

CHEMICAL RESISTANCE, STRENGTH AND DURABILITY OF ACRYLIC COMPOSITIONS

L. Shutenko

Kharkov National Academy of Municipal Economy

S. Zolotov

S. Voliuvach

M. Zolotov

Kharkov National Academy of Municipal Economy

Abstract

In connection with wide application of acrylic compositions as glues for joining construction elements and as protection covering in construction it is necessary to predict their durability as well as strength and application technology. That is why the problem of chemical interaction of acrylic compound and a filler is considered to be very important.

There are no experimental data concerning the influence on strength, chemical resistance and durability of acrylic compositions and corrosion actions.

The experiments on determining the influence on physical and mechanic and physical and chemical properties of corrosion action: water, solutions of nitric, hydro chloric and sulphuric acids and caustic soda, waste engine oil have been carried out by the authors.

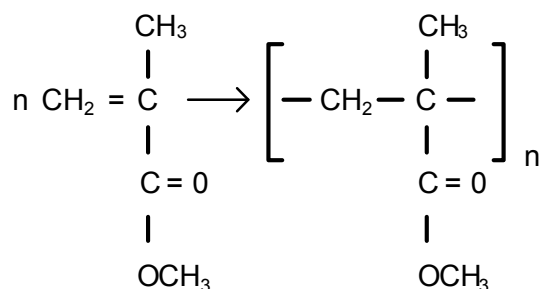
The experiments proved chemical resistance, strength and durability of acrylic compositions used as glues and covering.

Keywords: poly-acrylic glue, acrylic compound, filler, aggressive conditions, chemical resistance, spectrum analysis, phase analysis, thermal stability, physical and chemical properties.

INTRODUCTION

Due to wide use of acrylic compositions as glues for joining construction elements and as protection covering in construction it is necessary to predict their durability, strength and to improve the technology of glue compositions production. That is why the problem of chemical interaction of poly-acrylic compound as a binding material for glue with filler is considered to be very important.

The acrylic compound of cold hardening under consideration belongs to the group of mixed glue compositions on the basis of powder (polymethylmetacrylate) and liquid monomer (methylmetacrylate). Hardening occurs under the influence of oxidizing and rehabilitation system from benzoyl peroxide and dimethyl-aniline as a result of monomer polymerization:



50-75 mas. % of grinded quartz sand with the size of not more than 0,63mm is used as a filler for a glue composition [1-3].

EXPOSITION

Adsorption interaction characterizing physical and chemical properties of not only hardened but also forming polymer is considered by Yu. Lipatov [4] to be one of the main processes, determining the properties of filled polymer. It is explained by Yu. Lipatov as a result of boundary layer appearance on a hard surface of a filler having the structure and properties different from polymer in volume. Adsorption interaction of polymer with hard phase of a filler and additions causes the changes in boundary layer structure, temperature of thermodynamic and structural transitions, decreases the mobility of polymer chains and elements of permolecular structures and the number of conformations of a chain molecule of a given layer.

The interaction of adjoining phases is determined by molecule and surface phenomena and depends on chemical nature of polymer and fillers, chain regularity degree and permolecular regulation of polymer in permolecular formations. The interaction of permolecular structures occurs due to molecules interaction.

So, physical and mechanic and physical and chemical properties of polymer compositions can be changed within wide limits by changing the morphology of permolecular structures and the level of completion of spatial molecules of polymer binding material.

Long-term influence of corrosive media on acrylic composition has been investigated for studying its maintenance properties. Such corrosive media as water, 5% aqueous solution of nitric acid, 10% aqueous solution of hydrochloric and sulphuric acids, 10% aqueous solution of caustic soda and waste engine oil have been used.

Physical and chemical and physical and mechanic methods have been applied for the research. Spectral analysis has been used as physical and chemical method. It is based on the ability of a polymer substance to interact with the electromagnetic radiation field in infrared area of power spectrum. The changes of a form and the position of absorption strips caused by interaction of organic radicals with active centers on silicate surface have been revealed.

