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AQUEOUS COMPOSITIONS BASED ON MULTICOMPONENT HYDROPHILIZED POLYMER SYSTEM

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ABSTRACT

The purpose of this work is to develop compositions based on different types of HUPER with the addition of specific amounts of water that do not hinder the cross-linking of the unsaturated polyester. Hydrophilized unsaturated polyester resin (HUPER) diluted with specific amounts of water are presented. The unsaturated polyester resin (UPER) is modified with different reagents (cement, water glass, sodium hydroxide, sulfur) after which the addition of water is completely possible in technical terms. Water-diluted HUPER acquires new specific properties – visually it is more homogeneous, in certain cases it is gypseous, highly embossed and with relatively good strength indicators. The aqueous compositions of combined hydrophilizing agent of 13% SC/ 3.5% WG and 12% SC/7% WG demonstrate increased tensile strength by 50 to 70% and tensile elongation by 90 to 130%. Composites based on NaOH with small amounts of water (up to 15%) show increased tensile strength by up to 47% and increased tensile elongation by up to 100%.

1. INTRODUCTION

Unsaturated polyester resins are extremely universal in relation to their properties and applications. These are thermosetting materials that harden in the presence of the mainstream redox system of cyclohexanone peroxide (CHP) and cobalt naphthenate (CN). The interest in them is half century old, it is not waning but is even increasing in the last decade in a broad aspect of application. The literature reviews the development of polyester-based composites [1] and examines the types of fillers, properties and applications of composites. A comparison is given between different types of unsaturated polyester composites developed as insulating materials using date palm fibers as fillers [2], particles of waste rubber [3]. Some literature sources mention other type of waste material, such as bauxite residue. This has motivated the authors [4] to continually develop new techniques in order to recover waste material. An interesting point in the development of composites is the neutralization with seawater and subsequent assessment of the effect of filler content on strength indicators.

Currently, polymer concrete composites manufactured by industrial or agricultural waste are increasingly popular as the demand for concretes with high strength characteristics is growing. The meaning of their development is not only in high-strength characteristics but also in the acquisition of specific characteristics: high durability, reduced shrinkage, reduced permeability, chemical and heat resistance [5]. These exclusive characteristics of polymer composites allow for their specific application and make them a promising re-use alternative [6].

However, there is a limited number of studies indicating that it is possible to dilute UPERs with specific amounts of water after their hydrophilization with different modifiers. Accordingly, the use of the mainstream redox system of CHP and CN guarantees their hardening in the presence of different amounts of water. The inclusion of water can compete with the addition of waste material [7], since, depending on the hydrophilizing agent, the appropriate ratio and good interaction can homogenize the material, plasticize it, improve its appearance and embossment, and some strength characteristics and last but not least it can have a good economic result. The aim of this work is to develop compositions based on different types of HUPER with the addition of specific amounts of water that do not hinder the cross-linking of the unsaturated polyester.

2. MATERIALS AND METHODS

The following were used:

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

Sodium hydroxide (reagent grade ≥ 98%, pellets, anhydrous) – Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany.

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Sulfur powder (S), A.R. (purum p.a. ≥99%) – Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany.

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

Sodium silicate, 25% solution (Water glass, WG) – BEKO Water Glass and Detergents Factory, Troyan, Bulgaria.

Methods for preparation of aqueous compositions based on hydrophilized unsaturated polyester resin with various modifiers (SC, SC/WG, 33% aqueous solution of NaOH, sulfur powder, SC/sulfur) have been developed at constant CN/CHP ratio in relation to resin [8]. All aqueous compositions of HUPER were obtained at room temperature by continuous and vigorous stirring with successive addition of each of the components in chronological order as presented horizontally in Tables 1-4.

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.

Table 1 *Formulations for preparation of HUPER based on an individual modifier SC (compositions 2 - 4), of WG (compositions 5 - 7), and of a combined modifier SC/WG (compositions 8 and 9)*

Composition,№ / Formulation sequence	1	2	3	4	5	6
	UPER, [wt%]	CN, [wt%]	SC, [wt%]	H_2O, [wt%]	CHP, [wt%]	WG, [wt%]
1	95,2	1,4	-	-	3,4	-
2	76,8	1,0	13,0	6,5	2,7	-
3	55,2	0,8	28,0	14,0	2,0	-
4	43,8	0,7	36,0	18,0	1,5	-
5	91,4	1,4	-	-	3,2	4,0
6	87,6	1,3	-	-	3,1	8,0
7	83,8	1,2	-	-	3,0	12,0
8	74,2	1,0	13,0	6,2	2,6	3,5
9	71,5	1,0	12,0	6,0	2,5	7,0

