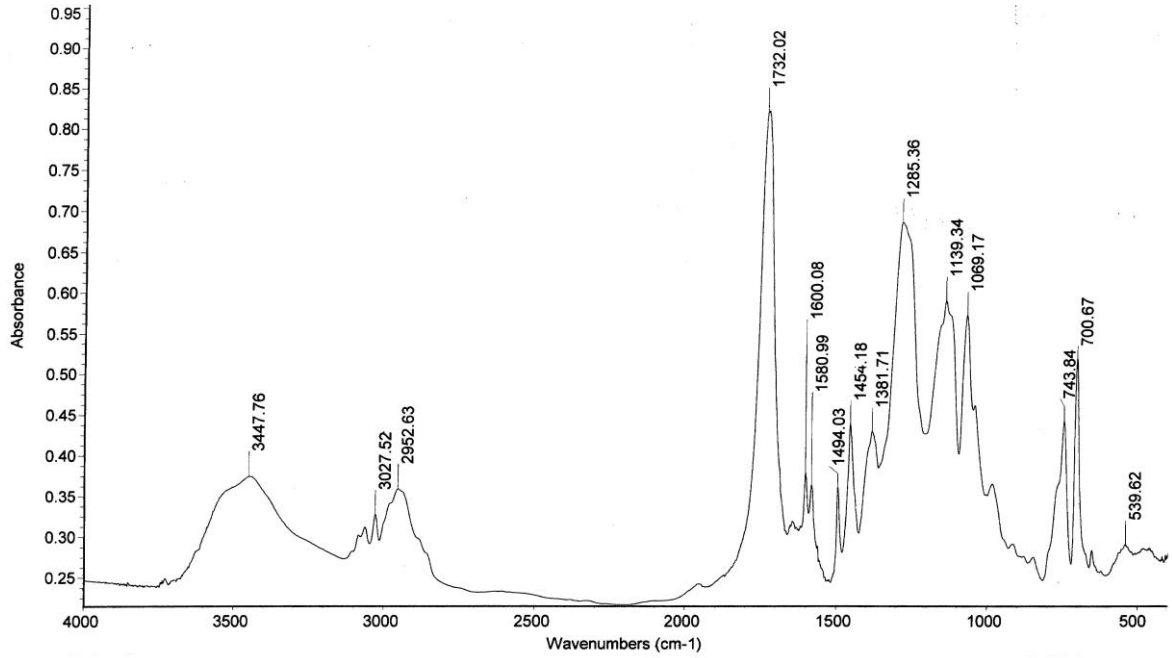


Fig. 4. IR spectrum of HUPER with 0.05 g sulfur and 0.6 ml 33% NaOH.

The association increases in the 3600 – 3000 cm^{-1} range as a result of the occurrence of intermolecular OH-bonds. The intensity also grows in the 1660-1520 cm^{-1} range. This could be explained with the ongoing process of interaction between the C=O group and NaOH. The addition of sulfur results mainly results in removal of the association caused by NaOH.

The sulfur and NaOH interaction form a range of compounds of sodium with sulfur derivatives, from S^{-2} to S^{+6}. Thereby, part of the hydrophilizing agent NaOH is eliminated reducing to a certain extent the interaction between the C=O group and NaOH.

It was found that the effect of inverse proportionality between curing time and amount of sodium hydroxide (at constant amounts of resin and sulfur) was only on only one side of the kinetic dependencies of interest. It is also essential to monitor the influence of water in relation to the sodium hydroxide/sulfur combination. This way, any possible changes in the initial effect could be reported. The results are presented in table 4.

Table 4. Influence of the amount of water on polymerization activity of hydrophilized resin. Amounts: UPER – 30 g; CHP – 1.2 ml; CN– 0.6 ml; 0.6 ml 33% NaOH; sulfur – 0.05 g

	Amount of water, g	Time [τ , min]	Temperature [Tmax, ˚C]
1	1	35	78,5
2	2	41	79
3	3	41	79
4	4	45	77
5	5	42	69

Of interest is the fact that water in amounts between 1 to 5 g, at constant sodium hydroxide/combination of 0.6 ml /0.05 g, do not inhibit the speed of polymerization process (Table 4). Those data should be followed in detail and be presented in a next work in the future.

Fig. 5 shows the IR spectrum for one of the compositions specified in table 4 (sample 5).

