Volume 1 Issue 1



Trade Science Inc.

Research & Reviews On Polymer

Full Paper

RRPL, 1(1), 2010 [35-42]

Influence of nature and concentration of silica on swelling (in water/acid environments) and structure of polyepoxy composites

Starokadomsky Dmitro*, Telegeev Igor

Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine, Kyiv, (UKRAINE) E-mail : stard1@mail.ru Received: 13th July, 2010 ; Accepted: 23rd July, 2010

ABSTRACT

It was determined that silica addition in epoxypolymer is able to activate swelling process in 11 solutions of the hydrochloric and nitric acids, and to reduce in water and concentrated nitric acid. By nature of influence on the swelling process silica are divided on coarsely dispersed (specific surface 50-100 m²/g), middle dispersed (100-300 m²/g) and finely dispersed (300-500 m^2/g). It was define that the swelling process of composites in 2-5 times intense in acids solutions than in water, and in nitric acid in 1,5-2 times is more intense than in the hydrochloric (5-10 % against 3-6 % after 100 days). The swelling curve does not reach saturation in acids unlike of water medium. It was explained by the processes of decomposing (dissolution), and in concentrated nitric acids the swelling reach 40-60 % and concludes for 6-8 days of decomposing producing foam solution. It is shown that the swelling of the filled composite material can be weaken noticeably in the field of 5 wt. % (comparing both with others concentrations, and with unfilled composites), in particular for water, solution of the hydrochloric and concentrated nitric acids. By microscopic techniques (SEM, AFM) it is shown that silica influence on the swelling process can be related to decrease in an amount of pores and its distribution and also appearance of a structure « silica agglomerates in polymer» and «polymer in silica agglomerates». © 2010 Trade Science Inc. - INDIA

INTRODUCTION

There is a permanently necessity of an increase of epoxypolymer (EP) material resistance (of decomposing, dissolution, swelling process) in various liquid mediums while exploitation. When using such material and adhesives in polygraphy their inactivity in organic solvents, in shipbuilding - to salt solution, in automobile industry - to acid and to alkaline conditions is required.

KEYWORDS

Silica; Specific surface; Filling; Concentration; Swelling; Acids; Epoxypolymer; Structure; Pores; Agglomerates.

For instance, losses of the adhesive stability of epoxy adhesives in polygraph business resulting to excess expenditure for restoring of printers and plotters impact dot matrix. High stability to acid mediums is required in construction and transport branches.

It is known^[1,2], that epoxypolymers is quite stable in the water, naphthenic, alkaline conditions, however are nonresistant in a number of practically relevant mediums, for example in concentrated solutions of the

Full Paper -

hydrochloric and nitric acids. It's undoubtedly narrows down a field of their application. Therefore the problem of improvement of epoxypolymers items and adhesives stability in various medium is actual. One of technological simple techniques of polyepoxides properties optimisation is filling.

Literature^[1-4] on influence of pyrohenic nanosilica (SiO) and other filling compounds on stability of polymers in liquid mediums is quite often confined by quality standards, for instance 2-3 mark scale (stable-instable, good-neutral-bad etc)^[2]. Meanwhile, most of composite items are exposed to exploiting at atmosphere or in aggressive environments. It has unpredictable agency to their properties sometimes. Integrated investigation of SiO influence with various particle dispersity on swelling process in acid mediums was the purpose of the work. Based on surface chemistry^[6] it is possible to expect that addition of such industrial nanofiller as pyrogenic high dispersed silica dioxide can influence significant to epoxypolymers swelling process. Silica self-structurization feature in oligomers and monomers allow supposing that it could enrich stability of EP in aggressive medium even in case of unmodified SiO surface.