Table 2 *Aqueous compositions of HUPER with NaOH as a modifier*

Composition,№ / Formulation sequence	1	2		3	4	5
	UPER, [wt%]	33% NaOH		H_2O, [wt%]	CN, [wt%]	CHP, [wt%]
		NaOH, [wt%]	H_2O, [wt%]			
1	95,2	-	-	-	1,4	3,4
2	93,0	0,8	1,7	-	1,3	3,2
3	82,7	0,7	1,5	10,0	1,5	3,6
4	70,2	0,6	1,3	23,7	1,2	3,0
5	56,0	0,5	1,0	39,0	1,0	2,5
6	46,7	0,4	0,9	49,1	0,9	2,0

Table 3 *Aqueous compositions of HUPER with sulfur as a modifier*

Composition,№ / Formulation sequence	UPER, [wt%]	S, [wt%]	H_2O, [wt%]	CN, [wt%]	CHP, [wt%]
	1	2		3	4
1	95,2	-	-	1,4	3,4
2	95,04	0,16	-	1,4	3,4
3	94,24	0,16	0,8	1,4	3,4
4	93,44	0,16	1,6	1,4	3,4
5	92,64	0,16	2,4	1,4	3,4

Table 4 *Formulations for preparation of HUPER based on an individual modifier SC and sulfur (compositions 2 and 3), and of a combined modifier SC/sulfur (composition 4)*

Composition,№ / Formulation sequence	1	2	3	4	5	6
	UPER, [wt%]	SC, [wt%]	S, [wt%]	H_2O, [wt%]	CN, [wt%]	CHP, [wt%]
1	95,2	-	-	-	1,4	3,4
2	76,8	13,0	-	6,5	1,0	2,7
3	95,04	-	0,16	-	1,4	3,4
4	76,64	13,0	0,16	6,5	1,0	2,7

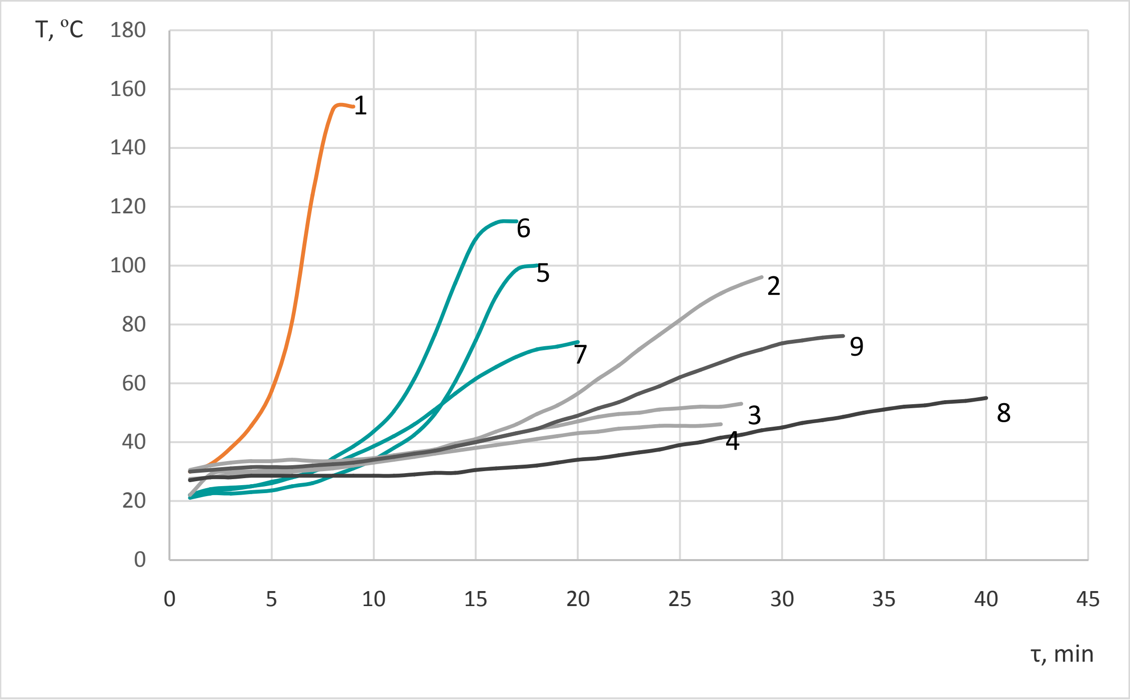

Fig. 1. Kinetics of polymerization process, where curve 1: – unmodified UPER; curve 2: 13.0 % SC; curve 3: 28,0 % SC; curve 4: 36,0% SC; curve 5: 4.0 % WG; curve 6: 8.0 % WG; curve 7: 12.0 % WG curve 8: 13% SC/ 3.5% WG; curve 9: 12.0% SC/ 7.0% WG. (according to Table 1)

