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DEVELOPMENT OF HYDROPHILIZED UNSATURATED POLYESTER RESINS BASED ON DIFFERENT TYPES OF MODIFIERS

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ABSTRACT

This work presents the modification of unsaturated polyester resin (UPER) with different types of hydrophilizing components – sodium hydroxide, sulfur and sulfate-resistant cement. A different type of hydrophilized unsaturated polyester resin (HUPER) was obtained based on this processing. The varieties of HUPER so obtained were compared on the basis of their hardening kinetics. When sodium hydroxide is used as a hydrophilizing agent minimum amounts of sodium hydroxide make it possible to choose a minimum gelation time. Unlike the sodium hydroxide, the hydrophilizing agent sulfur demonstrates that the increase in its amount results in lower gelation temperatures and increases the gelation time. A special feature of the third hydrophilizing agent sulfate-resistant cement was identified, whose amount does not affect the gelation time, i.e. it is maintained within certain limits (27-29 min). A comparison of strength values was made. With the hydrophilizing agent sodium hydroxide the test pieces retain their strength values in a broader range (2.99-4% tensile elongation, 14.98-18.62 MPa tensile strength, 1056.81-581 MPa Young's modulus). Where the hydrophilizing agent is sulfur these values are the lowest, and the sulfate-resistant cement increases to the greatest extent the tensile strength values (24.19 MPa) and percent tensile elongation values (8.23%), and to the lesser extent – the Young's modulus values (389.25 MPa).

1. INTRODUCTION

Hydrophilization of UPER resulting in multicomponent polymer systems has been the subject of our work over the last decade [1-4]. On the one hand, the related literature review is extremely abundant, as UPER-based materials have more than half a century of history involving the participation of different countries (USA [5], Japan [6], Germany [7], Poland [8], India [9]). On the other hand, however, there are too scarce data for hydrophilization of UPER resulting in a qualitatively new property – solubility in polar solvents as opposed to the basic, which is hydrophobic. Most of the literature for the last decades includes the results of filling the resin with natural and artificial fibers[10-14]. These works consider the extremely important technical aspect – strength properties of materials that are based on resins reinforced with the relevant fillers. The technical parameters of materials based on UPER remain essential for developing its hydrophilization. However, the primary objective of all these works that is also pursued by the writing team when developing the hydrophilization is to achieve resin curing with a conventional redox system even in the presence of diluent water. That's why resin technical parameters relating to the strength properties of the materials on which it is based are not extensively represented at the first glance.

This work includes a set of three hydrophilizing agents used in recent years. The role they play in the hydrophilization of resin is to change the chemical nature thereof – to turn it from hydrophobic into hydrophilic. This was achieved by giving ionic character to UPER, as a result of which it might be diluted with water without affecting its curing. Each selected hydrophilizing agent is a chemical modifier because it converts it from a molecular to ionic form. A comparative analysis of individual hydrophilizing agents was made in view of the use thereof in construction, architecture and other industrial sectors. Accordingly, it is of interest to further develop hydrophilization with specified modifiers also in the presence of water, which will be the subject of our future studies.

2. MATERIALS AND METHODS

The following were used:

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

Sodium hydroxide (reagent grade ≥ 98%, pellets, anhydrous) – Sigma – Aldrich.

Sulfur powder (S), A.R. (purum p.a. ≥99%) – Sigma – Aldrich.

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Sulfate-resistant blast furnace cement CEM III A-S 42.5 N SR (SC) – Devnya Cement, town of Devnya.

Sodium silicate solution (Water glass - WG) – BEKO Water Glass and Detergents Factory, town of Troyan.

Methods for obtaining compositions on the basis of unsaturated polyester resin hydrophilized with different amounts of sodium hydroxide, sulfur and cement have been developed, in which the percentage of water is always 50% with constant CN/CHP ratio in relation to resin. All specified types of HUPER were obtained at room temperature by continuous and intensive stirring with successive addition of each component in the chronological sequence given in Table 1-3. The mass of all components included in the modification of UPER was summed up and reduced to 100%. The tables below present the percentage composition (vertically) and the formulation sequence (horizontally) for preparing HUPER, with non-modified UPER used as a comparison.