The comparison of infrared spectra of films on inner and surface layers of acrylic compositions samples held in corrosion media for 12 months showed that the character of spectra of all samples was identical, only the intensity and correlation of some strips changed. So, infrared spectra of films on inner and outer layers of samples held in water fully coincide in intensity almost for all strips. In infrared spectrum of acrylic polymer sample: hardening material: sand (100:100:150) (fig.1) the strips appear at 3400 cm^{-1} caused by molecules of fixed water and free hydroxylic groups. The adsorption of water molecules is evident to occur on the surface and inner layer of samples. Moreover, the increase of absorption intensity of a strip 1070 cm^{-1} of valent fluctuations of bond $C-H$ of zigzag polymer chain sensitive to molecule configuration change. At the same time the appearance of new strips of 800 and 780 cm^{-1} , concerning the fluctuations of group $C-O-C$ has been observed. The same changes in infrared spectra of films occur under the influence of hydrochloric acid on the composition samples. The comparison of the spectra on inner and outer layers of acrylic compositions samples treated with hydrochloric and sulphuric acids

showed (fig. 2,3) that the intensity of strips absorption of infrared spectra on surface layers films was lower than that on inner layers. The intensity correlation change is indicative of the greater influence of acids on the surface layer.

Unlike the spectra considered above strips intensity on surface layer films treated with nitric acid (fig. 4) was higher than that on an inner layer. The intensity of a strip absorption in the field of 1400 cm^{-1} increases in infrared spectra of samples treated with H_2NO_3 and H_2SO_4 and its splitting is observed. Deformation symmetric fluctuations of a bond $-CH$ in oxymethyl group $-O-CH_3$ and symmetric fluctuations of a bond $-CH$ in methyl group CH_3 appear in this field. Mention should be made that no great changes in the character and intensity of a strip of valent fluctuations of group $C=O$ at 1720 cm^{-1} have been observed. Besides, the intensity of strips of 1070 , 990 and 960 cm^{-1} in spectra of films on samples inner layers treated with acids, alkali solutions and water increased and it was caused by fluctuations of flat zigzag chain and valent fluctuations of groups $C-O-C$ and CH_3O . And the intensity of strips in the field $1300-1100\text{ cm}^{-1}$ related to intramolecular interaction of complicated etheric bond also increased. The strips at 3400 cm^{-1} appear in all samples of films obtained from inner layers.

When treated with alkali infrared spectrum of acrylic composition samples did not show any changes as compared with a sample spectrum treated with water (fig. 1). Both samples are much similar to strips intensity in the field $1200-1700\text{ cm}^{-1}$ and $2800-3000\text{ cm}^{-1}$.

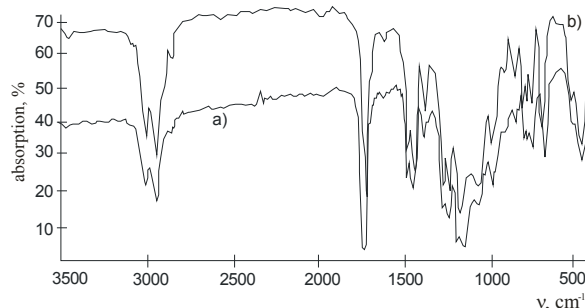


Fig. 1. Infrared spectra of acrylic composition samples held in water: surface (a) and inner (b) layers

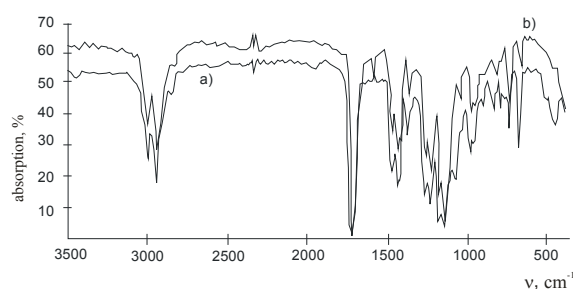


Fig. 2. Infrared spectra of acrylic composition samples treated with hydrochloric acid: surface (a) and inner (b) layers