3. RESULTS

3.1. Aqueous compositions of HUPER with WG, SC and SC/WG

Figure 1 presents kinetic dependencies temperature/time obtained as a result of hydrophilization of resin with an individual hydrophilizing agent WG, and with SC. They show that when only using WG kinetic curves have more pronounced extreme character: clearly defined gelation points in less time. The application of SC alone as a hydrophilizing agent demonstrates that the gelation points correspond to larger times and lower temperatures. Since the use of SC as a hydrophilizing agent is technically conditional on a specified amount of water [9], hydrophilization with a two-component modifying system in different ratios have been developed (Table 1, Fig. 1 curves 8 and 9).

Hydrophilized systems based on individual hydrophilizing agents and modified unsaturated polyesters were developed with a combination of both hydrophilizing agents. Difference in the kinetics of individually hydrophilized systems and those hydrophilized in combination are the reason to study and compare the strength indicators of those systems. As a final result, the combined hydrophilizing agent constitutes one of the components of comparative analysis (Fig. 2). The leading reason for adding WG are the improved values of strength indicators in specific ratios (SC/WG: 13%/3.5%; 12.0%/7%). For pure UPER, the tensile strength is 15 MPa with Young's modulus of 1056 MPa and tensile elongation – 3%. Mechanical characteristics show an increase between 50 and 70% for tensile strength, between 90 and 130% for tensile elongation, and a 45% decrease in the Young's modulus.

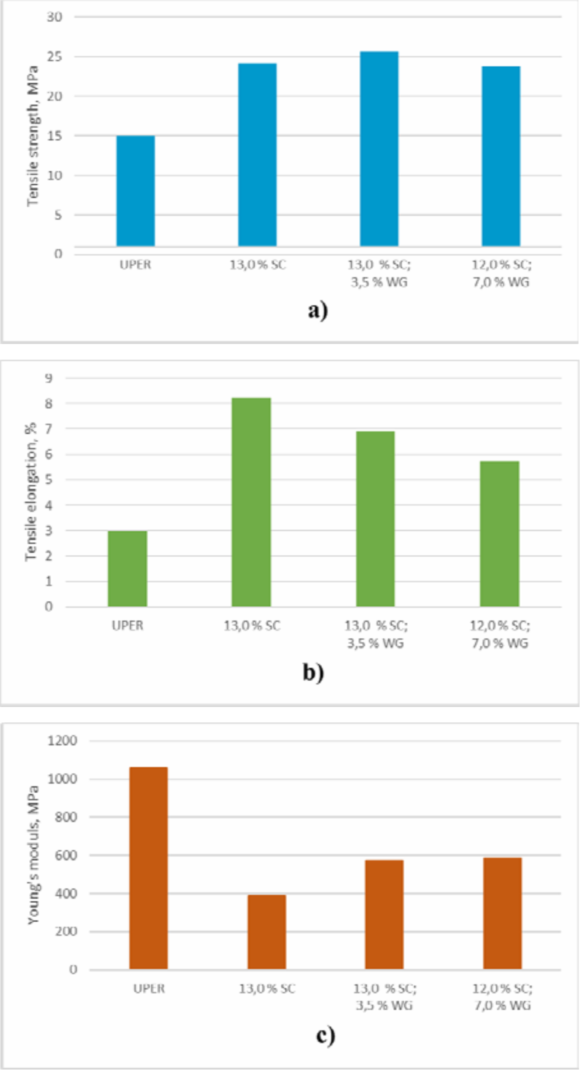

Fig. 2. Data on a) tensile strength b) tensile elongation, and c) Young's modulus of polymer compositions based on SC and WG