Table 1 *Percentage composition and formulation sequence for the preparation of NaOH-based HUPER*

Composition,№ / Formulation sequence	UPER, [%]	NaOH, [%]	CN, [%]	CHP, [%]
	1	2	3	4
1	95.23	-	1.41	3.36
2	94.93	0.30	1.41	3.36
3	94.67	0.80	1.29	3.24
4	94.27	1.40	1.17	3.16

Table 2 *Percentage composition and formulation sequence for the preparation of S-based HUPER*

Composition,№ / Formulation sequence	UPER, [%]	S, [%]	CN, [%]	CHP, [%]
	1	2	3	4
1	95.23	-	1.41	3.36
2	95.20	0.03	1.41	3.36
3	95.13	0.10	1.41	3.36
4	95.07	0.16	1.41	3.36

Table. 3 *Percentage composition and formulation sequence for the preparation of SC-based HUPER*

Composition,№ / Formulation sequence	UPER, [%]	CN, [%]	SC, [%]	H_2O,[%]	CHP, [%]
	1	2	3	4	5
1	95.23	1.41	-	-	3.36
2	76.92	1.14	12.80	6.41	2.73
3	55.52	0.82	27.80	13.9	1.96
4	43.48	0.65	36.20	18.13	1.54

Dumb-bell test pieces type 1BA were tested for tensile strength by means of HZ-1005 Computer-type Tensile Testing Machine at a test speed of 100 mm/min according to ISO 527-1:2019, ISO 527-2:2012

3. RESULTS AND DISCUSSION

Three characteristic points were selected, including the time studied and the respective gelation temperature for each of the hydrophilizing agents. The results obtained form the basis for monitoring and comparing the kinetic behavior of the hydrophilized resin with the relevant modifier. This, on the one hand, enabled the selection of a specific hydrophilizing agent in terms of curing temperature and, on the other hand, an attempt was made to find out the concentration at which the maximum degree of cross-linking is reached.

Figure. 1 presents the kinetic dependencies T /τ of compositions referred to in Table 1, which demonstrate that the increase in sodium hydroxide results in a corresponding reduction in the gelation temperature. On the other hand, the gelation time, which is usually different for individual compositions, is not directly proportional to the amount of sodium hydroxide. For example, in composition 4 (Table 1), the maximum amount of hydrophilizing agent corresponds to the shortest gelation time.

It can be inferred from kinetic dependencies that the minimum amounts of sodium hydroxide give better results when selecting a minimum gelation time.

Figure 2 presents the kinetic dependencies T /τ of the compositions referred to in Table 2, which demonstrate that the increase in the amount of the sulfur hydrophilizing agent leads to reduction in the gelation temperature but also to increase in the gelation time.

Figure 3 presents the kinetic dependencies T /τ of the compounds referred to in Table 3, which demonstrates a continuation of the general trend to reduction in the maximum temperature at greater amounts of hydrophilizing agent. A particular feature of the specific hydrophilizing agent is that the gelation time does not depend on the amount of the hydrophilizing agent, i.e. it is maintained in certain limits. Therefore, at lower temperatures, without a specified gelation peak, the cross-linking processes take a very long time. As it should be provided that the cross-linking process is hard to control in relation to the processing of the material and its portability to different points, additional modification is required – through a filler. Thus, in fact, both the gelation time and the maximum curing temperature will be controllable.

The mechanical tests (Fig. 4-6) demonstrate that the test pieces containing NaOH as a hydrophilizing agent keep their strength values (tensile strength, percent tensile elongation and Young's modulus) at a broader range. When sulfur is used as a hydrophilizing agent these strength values are the lowest. The review of mechanical tests shows that SC used as a hydrophilizing agent increases to the greatest extent the tensile strength values, and the percent tensile elongation values, and to the lesser extent – the Young's modulus values. Therefore, the properties of the resin hydrophilized with sulfate-resistant cement were improved most significantly.