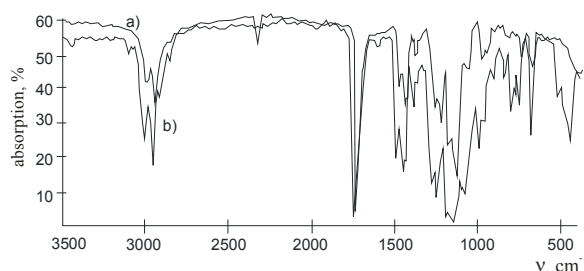


Fig. 3. Infrared spectra of acrylic composition samples treated with sulphuric acid: surface (a) and inner (b) layers

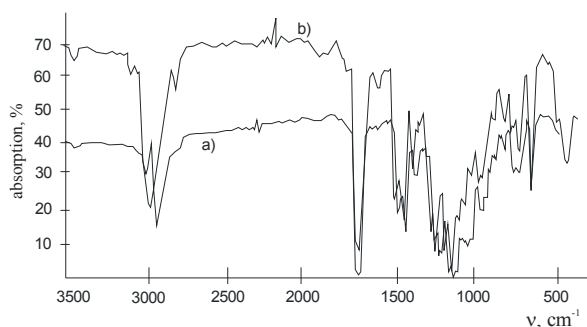


Fig. 4. Infrared spectra of acrylic composition samples treated with nitric acid: surface (a) and inner (b) layers

The changes occurred in a frequency field 3500–4000 cm^{-1} . When treated with alkali hydrolysis of complicated etheric bond may be observed, but the frequencies of $-\text{COOH}$ -group do not appear in a sample spectrum as overlapping of strips of complicated etheric and carbocryle groups may occur. That is why it is impossible to speak synonymously about possible changes in chemical nature of polymer solution.

When treated with oil absorption intensity increase was observed in the field of 1465 and 3000 cm^{-1} , which could be caused by valent fluctuations of saturated oil groups.

From the data obtained it can be concluded that in corrosive media some splitting of complicated etheric bond and formation of molecule interaction with water and other reagents may occur.

Phase analysis of samples held in mentioned above corrosive media was carried out using X-ray diffractometry. The analysis of X-ray photographs (fig. 5) shows that phase structure of the investigated material does not change under different chemical influence: diffractograms contain only diffractive maximum of quartz.

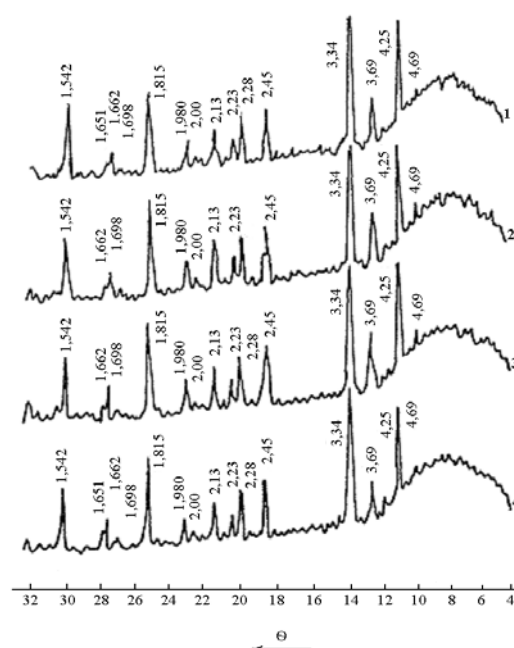


Fig. 5. X-ray photographs of acrylic polymer solution after long-term influence:
1 – normal temperature and humid conditions;
2 – water medium; 3 – waste engine oil;
4 – atmosphere

While investigating thermal stability of samples in mentioned above corrosive media derivatorgrams were made. The analysis of derivatorgrams curves (the velocity of mass changes (table 1) of acrylic solutions samples showed that the process of thermal destruction started at temperatures 175, 145, 185, 210, 160 $^{\circ}\text{C}$ and lasted till the temperature was 270, 210, 240, 260, 250 $^{\circ}\text{C}$ with constant velocity (table 1). Mass losses were equal to 5, 4, 4, 5, 6, 5 %. At elevated temperatures the velocity of mass changes increased. The processes reached their maximum at 380, 390, 390, 370, 380, 410 $^{\circ}\text{C}$ and were over with mass losses equal to 40, 53, 55, 45, 48, 52 %.