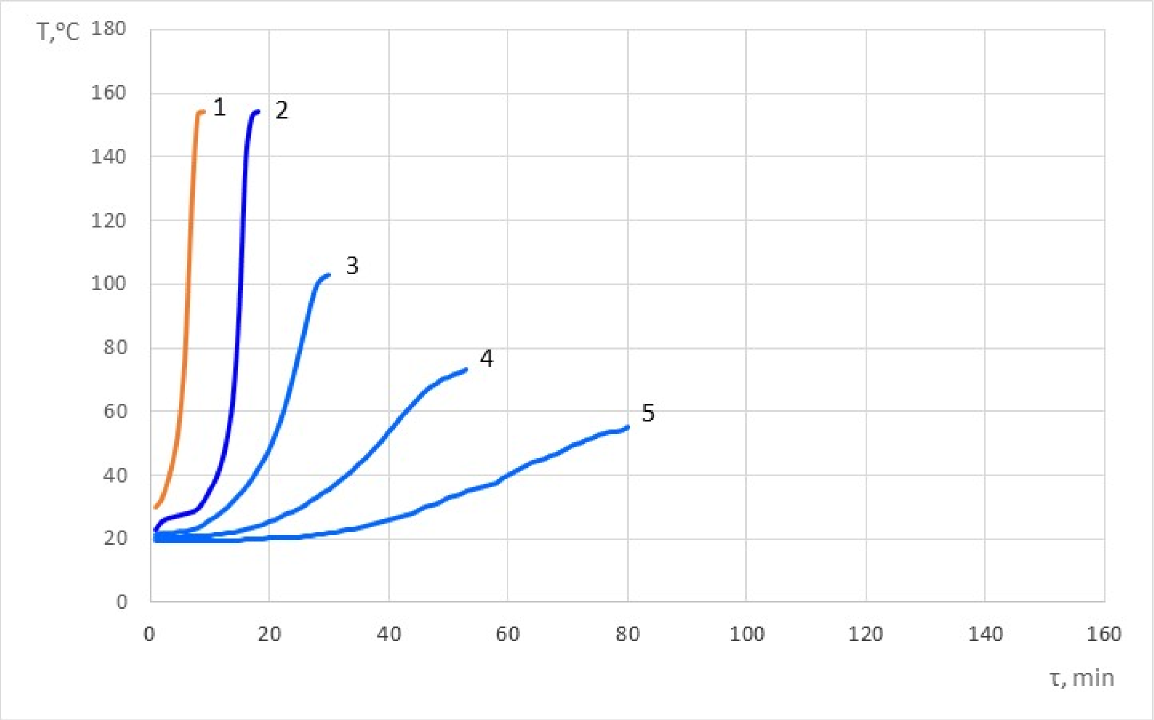

Fig. 3. Kinetics of polymerization process, where curve 1: unmodified UPER; curve 2: 0.8% NaOH/1.7% H_2O; curve 3: 0.7% NaOH/11.5% H_2O; curve 4: 0.6% NaOH/25% H_2O; curve 5: – 0.5% NaOH/40% H_2O; curve 6: 0.4% NaOH /50% H_2O (according to Table 2)

3.2. Aqueous compositions of HUPER with NaOH

Fig. 3 presents the kinetic dependencies temperature/ time of compositions referred to in Table 2 showing that the addition of water in different amounts between 25 and 50% is absolutely possible and does not prevent the hardening but results in gradual decrease in maximum temperature and increases the gelation time.

It was found that the addition of small amounts of water to the HUPER composition (Fig. 4) demonstrates higher strength characteristics (increased tensile strength by up to 50% and increased tensile elongation by up to 100%).

In compositions with 40-50% water content strength indicators do not improve (decreased tensile strength by up to 87% and decreased tensile elongation by up to 17%) but that materials based on them acquire a gypseous nature. However, they can be used in orthopedics where mechanical characteristics are not required to reach maximum values as they are used in the human body. Therefore, composites obtained with small amounts of water up to 15% can be used, on the one hand, as carrier materials in construction [10], and on the other hand they can be used with larger amounts of water (25-50%) for architectural decorations, including as orthopedic materials [11].