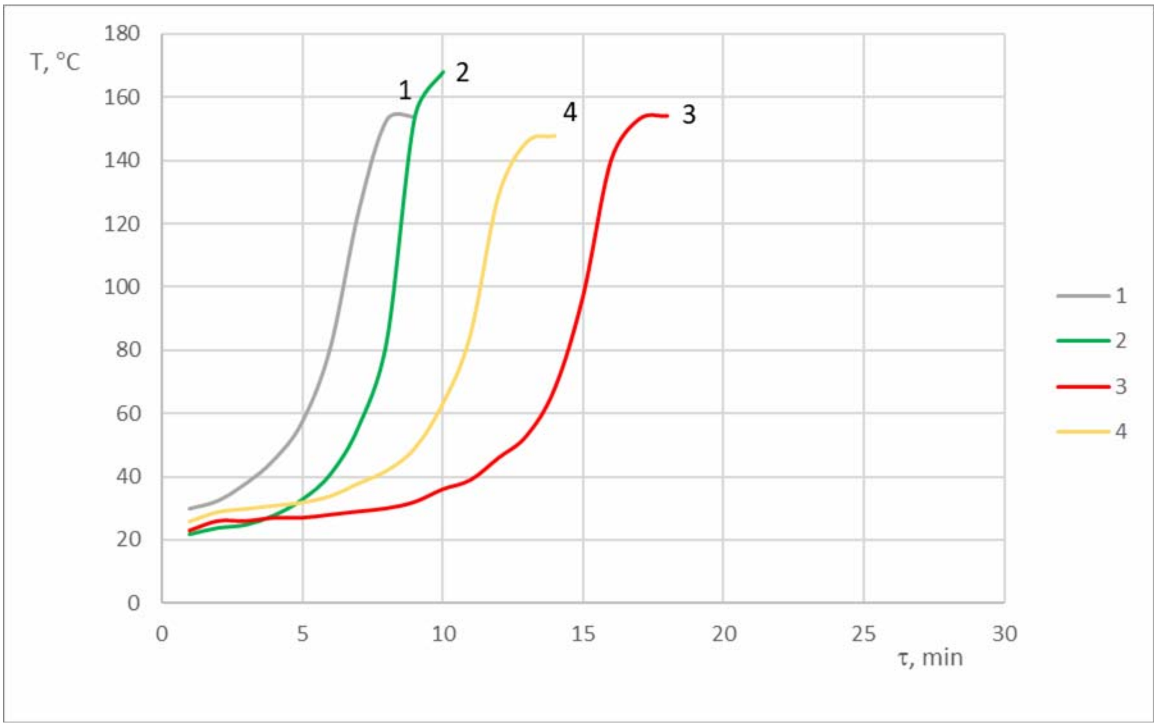

Fig. 1. Kinetics of polymerization process,

where curve 1: 0% NaOH; curve 2: 0.30% NaOH; curve 3: 0.80% NaOH; curve 4: 1.40% NaOH, according to Table 1

