POLYESTER/SILICATE COMPOSITES

ПОЛИЕСТЕРНО-СИЛИКАТНИ КОМПОЗИТИ

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Abstract

This work is a continuation of the HUPER development, as in this study hydrophilization was performed by different types of cement (grey cement and medical cement). It was established that alkaline hydroxides in the cement "milk" composition traditionally perform the preselected role of a hydrophilizer. Water was used as a second dispersing component, which can not only homogenize the composition of the prepared composite material. A third component was introduced (water glass), which was studied due to its dispersing role towards the resin/cement/water system. Mechanical strength characteristics (mostly impact characteristics) characterizing the shape, dimensions and integrity of the operational product were studied based on the obtained composition in various proportions of components.

KEYWORDS: hydrophilization, resin/mineral disperse system, cement, water glass.

1. Introduction

The development of composites based on hydrophilized unsaturated polyester resin (HUPER) could be accomplished not only by methods described in previous works [1-5] but also with different types of cement (Sulfate-resistant blastfurnace cement and medical cement). The addition of cement affects the curing behavior compared to the unmodified resin, which is important for tracing the polymerization. The investigation of mechanical indices of the compositions obtained is another essential task in terms of their main purpose as polymer/silicate composites. Some literary sources review the role of cement as a supplement demonstrating the various advantages of modified resins: for obtaining artificial stone [6]; possibilities for producing repair materials [7]; for strength and elasticity modulus optimization [8]. Cement-based composites were also obtained as cement was used as a filler in a fiberglass/polyester resin matrix in view of sea-water resistance [9].

The purpose of this work is the development of UPER-based compositions in view of their application as composite materials – polymer concrete, fiberglass, etc.

2. Materials and methods

2.1. Materials

We used:

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

Medical two-compound zinc phosphate cement in the form of powder, ADHESOR® - „SpofaDental" (MC).

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

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

2.2. Methods

Methods for obtaining compositions based on unsaturated polyester resin (UPER) hydrophilized with different types of cement (SC and MC) have been developed at fixed amount of water compared to cement (50%) in the presence or absence of WG, at fixed CN/CHP ratio compared to resin.

Charpy impact strength tests have been performed to test pieces using Ceast 6545/000, Great Britain. A test piece fixed next to its ends as a horizontal beam is hit by a single pendulum impact. The impact direction is in-between the supports holding the test piece at fixed speed of 50 mm/min. The impact energy absorbed by the test piece is reported.

Test pieces were tested for pressure strength by dynamometer Instron 4203, Great Britain. The test piece is pressure loaded at a fixed rate of strain of 50 mm/min, until destroyed.

3. Results and discussion

Polymeric compositions have been developed with various quantities of SC at a constant cement to water ratio (2:1), the same amount of UPER curing in the presence of CN/CHP redox system (table 1). A composition without SC was produced for comparison.

The polymerization of UPER was traced in the presence of different percentage of SC compared to resin. It was found that with increase in its amount, within the range from 10% to 40%, the maximum temperature gradually decreased from 140 to 60 ˚C (fourfold decrease). The kinetics of the polymerization process of UPER in the absence of SC shows that the unmodified resin has the highest curing temperature and the least gelation time (fig.1).

Table 1. Data on the obtaining of composites based on UPER hydrophilized with different quantities of SC. Quantities: UPER – 30 g, CN – 0.5 ml, water – 50% vs. SC quantity, CHP – 1 ml

Composition No.	SC quantity %	Time [τ, min]	Temperature T max., ˚C]
1	-	9	154
2	12.82	14	139.5
3	21.50	22	124.5
4	27.78	27	101
5	32.52	30	84.5
6	36.23	35	70.5
7	39.21	37	61.5

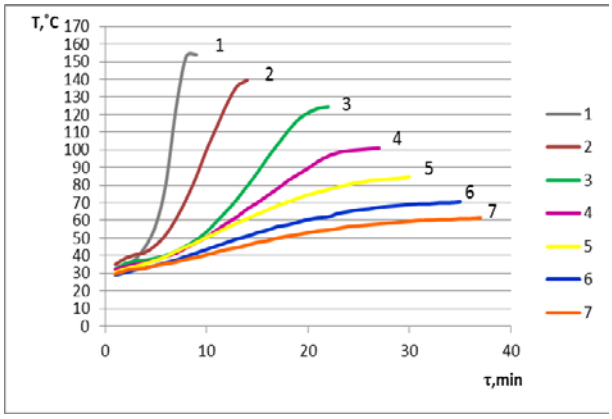

Fig. 1. Kinetics of the polymerization process, where curve 1 – 0% SC, curve 2 – 12.82% SC, curve 3 – 21.5% SC, curve 4 – 27.78% SC, curve 5 – 32.52% SC, curve 6 – 36.23% SC, curve 7 – 39.21% SC (according to Table 1)

The impact and pressure strengths of the compositions in table 1 have been studied as shown in fig. 2 and fig. 3, respectively.
Fig. 2 shows that the increased percent content of SC results in increase of the impact strength compared to the zero sample, as such dependency is of extremal nature – at about 22 ±2% and 35±2% SC reaches maximums and at 27±2% and 35± % SC reaches minimums.