EXPERIMENTAL

Standard epoxypolymer template based on ED-20+12.5 wt.% of polyethylene-polyamine PEPA was used as experimental models. It was filled with silicas À-50, À-100, À-175, À-300, À-455 (number correspond to the value of specific surface area in m^2/g). Used silicas: A-50-Degussa (Germany), remaining -Kalush factory ISC NASU (Ukraine). The concentration of filling compounds was C=1, 3, 5, 10, 20 wt. %. Aerosils was load into a warm polymer template, mixed and keep during 1-2 months, periodically realizing additional mixing of a warm composition. The composition warmed up, loaded 12.5 wt.% of PEPA, intensive mixed 5-10 minutes after completion of 'ripening' process. It is significant that vacuum pumping of final mixing has been considered as ineffective, and was not made because of high viscosity of compositions (especially highfilled) and high speed of primary gelation of process of solidification. Mixing of composition was car-

Research & Reviews Dn Polymer rying out by spiral motion ('mini-mixer') of inert needle. Then composition warmed up (70-90°Ñ) for 2-3 minutes for the maximum deleting of the individual macrobubbles of air. After composition homogenization was cured on air at an indoor temperature and the subsequent exposure of the solidified samples under normal conditions during 3-4 months. After that, without additional thermal processing, formated samples placed in a liquid medium. The cured samples with diameter of 1 cm, width of 2-3 mm and average weight 0.2-0.3 g were used for learning of swelling process of filled compositions. Swelling process was investigated by samples weight change (platters 10×1 mm) in water, in 11 solutions of nitric and hydrochloric, and also concentrated nitric acids. Swelling degree measured by a mass change of samples $q = ((m_1 - m_2)/m_1) \times 100 \%$ $(m_1 \text{ and } m_2 \text{ - current and initial mass of a samples}),$ dried 40-60 minutes at indoor temperature. Samples were investigated by SEM and AFM-microscopy by standard procedure. The structure of the composites was determined by FT-IR (Thermo-Nicolett).

RESULTS AND DISCUSSION

Swelling of EP with SiO

As it is known, stability of epoxy polymers in water is highly important (the limiting swelling process ranged in 1-2 %): curves q-t for this samples it is shown in figure 1(e, f). However, in a number of aggressive environments, first of all in acid, swelling process is much more intensive, than in water. The q index and the swelling process in acids are in 2-3 times higher, than in water (Figure 1). The short-term field of outwashing is appear in water during the first hours of an exposure (during of the first 10-30 minutes q value is negative), that it is not noticeable at an exposure in acids. Instead of water medium, in acid mediums the common feature - is lack of threshold of limiting swelling process on a curve. The swelling processes curve q (t) in an acid do not saturate, but may have inflexion point (Figure 1) when swelling process slow down (Figure 2), after one growth q (t) is resume - probably as a result of dissolution (decomposing) processes. It allows considering, that two processes - swelling processes and (gradually accelerated) dissolutions/decomposition is combine in

Full Paper

wt.%	A-100			A-175			A-300		
	hydrochloric	nitric	water	hydrochloric	nitric	water	hydrochloric	nitric	water
0	2,55	3,19	1,83	2,55	3,19	1,83	2,55	3,19	1,83
1	2,77	4,08	1,76	2,65	3,36	1,85	2,84	3,45	1,6
3		4,88			3,94			6,27	
5	2,38	4,51	1,38	2,68	5	1,47	2,38	7,65	1,54
10	3,56	6,04	1,67	2,96	6,19	1,69	4,54	9,59	1,76
20	4,77	8,87	1,43	6,23	11,94	1,68	4,68	14,21	2,25
wt.%	A-455						A-50		
	hydrochloric	nitric	water			wt.%	hydrochloric	nitric	water
0	2,55	3,19	1,83			0		3,19	
1	3,37	5,05	1,76			1		4,57	
3		4,76				3		5,92	
5	3,24	7,07	1,69			5		5,2	
10	3,68	8,19	1,51			10		7,7	
20	4,45	20,19	1,69			20		9,11	

TABLE 1 : Dependence of swelling value q on concentration of SiO, at an exposure of 90 days (for the hydrochloric-88, for water and nitric - 95)

acid. Really, samples after 3-4 months turn yellow in HCl, and in HNO3 - turn brown, take elasticity, and at high fillings up are scattered. Obviously, this determines very fast swelling process with decomposing in 7-10 days in concentrated nitric acid (Figure 2Å). According to the received data, there is a livelier swelling process (and decomposing) aggregates in nitric acid, than in the hydrochloric. So, a virtual velocity of swelling process and value q in nitric acid (especially at later phases) in 1,5-2 times above (Figure 1 and 2, TABLE 1).