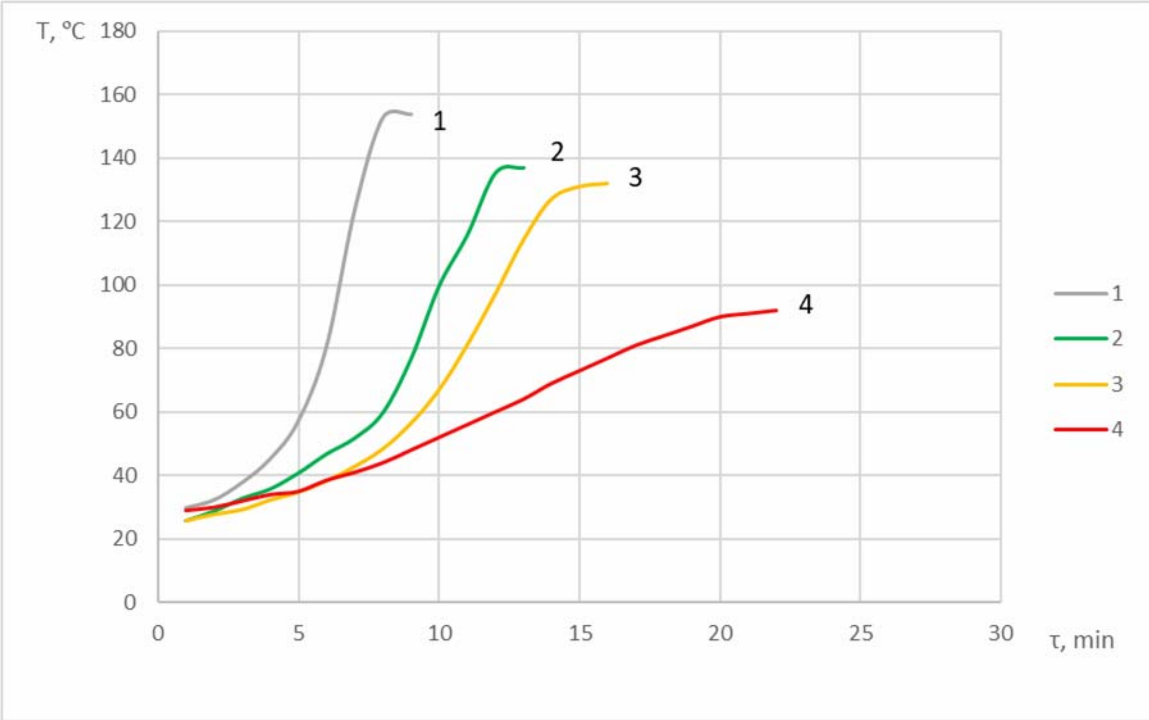

Fig. 2. Kinetics of polymerization process,

where curve 1: 0% S; curve 2: 0.03% S; curve 3: 0.10% S; curve 4: 0.16% S, according to Table 2

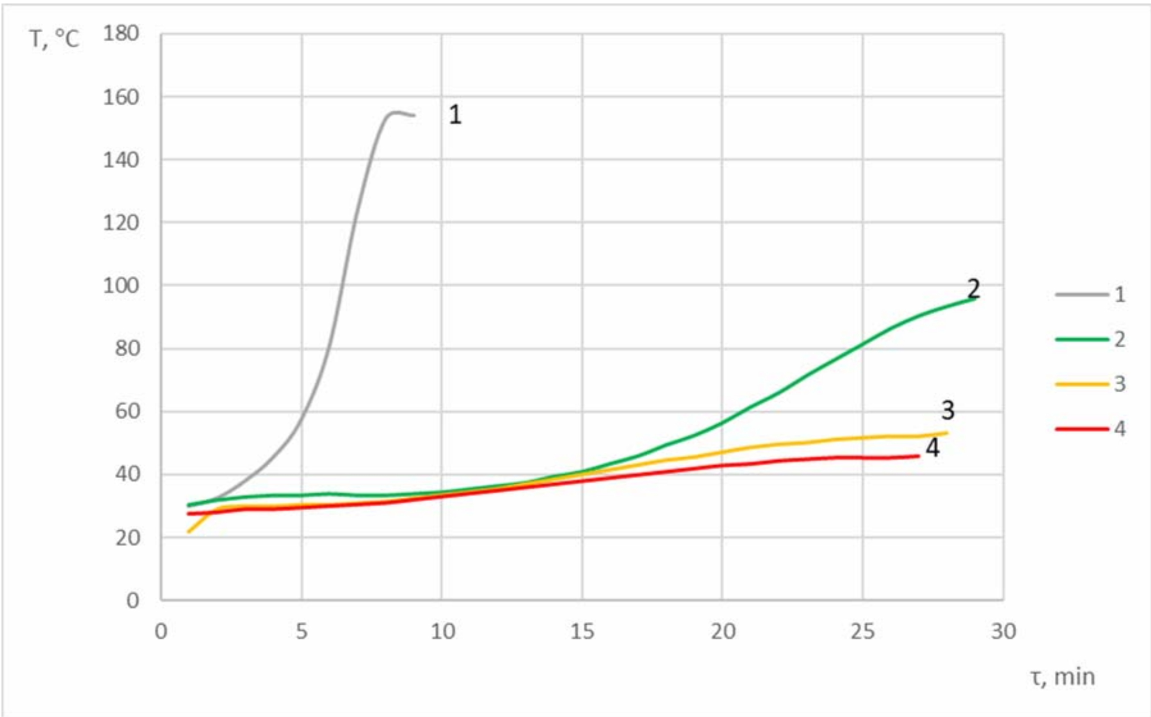

Fig. 3. Kinetics of the polymerization process, where curve 1: 0% SC; curve 2: 12.80% SC; curve 3: 27.80% SC; curve 4: 36.20% SC