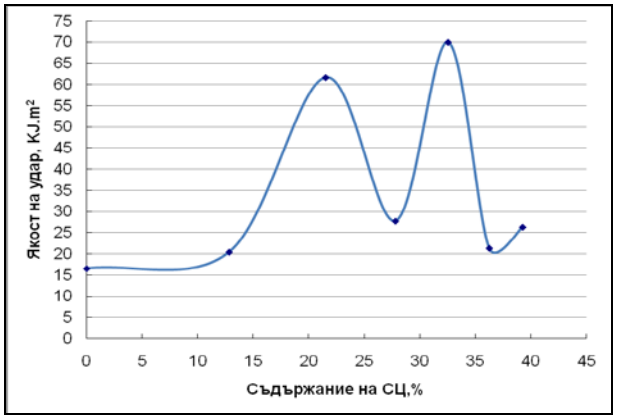

Fig. 2. Data on the impact strength when changing the SC quantity (according to Table 1).

Fig. 3 shows the change in the pressure strength according to the SC quantity, where the most significant increase is at 15% SC. Further increase in the cement quantity does not lead to significant increase in that inedx, while the high value trend is preserved.

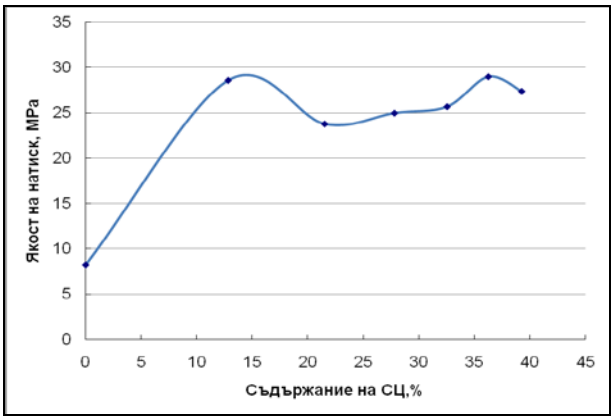

Fig. 3. Data on the pressure strength when changing the SC quantity (according to Table 1).

The influence of a third component (WG) was studied and for that purpose, compositions at fixed amount of SC (21,5%) were developed. The respective composition in the absence of WG was produced for comparison (No. 1, table 2).

Table 2. Data on the obtaining of composites based on UPER hydrophilized with the same quantity of SC when changing the amount of WG. Quantities: UPER – 30 g, CN – 0.5 ml, SC – 21,5%, water – 50% vs. SC quantity, CHP – 1 ml

Composition No.	WG quantity %	Time [τ, min]	Temperature [T max., ˚C]
1	-	22	124.5
2	2.52	42	97.5
3	4.91	41	90.5
4	7.18	35	99.5
5	9.36	39	83.5
6	11.43	39	75.5

The kinetics of polymerization processes was traced according to the WG content and the strength indices of such compositions and certain main conclusions were made concerning the obtained result. Those conlcusions will be presented in our following works.

Polymeric compositions have beem also developed with different quantities of MC (MC:water=2:1), at a fixed amount of UPER and redox system (table 3).

Table 3. Data on the obtaining of compositions based on UPER hydrophylized by different quantities of MC. Quantities: UPER – 30 g, CN – 0.5 ml, water – 50% compared to MC quantity, CHP – 1 ml

Composition No.	MC quantity %	Time [τ, min]	Temperature [T max., ˚C]
1	-	9	154
2	12.82	21	148
3	21.50	34	122.5
4	27.78	39	109.5
5	32.52	46	96
6	36.23	92	68
7	39.21	94	59

The polymerization of UPER in the presence of different percentage of MC compared to resin was traced.
In that case, it was found that the change in MC, in quantities from 10 to 40% (analogically to SC), affects to a greater extent the maximum temperatures (they decrease almost three times), while the curing time increases four times similarly to SC.

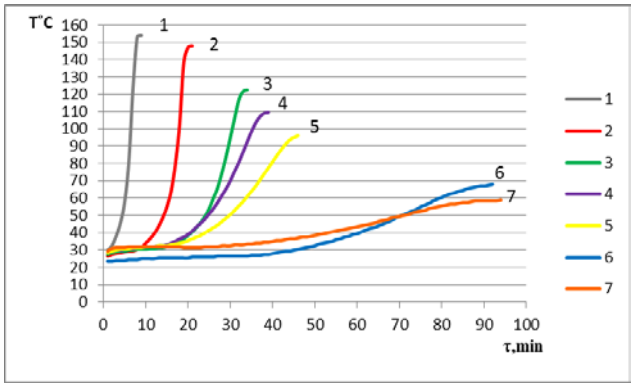

Fig. 4. Kinetics of the polymerization process, where curve 1 – 0% MC, curve 2 – 12.82% MC, curve 3 - 21.5% MC, curve 4 – 27.78% MC, curve 5 – 32.52% MC, curve 6 – 36.23% MC, curve 7 – 39.21% MC (according to Table 3)