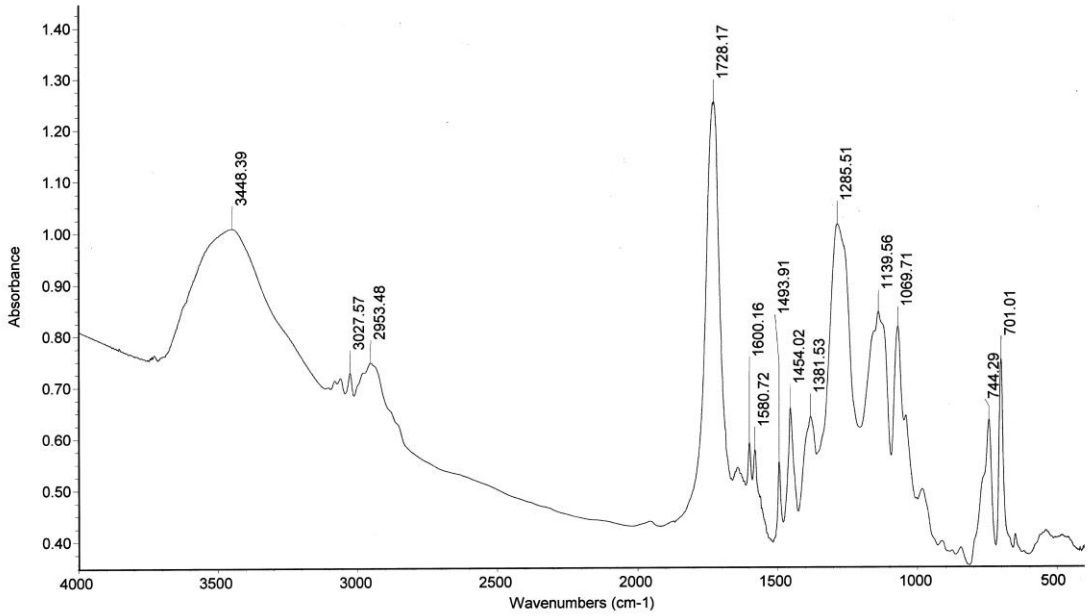


Fig. 5. IR spectrum of HUPER with 0.05 g sulfur, 0.6 ml 33% NaOH and 5 ml water.

In order to get a more complete picture of water influence, we made an IR spectrum of a composition including a larger amount of water (5 ml). We observed an increase in the background in the 3600-2000 cm^{-1} $\nu(OH)_{assoc.}$ range as compared to the respective composition without water, which is a result of intermolecular OH-bonds and tablet opacity. Absorption is also observed at 1637 cm^{-1} for deformation vibration of OH-groups.

Table 1 shows that the addition of water to the multicomponent combination decreases the polymerization dynamics, which at 0.6 g NaOH passes through the maximum.

Studies, the results of which are demonstrated in this publication confirm the previously established possibilities of hydrophilization of UPER with NaOH, sulfur or a combination of them. All hydrophilized resin compounds preserve their polymerization ability, which is influenced by the composition of hydrophilizing additives and their quantitative relationship.

It is supposed that the phase state of resin compositions influences the processes ongoing in them.

Based on experimental data, we can develop a hypothesis of the mechanism of processes of hydrophilization and polymerization and their mutual influence. In general terms, it is expressed in the formation of a two-phase system consisting of a hydrophobic (organic) and hydrophilic inorganic phases. At first, the hydrophilic phase emulsifies in the organic phase. The cobalt soap, which is a promoter of the polymerization process, is an emulsion stabilizer. Reactions of hydrophilization, and subsequently of polymerization initiation, pass on the interphase surface. Hydrophilization is due to the interaction of sulfur, NaOH and the mixture of sulfur and base on polyester surfaces. NaOH forms salts with the end carboxyl groups of UPER. In the excess of base, it also attacks part of the ester in polyester chains by fragmenting them. As a result, in the presence of moisture, macromolecular ionic soaps are formed. They cause phase inversion, as the hydrophilic phase turns into a medium and the hydrophobic phase becomes a disperse one.

Initiation of polymerization passes on interphase surfaces where the cobalt soap reacts with peroxide dissolved in the organic phase decomposing it into radicals. They initiate the polymerization.

Most of the experimental work shows that the binding of the sulfur component in the three-dimensional network of the resin is most effective as a hydrophilizer at a quantity of 0.08%. At a quantity of 0.16 to 0.32%, the sulfur plays the role of a component inhibiting the kinetics. Of interest is the fact that water in amounts between 1 to 5 g, at constant sodium hydroxide/combination of 0.6 ml /0.05 g, do not inhibit the speed of polymerization process (Table 4). Those data should be followed in detail and be presented in a next work in the future.

CONCLUSION

Studies were performed to obtain polymerizing compositions of hydrophilized unsaturated polyester resins. Sulfur and NaOH were used as hydrophilizing agents.

The base reacts with carboxyl groups of polyester macromolecules, which form long-chain ionic soaps. If NaOH and sulfur are in excess, they attack the ester bonds in macromolecules by fragmenting them and increasing the quantity of carboxyl groups.

An IRS analysis found that the increase in the quantity of hydrogen bonds is an indication of proportional increase in the content of carboxyl groups.

Concentrations of hydrophilizing agents and their proportions influence the dynamics of polymerization processes. If used moderately they accelerate the polymerization processes.

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