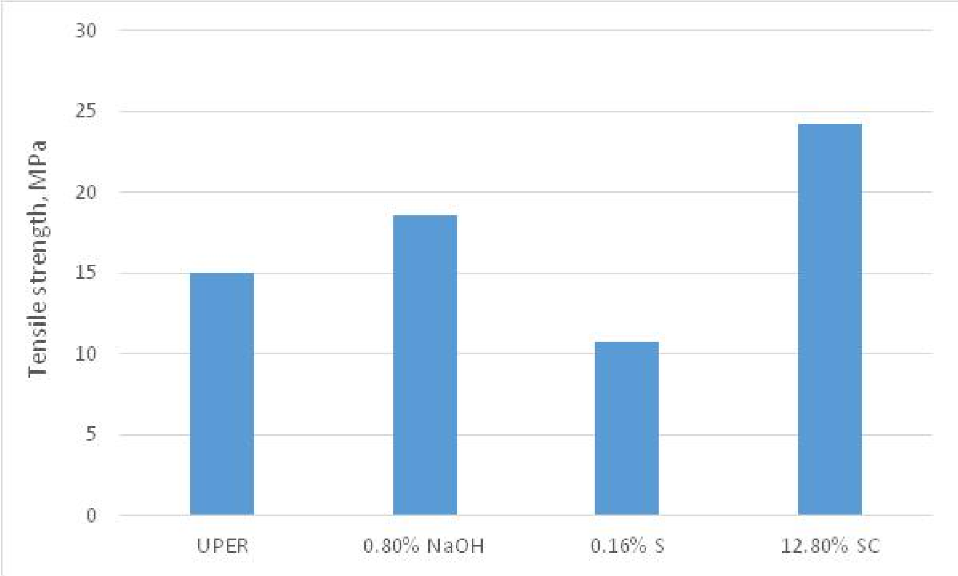

Fig. 4. Tensile strength data for polymeric compositions obtained by different modifiers (according to Tables 1, 2 and 3)

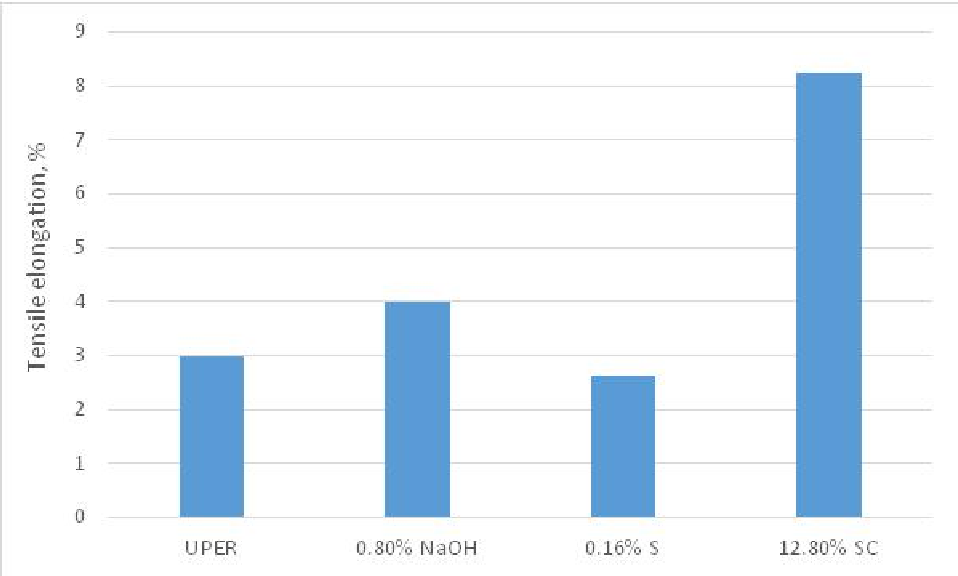

Fig. 5. Tensile elongation data for polymeric compositions obtained by different modifiers (according to Tables 1, 2 and 3)