Investigation of dependence of SiO concentration on swelling value q(C) has shown a number of interesting regularities. It is not linear more often, and in some cases is nonmonotone. Accurate correlation of decrease of swelling value q(C) with SiO concentration increase is observe for finely dispersed SiO (i.e. with a minimum size of particles) - À-455 and (for nitric) À-300, in remaining cases, it is disturbed already at 5 wt.% (TABLE 1, Figure 2, 3).

The analysis has shown, that small addition (in range of 1 wt. %) not always result in to an noticeable modification of a swelling process curve line and it almost coincides with a curve line of an unfilled composite material (Figure 1à; Figure 2a). But for the majority of SiO in HNO3 and HCl (and for high-disperse À-300 and À-455 - also in water, Figure 1), difference from initial (0 wt. %) curved line has already well noticeable even at 1 wt. % (Figure 2, Figure 3, TABLE 1).

In solutions of acids (and for water), at 5 wt. % it is less intensive swelling process in comparison with adjacent concentrations. It apparently explains by consolidation of the polymer net and appearance of a frame from SiO particles (TABLE 1, Figure 1 and Figure 2). Regularly watched in most cases (till 25 composites from 4-5 types of silica in acid and even in aqueous mediums) swelling degree decrease in range of 5 wt.% can be evidence of the existence of optimum concentration of an aerosil, from the point of view of chemical resistance of composites to action of aggressive mediums. Tendency of lowering of swelling process in the field of 5 wt.% drops with growth of specific surface of SiO, especially it is visible in 1M nitric acid, where even for middle dispersed composites À-175 and finely dispersed À-300, À-455 swelling process increases with filling growth (Figure 2b-d). From here follows that at certain concentrations of SiO and in dependence on its specific surface the specific frame of a composite material with heightened polymeric net density can be formed.

At high C, the swelling degree increase in comparison both with 0 wt. %, and with 1-5 wt. % (Figure 1, Figure 2) is watched. As a rule, at transition from 5 to 10 and especially 20 wt. % clear positive correlation $q\sim$ C (Figure 1à, b, g, Figure 2 b-d, TABLE 1), some-





times with repeated growth q (Figure 1 and, Figure 2 b-d) is watched. Apparently, a determining factor of swelling in acid solutions at high fillings becomes loosening as the polymer net, and also aggregate (coagulation) frame of particles of a filler, with availability (the more it is the higher filling) islets inclusion of a filler (Figure 4). At the same time, this rule of proportionality q~C has quite a lot of exceptions, for example curves for samples with 10 and 20 wt.% À-300 in the hydrochloric and À-50 in nitric acid are identical (Figure 1b, Figure 2À). At growth or lowering of an acid the regu-

larity q~C stops to show, that is visible on example of composites in concentrated nitric acid and water (Figure 2Å, Figure 1d and e). We will notice, that swelling process growth at filling 10 wt. % (compared with 0 wt. %) does not mean worsening of hardness of a composite. For example under our data (in article are not brought), compression strength of composites and hardness on the adhesive displacement (at pasted together metal or glass-fiber plates) do not lower compared with unfilled polymer.

Systematise the received experimental data is pos-



Figure 2 : Swelling process of epoxy polymers from 0-20 wt.% of SiO (unmodified) in 1Ì to hydrogen nitrate and (for comparison) the concentrated nitric

sible, by having parted on character of influence of SiO on 'coarsely dispersed' and 'finely dispersed' groups. The behaviors of composites with À-175 (Figure 1 and 2) displays, that can exist also the intermediate group «middle dispersed» SiO, generalize properties of other groups. Finely dispersed SiO display the influence even at small concentrations (especially for À-455) is more often, and dependence q~C which one strengthens with growth of specific surface of SiO is characteristic for them. In fact, for finely dispersed SiO as a rule, of concentration growth gives swelling process growth (Figure 1, Figure 2). For coarsely dispersed SiO, naturally comparative decrease of intensity of swelling process at 5 wt.% when the swelling process curve lays down below curves for 3 wt.% (Figure 2a, 2b) and even for 0 and 1 wt.% (Figure 1a, b).