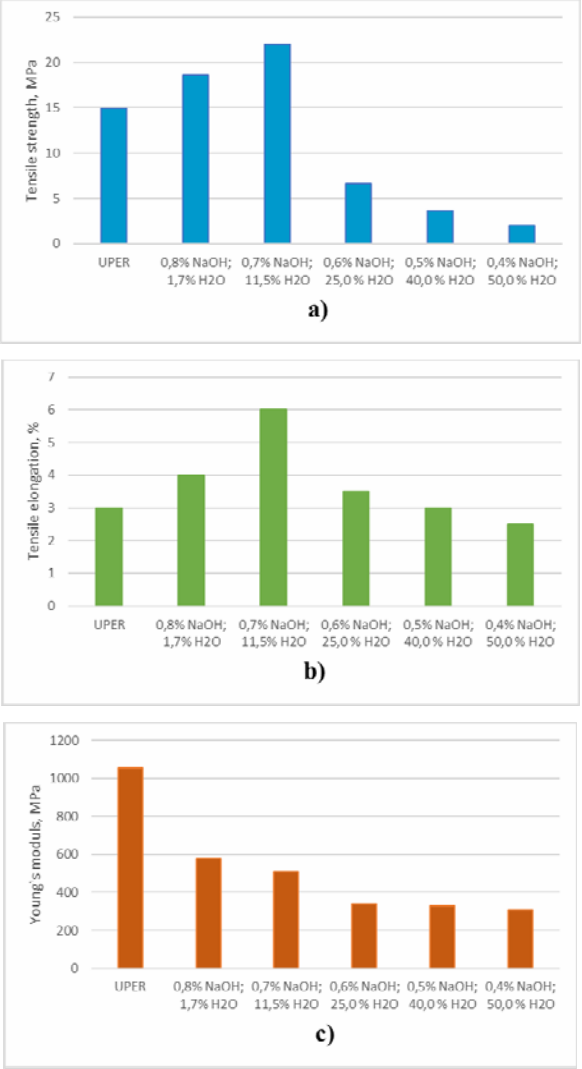

Fig.4. Data on a) tensile strength b) tensile elongation, and c) Young's modulus of polymer compositions hydrophilized with sodium hydroxide

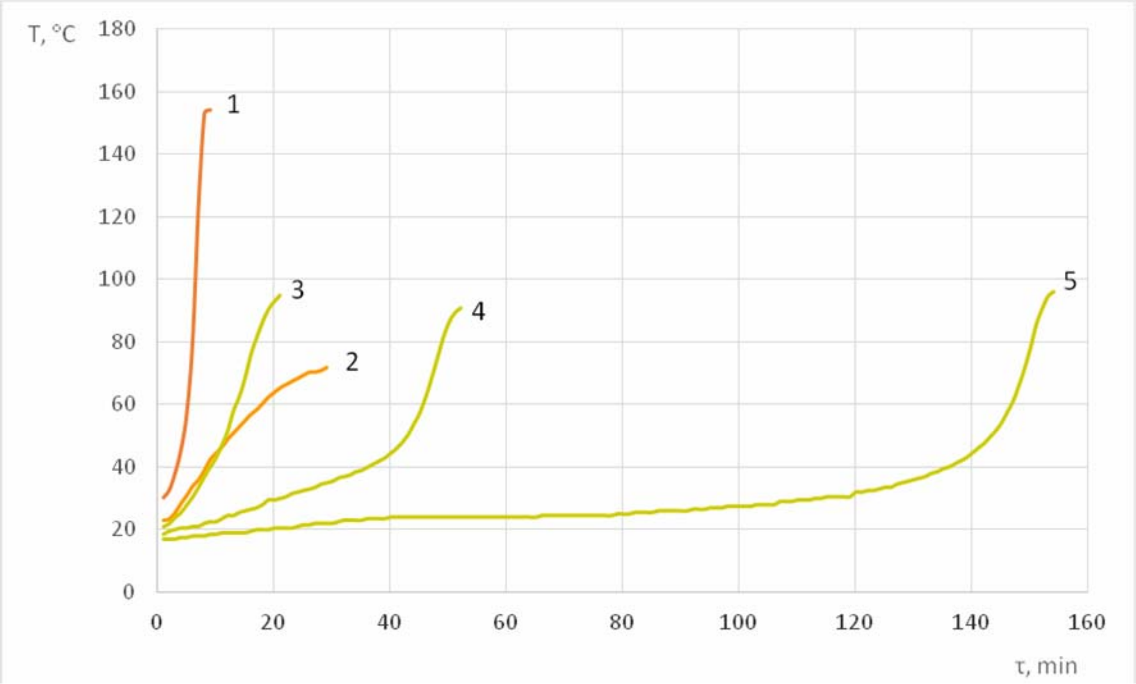

Fig. 5. Kinetics of polymerization process, where curve 1: unmodified UPER; curve 2: 0.16% S; curve 3: 0.16% S /0.8% H_2O; curve 4: 0.16% S/ 1.6% H_2O; curve 5: 0.16% S/ 2.4% H_2O (according to Table 3)

3.3. Aqueous compositions of HUPER with S

It can be observed that the amounts of the hydrophilizing agent sulfur, which are possible to be added to the unsaturated polyester resin, are very small – some 0.16 % (Table 3, Fig. 5)

Fig. 5 presents the kinetic dependencies temperature/ time of compositions referred to in Table 3 showing that the addition of water does not prevent the hardening but results in increases the gelation time. Nevertheless, aqueous compositions based on sulfur as a hydrophilizing agent show the following special feature – amounts of water vary between 5-15 times more in proportion to the quantity of sulfur. Therefore, these high amounts of water relative to sulfur appears to be small quantity in relation to the entire system (0.8-2.4%, Table 3).