Table 1 – The temperature of the main thermal effects

№	Chemical reagent	The main temperatures, t°C			
		Thermal destruction	Endo-effect	Exo-effect	End of the process
1	Water medium	175	320	380	270
2	5% solution of hydrochloric acid	145	335	390	210
3	10% solution of nitric acid	185	315	370	240
4	10% solution of sulphuric acid	210	310	380	260
5	10% solution of caustic soda	160	300	410	250

According to the curves of differential and thermal analysis the samples decomposition and evaporation of volatile products occurred until the temperatures were equal to 320, 335, 315, 310, 300 °C. It resulted in peak indices of thermal energy absorption on endothermic curves. Endothermic effect on the curves of derivatorgrams was followed by marked peak of exothermal effect connected with combustion of non-volatile part of thermal destruction products of the composition under investigation. The maximum of exothermal effect was observed at 380, 390, 390, 370, 380, 410°C. The analysis of table 1 show that thermal effects and the velocity character of destruction process are almost identical.

The method of temperatures comparison corresponding to 5, 10 and 15% of mass losses was applied for estimating thermal stability of polymer solution. Thermal stability of a surface and an inner layer was investigated for each sample. The results are given in table 2.

Table 2 – Thermal stability of acrylic polymer solution samples

№	Layers	Chemical reagent	The temperature at which mass losses are equal to (%)		
			5	10	15
1	Normal conditions		287	310	329
2	surface	H ₂ O	286	307	319
	inner	H ₂ O	283	307	318
3	surface	HCl solution	272	297	311
	inner	HCl solution	274	307	322
4	surface	H ₂ NO ₃ solution	282	306	318
	inner	H ₂ NO ₃ solution	288	314	328
5	surface	H ₂ SO ₄ solution	268	294	307
	inner	H ₂ SO ₄ solution	270	397	315
6	surface	KOH solution	272	398	314
	inner	KOH solution	274	304	318

The data obtained showed that the temperatures characterizing decomposition of the investigated compositions in surface and inner layers do not differ greatly.

The samples, treated with water and nitric acid for 12 months are known to have the highest thermal stability.

Thermal stability indices of samples treated with hydrochloric acid and alkali are almost identical. Samples treated with sulphuric acid are characterized by the highest thermal stability.

Physical and mechanic investigation showed that visual appearance and the size of samples did not change. Under the influence of water, acids, alkali and waste engine oil only mass changes were observed (fig. 6a). In the first 70-80 days of treating the samples with chemical reagents sharp mass increase was observed. Treatment with sulphuric acid caused 0,78% increase of mass, with nitric acid 0,67% and with caustic soda – 0,42%. After 80, 120, 160, 130, 150 and 180 days of treatment with acids, water, oil and caustic soda no mass changes were observed (fig. 6a).

The coefficients of diffusion *D*, sorption *S* and permeability *P* and the mass of chemical reagent absorbed by a treated sample *M_p* (table 3) were calculated on the results of experiments.

Absorption of water is 2,2%, of waste engine oil – 1,3%, of hydrochloric acid – 3,9%, of sulphuric acid – 3,85%, of nitric acid – 3,5% and of caustic soda – 1,55%.