Positive correlation of swelling degree and specific surface of filler at 20 wt. % is also visible. It was explained by amplification of a self-aggregation of SiO in polymer and, accordingly, a irregular distribution of a



Figure 3 : SEM - and the AFM-photos of epoxypolymer (in various scales) unfilled (a-g) and filled. In brackets year of composition manufacture is mentioned

filler with growth of specific surface of particles.

Apparently from figure 1, swelling degree q of samples in HCl (3-5 % after 100 days) in 2-3 times exceeds indexes q (1.5-2 %) in water. In HNO3, an index q still higher, that is especially visible at high fillings, for which after 100 days q=9-15 %, and sometimes also 17-20 % (Figure 2d). For acids, several times higher and value of a effective velocity of swelling (accordingly 0,05 and to 0,1 %/per day accordingly in the chlorhydric and nitric), than in water (0,025 %/per day). Similar data q (t) are received for other SiO in the chlorhydric and nitric acids. As a whole, filling intensifies swelling process in acids while in water (Figure 1d, e, see also^[8]) weakens it.

Filled epoxypolymer structure

Experimentally observable change of swelling process in consequence of filling should be the result of restructuring of polymer under the influence of filling. In fact, both from SEM-photo, and from AFM-images it is visible (Figure 3), that the whole surface of unfilled epoxypolymer is covered by pores. The porosity is not

related to application of porophore and to quality of reagents (it is showed in samples from different parcels of resin and a curing agent), and is characteristic for epoxypolymer received on an ordinary process engineering (in a household activities, on service, on production etc). It is possible that, the appearance of pores is connected to the presence of micro-bubbles of air (coming with an aerosil or during mixing), with presence of a moisture and admixtures in reagents, local exotherms at solidification, etc. In it's microstructure, as we can see, polymer is rather similar not to a stone monolith, but to a «bread or cheese in a cut». Pores represent paraboloidal formations with diameter of cut 0.5-1 of micrometers (by SEM data) and less (according to ASI). Their concentration is sizeable enough - sometimes till 70-80 per 100 mcm² (Figure 3à), or 20-25 vol. % by Rosivale method (the ratio of length of the cutting a surface segment passing through pores, to total length^[7]). The porosity obviously also determines comparatively intense character of swelling in acid mediums unadulterated polymer.

The quantity of pores decrease and influence on



Figure 4 : FTIR spectrums (reflectances) of epoxypolymers - 0 % without an exposure in HNO3 (on fig. 4À) and exposure 4 month in 1Ì HNO3 solution: A) 0, 1, 10 and 20 wt.% À-100; B) 0, 1, 10 and 20 wt.% À-455

their locating will allow to reinforce stability of a composite material and to reduce swelling process. It is achieved by SiO addition at which, nanoparticles form optimum structure of their own frame in polymer.

From literary data it is known^[3-6,8], that SiO is capable to form in non-harden polymer and other liquid mediums proper structures (chains, accumulations) of the aggregates forming agglomerates. It is visible from figure 3, that injection of little amounts of an aerosil (1-3 wt.%) result in visible lowering of an amount and enlargement of pores. On AFM-images (Figure 3j, k), 'nano-islets' of agglomerates of SiO in the measurement till 0.1-0.5 micrometers alternating with rare large pores are also visible. Thus, the surface of polymer from porous, but 'comparatively smooth' (when the dimensions of heterogeneities do not exceed 0.3 microns, figure 3 a, b) turns into much more rough (Figure 3 j, 1). Enlargement of pores is good noticeable also on SEMphotos figure 3e. As we see, even at 1 wt. % of filling the composite material has two phases: relatively it is «SiO in polymer» (Figure 3e) and «polymer in SiO» (Figure 3f) - in last SiO agglomerates have spongy (chondroid) frame. In a phase «the SiO in polymer» we can see noticeably smaller, than in unadulterated polymer, the quantity of pores in which individual particles or SiO agglomerates can be situated: on figure 3d it is visible such single pore on square 100 mcm². On more large-scale picture (Figure 3g) both phases of the polymer composite are clearly distinguishable.