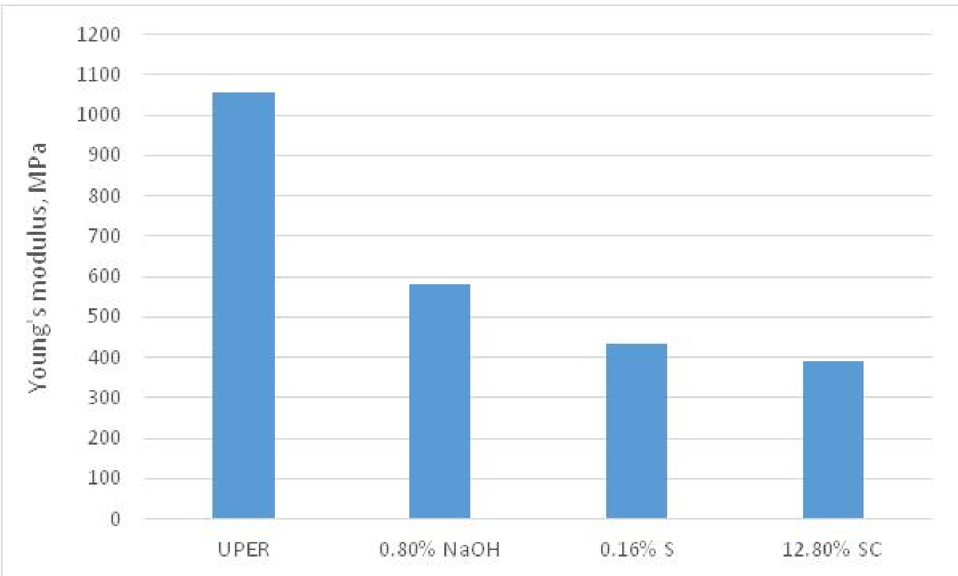

Fig. 6. Young's modulus data in polymeric compositions obtained by different modifiers (according to Tables 1, 2 and 3)

The kinetic dependencies with NaOH as a hydrophilizing agent lead to the conclusion that minimum amounts produce better results as regards to the selection of minimum gelation time together with high curing temperatures. With sulfur as a hydrophilizing agent it appears that the increase in its amount results in higher gelation temperatures and a corresponding increase in the time to reach the gelation point. When sulfate-resistant cement is used as a hydrophilizing agent, the gelation time does not depend on its amount, i.e. it is maintained within certain limits.

The mechanical tests carried out with the three hydrophilizing agents lead to the conclusion that the test pieces with the hydrophilizing agent NaOH retain their strength values in a broader range; where the hydrophilizing agent is sulfur these values are the lowest, and the sulfate-resistant cement increases to the greatest extent the tensile strength values and percent tensile elongation values, and to the lesser extent – the Young's modulus values.

4. CONCLUSION

HUPER was developed based on three modifiers and their kinetic and strength properties have been observed by comparison to the corresponding characteristics of non-modified UPER. It was found that when the hydrophilizing agent is NaOH, the increase in its concentration leads to reduction in the gelation temperature. A composition was obtained in which the maximum amount of hydrophilizing agents corresponds to a minimum gelation time. Test pieces with the hydrophilizing agent NaOH retain their strength values in a broader range (2.99-4% tensile elongation, 14.98-18.62 MPa tensile strength, 1056.81-581 MPa Young's modulus). With sulfur as a hydrophilizing agent the increase in its concentration leads to reduction in the gelation temperature and to increase in the gelation time. The strength values for the test pieces hydrophilized with sulfur are the lowest. When sulfate-resistant cement is used as a hydrophilizing, the increase in its concentration leads to reduction in the gelation temperature, and the gelation time is maintained within certain limits (27-29 min), the cross-linking processes take a longer time at lower temperatures without a specified gelation peak. Test pieces with the hydrophilizing agent SC increase to the greatest extent in tensile strength values (24.19 MPa) and percent tensile strength (8.23%) and to the lesser extent – the Young's modulus values (389.25 MPa). There is therefore improvement in the properties of the resin hydrophilized with sulfate-resistant cement.

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