Sulfur as a hydrophilizing agent demonstrates the lowest strength indicators (Fig. 6).

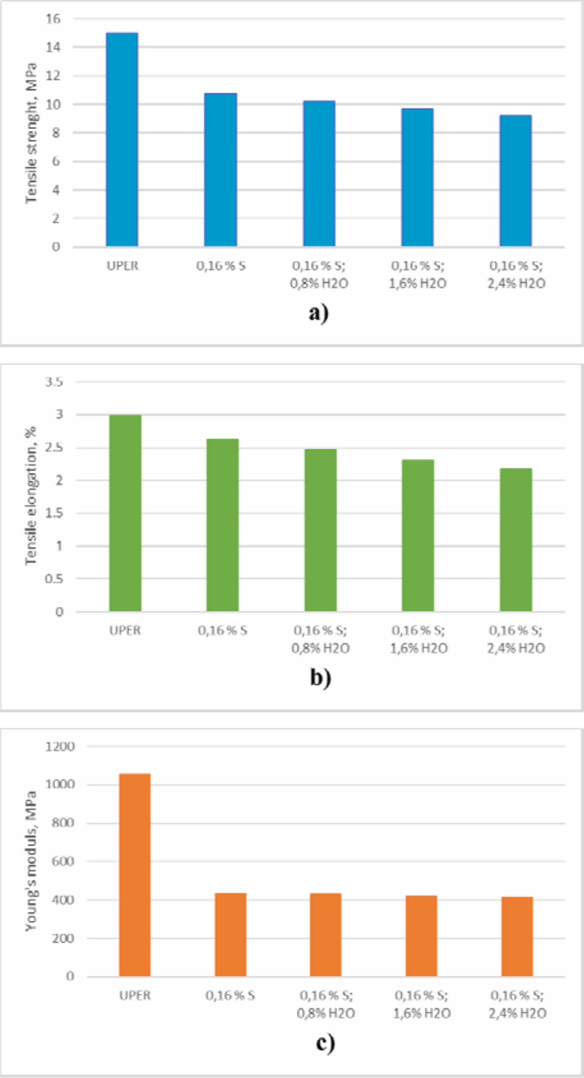

Fig. 6. Data on a) tensile strength b) tensile elongation, and c) Young's modulus of polymer compositions hydrophilized with sulfur