Table 3 – Coefficients of diffusion, sorption and permeability

№	Chemical reagent	Coefficients			Absorption of chemical reagent <i>M_p</i> , %
		Diffusions <i>D</i> , cm ² /c	Sorptions <i>S</i> , g/cm ³	Permeability <i>P</i> , g·cm/cm ² ·c	
1	Water	0,35	0,024	0,011	0,33
2	Waste engine oil	2,1	0,12	0,049	0,24
3	10% hydrochloric acid solution	0,45	0,052	0,023	0,77
4	10% sulphuric acid solution	0,39	0,027	0,026	0,79
5	5% nitric acid solution	0,63	0,059	0,053	0,68
6	10% caustic soda solution	0,9	0,020	0,022	0,43

The strength of acrylic compositions tested on compression increased during the first 60 days by 11,8; 9,2; 8,5; 6,8; 6,0%. During the next 400 days strength reduction was equal to: for water – 14,7%, for hydrochloric acid – 1,48%, for sulphuric acid – 1,8%, for caustic soda – 3,6%, for oil – no strength reduction was observed. Under the influence of nitric acid strength reduction by 13,4% was observed during the first 330 days. The strength did not change later (fig. 6b).

The investigation of corrosion resistance of acrylic composition showed that long-term influence on corrosive media does not exert an adverse effect on its physical and mechanic properties. The strength reduced by 14,7% and the mass of samples increased only by 0,87%.

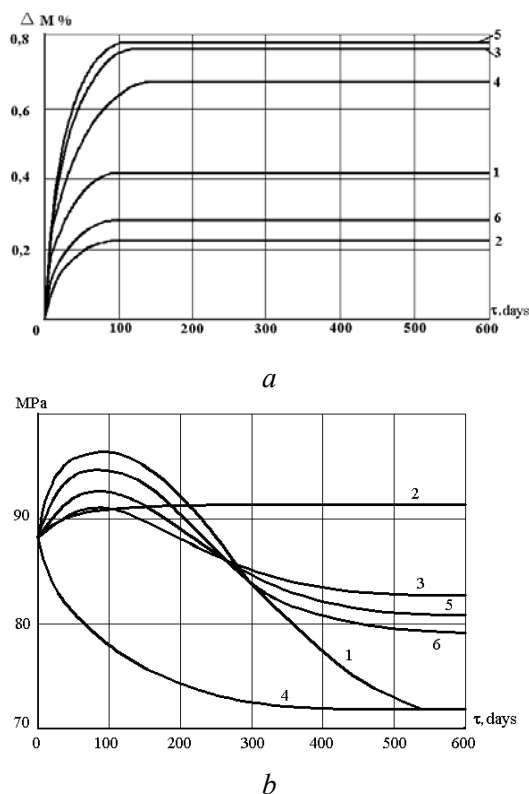


Fig. 6. The change of mass and strength of acrylic composition samples under the influence of corrosive media:
1 – water; 2 – waste engine oil; 3 – hydrochloric acid solution; 4 – nitric acid solution; 5 – sulphuric acid solution; 6 – caustic soda solution

CONCLUSION

So, acrylic compositions possess sufficient chemical resistance, strength and durability and can be used as materials for reliable protection of construction structures from corrosion, as well as for glue joining of construction elements.

REFERENCE

- [1] Zolotov S. Adhesive on the Basis of Acrylic Compound to Join Concrete and Reinforced Concrete Elements // Science, Education and Society: 11 International Scientific Conference University of Zilina. Slovak Republic, part I, 2003. – P. 323-325.
- [2] Золотов С.М. Акриловые клеи для усиления, восстановления и ремонта бетонных и железобетонных конструкций // Будівельні конструкції: зб. наук. праць. – К.: НДІБК, 2003. – Вип. 9. – С. 440-447.
- [3] Shutenko L., Zolotov M., Zolotov S. Compositions on the basis of acrylic polymers for repairing cement-concrete pavements and reinforced concrete bridge structures // Proceedings of the 1st Polish Road Congress. – Warsaw, October 4-6, 2006. – P. 443-450.
- [4] Липатов Ю.С. Физико-химия наполненных полимеров. – К.: Наукова думка, 1987. – 167 с.