The impact and pressure strengths of the compositions in table 3 were studied and are shown in fig. 5 and fig. 6, respectively.
Fig. 5 demonstrates that the change in that mechanical index goes minimums and maximums, as the zero sample was also used for that purpose (in the absence of MC according to composition No. 1 from table 3). It follows from fig. 6, that the pressure strength grows proportionately to the increase of MC up to 22±2%, and on subsequent increase of MC up to 40% the mechanical index decreases on the background of slightly attentuating extrema.

Fig. 5. Data on the impact strength when changing the MC quantity (accordong to Table 3)

Fig. 6. Data on the pressure strength when changing the MC amount (according to Table 3)

The data on the influence of the third component, WG, when developing composities with MC, are shown in table 4.

Table 4. Data on the obtaining of composites based on UPER hydrophilized with the same quantity of MC when changing the WG amount. Quantities: UPER – 30 g, CN – 0.5 ml, MC – 21.5%, water – 50% compared to the SC quantity, CHP – 1 ml

Composition No.	WG quantity %	Time [τ, min]	Temperature [T max., ˚C]
1	-	122.5	34
2	2.52	58	113
3	4.91	31	114.5
4	7.18	35	100
5	9.36	50	83
6	11.43	43	66.5

The kinetics of polymerization processes of such compositions was traced and the impact and pressure strengths were studied. Those results shall be presented in the future.

4. Conclusion

There are alternating maximums and minimums and it is determined by different factors, polyemrization first; moreover, there may be emulsion of cement milk in the resin, as at higher concentrations, there will be emulsion of resin in the cement milk, respectively. Therefore, phase inversion could be expected at higher concentrations. It can be assumed that the emulsion containing drop-shaped cement milk cures before the resin and vice versa, where cement cures slowly, resin cures first. It could be expected that interpenetrating polymer/silicate networks have been obtained. In such cases, curves necessarily follow minimums and maximums and when the curves are of the right Gaussian character, it would mean that polymer-silicate mechanical blends were obtained. At the same time, although the polymer and silicate are two different skeletons, they are interconnected because each resion molecule has turned into soap. And the soap moistens and interacts with cement, which does not inhibit the resin polymerization. Indeed, we have a lot of mazimums and minimums and very complex processes are under way, apparently depending on the polymerization process activity, sample compositions and structure formation processes. The completion of the polymerication process puts an end to resin curing and cement curing.

5. References

1. Radenkov, M., V. Trenev, V. Dikov, R. Cherkezova, Ph. Radenkov. On the noxious influence of the excess of moisture during polymer concrete obtaining. *Mechanics and Technology of Composite Materials.* 2009, 238-42.

2. Radenkov, M., V. Trenev, V. Dikov, R. Cherkezova, Ph. Radenkov. An Approach to Eliminate the Adverse effect of Increased Humidity on Formation of Polymer Concrete. *Mechanics and Technology of Composite Materials.* 2009, 242-48.

3. Черкезова, Р; 2001. Многокомпонентна полимерна система на основата на хидрофилизирана ненаситена полиестерна смола и методи за получаването й. BG Patent 63168.

4. Cherkezova, R; An. Topliyska, F. Radenkov, B. Milosheva. Dynamics of hardening of polyester-silicate adaptive compositions for binding silicate concrete with polyester polymer concrete. *Journal of polymer engineering*. 2005, 1(25), 11-21.

5. Cherkezova, R., Ph. Radenkov, M. Radenkov, T. Hristova, K. Zafirova, N. Todorov, A. Popov. 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. In: Materials, Methods & Technologies, 26-30 June 2016. *J. Int. Sci. Pub.*, 10, 2016.

6. Sarami, N., L. Mahdavian. Comparison of artificial stone made from sludge stone with travertine stone waste of stone cutting factory. *Int. J. Eng. Res. Africa*, 23, 2016, 64-71.

7. Adi Kristiawan, S., A. Bekti Prakoso. Flexural behaviour of patch-repair material made from unsaturated polyester resin (UPR)-mortar.In: International Conference on Advanced Materials Engineering and Technology, ICAMET 2015; Kaohsiung; Taiwan; 4 - 5 December 2015. *Materials Science Forum, 857, 2016, 426-30.*

8. Gupta, S.U.C., V.N. Pillai, S.S. Gupta. Development of hovercraft landing base/platform at seashore by cementicious MF polymer sea-sand composites. *Recent Innovations in Chem. Eng*, 8(1), 2015, 43-56.

9.Shettar, M., P. Hiremath. Effect of seawater on mechanical properties of GFRP with cement as filler material for fishing boat application. *Int. J. Appl. Eng. Res.*, 10(19), 2015, 40027-30.