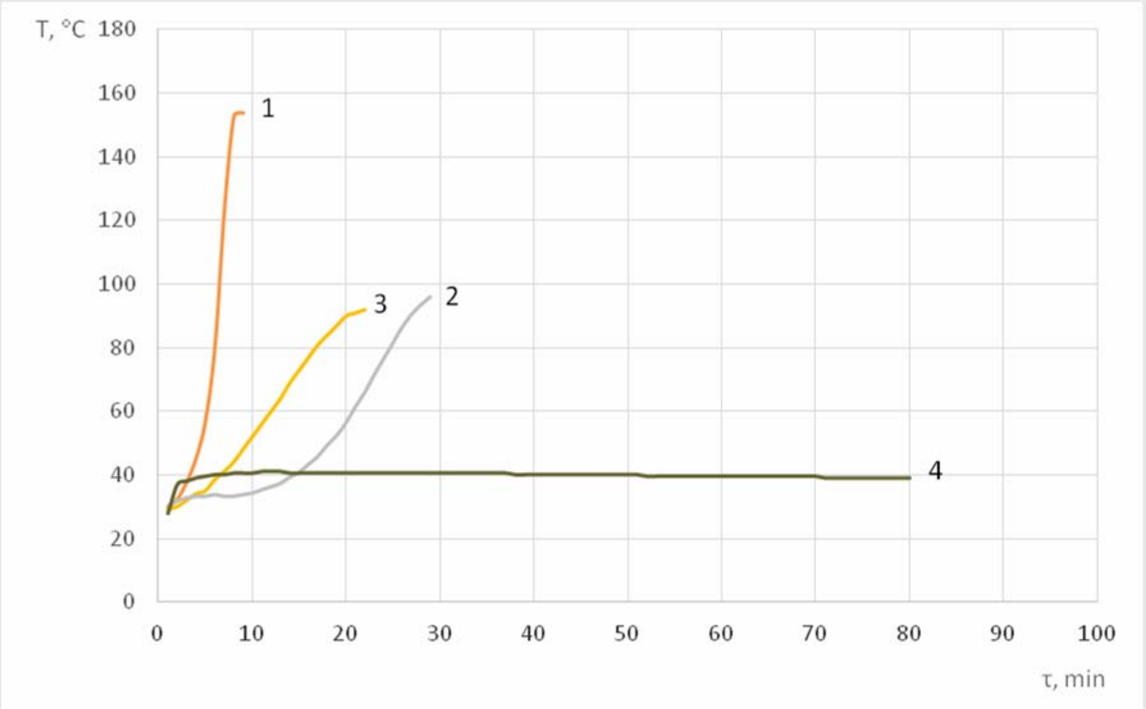

Fig. 7. Kinetics of polymerization process, where curve 1: unmodified UPER; curve 2: 13.0% SC; curve 3: 0.16% S; curve 4: 13.0% SC/0.16% S (according to Table 4)

3.4. Aqueous compositions of HUPER with SC/S

The idea to add SC as a second hydrophilizing agent is based on the following fact: it is observed that this hydrophilizing agent can be added in much larger amounts than those of sulfur (around 13%, i.e. 80 times more). Nevertheless, aqueous compositions based on SC as a hydrophilizing agent and diluent water demonstrate another special feature: amounts of water are exactly 50% relative to SC. It appears that this limited percentage of water to SC is a large amount in relation to the entire system (6.5-18%).

A system of two hydrophilizing components (sulfur and SC) was thus built (Table 4, Fig. 7), where small amounts of sulfur are compensated by large amounts of water because of SC, and small amounts of water are compensated by large amounts of SC because of sulfur.

Figure 7 presents kinetic dependencies temperature/time obtained as a result of hydrophilization of resin with an individual hydrophilizing agent S, and with SC. They show that when only using S or SC kinetic curves have clearly defined gelation points in less time. The application of two-component system of sulfur and SC with corresponding amounts of water as a hydrophilizing agent demonstrates that the gelation points correspond to larger times and lower temperatures.

Strength indicators with SC as a hydrophilizing agent have the highest values (tensile strength is 24 MPa and tensile elongation - 8%). Studies have been carried out to check the mutual influence of both hydrophilizing agents on those strength indicators. They showed that, unlike other combinations in which both hydrophilizing agents have a reinforcing effect (Fig. 2), sulfur has no additive effect in this case (Fig. 8).

The two-component system of sulfur and SC with corresponding amounts of water to each of them is an interpenetrating hydrophilizing network in the unsaturated polyester resin.

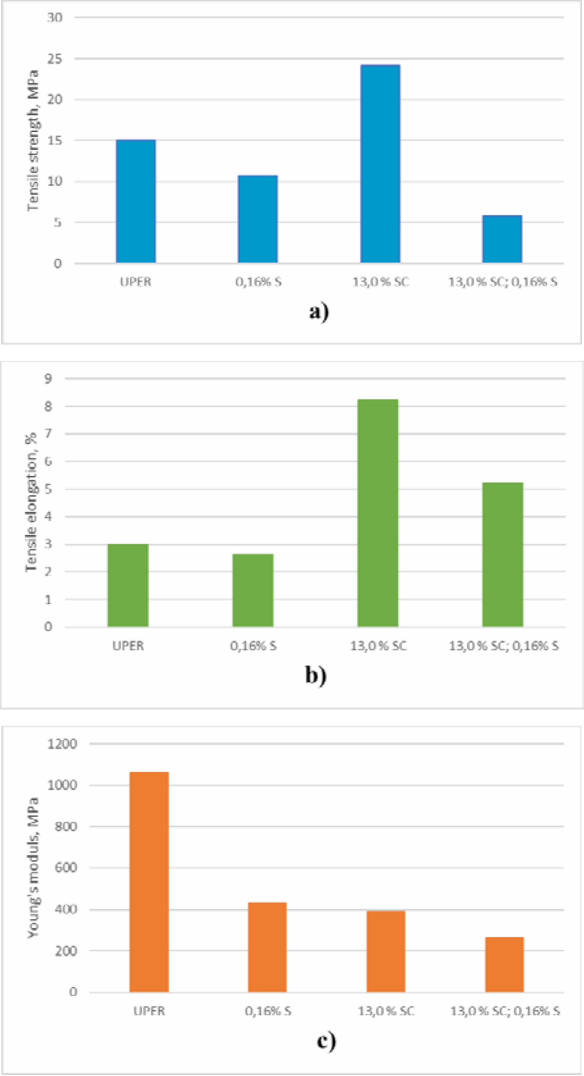

Fig. 8. Data on a) tensile strength b) tensile elongation, and c) Young's modulus of polymer compositions based on SC and sulfur

4. DISCUSSION

Various types of hydrophilizing agents (SC, WG, NaOH, S) were developed; they modify UPER and give it a chemical and technologically nature that is different from its natural essence: from hydrophobic character it acquires hydrophilic properties. The resulting HUPER acquires an important property: it can be diluted with a specific amount of water that is characteristic of different hydrophilizing agents without preventing the hardening of samples when using the resin-specific redox system. Kinetic dependencies temperature/time resulting from resin hydrophilization with individual hydrophilizing agents, different combinations thereof and addition of a specified amount of water to each of them were presented. Where only WG is used, kinetic curves have more pronounced extreme character, and where only SC is used as a hydrophilizing agent gelation points correspond to larger times and lower temperatures. This is probably related to a specific amount of water, which is technically applied when developing the resin. With NaOH as a hydrophilizing agent, the kinetics of hydrophilization not only shows highly expressed speeds of hardening but also possibilities to add water in relation to the entire system varying widely from 25 to 50 %. With SC, they are up to 18 % but cannot change, which impedes the examination of the dependency, a second modifier is used therefore, WG. With sulfur as a modifier, the possibilities for its inclusion as a hydrophilizing agent are very limited – some 0.16%. An essential characteristic related to the addition of water was considered, which has a very high share (80-95%) in relation to the sulfur amount, which however is extremely small in relation to the entire system (not exceeding 2.5%). That enabled the inclusion of SC as a second hydrophilizing agent to help compensating small amounts of sulfur by large amounts of water because of SC, and small amounts of water to be compensated by large amounts of SC because of sulfur. Consideration was given to the possibility for the occurrence of interpenetrating networks in UPER.

The differences in kinetics of individually hydrophilized systems and those hydrophilized with a combination of hydrophilizing agents is the reason to study and compare the strength characteristics of those systems. In the end, the combined hydrophilizing agent is one of the components of the comparative analysis. The main reason for adding WG were the improved values of strength indicators at specific ratios (SC/WG: 13%/3.5%; 12.0%/7%). The resulting composites based on sodium hydroxide with small amounts of water (up to 15%) show higher strength characteristics: increase in the tensile strength by up to 47% (from 15 MPa to 22 MPa), increase in the tensile elongation by up to 100% (from 3% to 6 %). They can be used as carrier materials in construction. On the other hand, with larger amounts of water (25 – 50%), the strength indicators decrease: tensile strength is reduced by up to 87% (from 15 MPa to 2 MPa), and tensile elongation is reduced by up to 17% (from 3% to 2.5 %), however materials based on them find practical use as architectural decoration, including as orthopedic materials. The lowest strength indicators are demonstrated with sulfur as a hydrophilizing agent. On the other hand, strength indicators with SC as a hydrophilizing agent are of the highest values. Studies have been carried out to check the mutual influence of both hydrophilizing agents on those strength indicators. They showed that, unlike other combinations in which both hydrophilizing agents have a reinforcing effect, sulfur has no additive effect in this case. This a clear proof that in some cases the use of hydrophilizing agents in combination is a result of their interpenetration but in other cases it only results in the formation of mechanical mixtures thereof.

CONCLUSION

Hydrophilization with different reagents (SC, WG, NaOH, S) results in chemical modification of UPER. Kinetic dependencies temperature/time show that when using WG and NaOH, kinetic curves have more pronounced extreme character while SC and S as a hydrophilizing agents demonstrate that the gelation points correspond to larger times and lower temperatures.

This chemical modification allows the HUPER to be diluted with specific amounts of water and subsequently cured. As a result deluted- HUPER acquires new properties. The aqueous compositions of combined hydrofililizing agent of 13% SC/ 3.5% WG increase the tensile strength from 15 MPa to 25 MPa (70 %) and tensile elongation increased from 3 % to 7 % (130%) and decrease in the Young's modulus from 1056 MPa to 575 MPa (45 %). It was found that the HUPER with NaOH diluted with 11,5% water demonstrates increased tensile strength from 15 MPa to 22 MPa (47 %) and increased tensile elongation from 3 % to 6 % (100%). SC as a hydrophilizing agent has the highest strength indicators while aqueous compositions of HUPER with sulfur demonstrate the lowest strength indicators. The aqueous compositions of 12,8 % SC/ 0.06% S decrease the tensile strength from 15 MPa to 13 MPa (13 %), increase the tensile elongation from 3 % to 4.2 % (40%) and decrease the Young's modulus from1056 MPa to 523 MPa (50%).

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