It is visible from figure 4, FTIR of samples after an exposure in nitric acid noticeably differ from infra-red spectrums initial only in the field of 2200-2800 and 1757 cm⁻¹ (intensity increase). Thus the position of all signals

does not change, new stripe are not appearing. About the same takes place after polymer filling. Influence of a filler is showed in the way that, comparative intensity of some signals is changing (without change of location) for example 1885, sometimes 2200 cm⁻¹. At the same time, intensity of signals 1885 (deformative of benzene ring^[6]), 2800-3000 (It - $\tilde{N}I_2$ -, $\tilde{N}I_3$ -), 1610 cm⁻¹remains without changing. From this it is possible to conclude, that an exposure in thin nitric acid inflated epoxycomposite does not changes its chemical composition.

At the same time, it is possible to speak about major changes of structure of a composite with a filling, swelling process becomes their indicator. First of all, it is a question of enlargement of agglomerates with growth of a filler concentration. Already at 1 wt. % of filling agglomerates are clearly visible on received SEM - and the AFM-images (Figure 3). The influence of proper structures of SiO at small fillings (1 wt. %) is showed in visible growth of degree of swelling, especially in nitric acid (Figure 2). Enlargement of agglomerates, possibly, firstly leads to regulating, and then to enlargement C - to loosening of the polymer net and a frame from aggregates of a filler. Imposition of these two impacts structuring and loosening, is most obviously displayed at filling 5 wt. %, when there is a swelling value decrease (and not only in polyepoxides, but also polyetheracrylates^[5]), and also at 10-20 % because of an loosening swelling process strongly increases.

CONCLUSIONS

The behavior of unfilled polyepoxides in 11 acids



Full Paper 🗆

solutions is defines by lack of the limit degree of swelling: on an swelling process curved line for 60-80 days of an exposure there is a field «quazisaturation» after which swelling process renews. Outside of dependence from the specific surface, all silicas influence on swelling process in each medium in a similar way. At the same time, it is possible to evolve three groups of SiO coarsely dispersed (specific surface till 100 m²/g), middle dispersed (100-300 m^2/g) and finely dispersed (300-500 m²/g). According to studies, coarsely dispersed silicas differ more strongly and expressed influence on epoxypolymer swelling process (and therefore on structure), than superfine. At the same time, with growth of specific surface of SiO becomes more and more expressed a direct relation between its concentration and swelling degree of a composite material is formed.

Swelling process epoxypolymers in acids is nonmonotone depends on concentration of silica and in a certain measure depends on its specific surface. Small additions (within 1 wt. %) not always noticeably influence the swelling process curve, but with growth of filling swelling process in the hydrochloric and nitric acids it strengthen. At the same time there is a field of concentrations of silica (in environs 5 wt. %) where swelling process in acid and aqueous mediums is relaxed, especially for coarsely dispersed SiO. Most actively swelling process growth in an acid goes at high concentrations of silica - at 10, and especially at 20 wt.% (Figure 2). At filling 20 wt.%, correlation of growth of the swelling process in 1Ì nitric acid with growth of specific surface of a filler is clearly visible. Received by AFM images of a epoxycomposites surface show irregularity of allocation of nanoparticles in polymer and shaping «nanoislets» from silica agglomerates. At the same time, pore size is enlarged, and their quantity lowers, with strengthening of a relief of a surface. It can be evidence of forming in a filling composite material as inspissations in polymer structure, and a proper frame from particles of filler, and also about forming of different defects, at different concentrations of composites that change swelling. In levelling of a strengthening effect owing to filling, the non-optimum aggregation and irregular allocation of particles of nanosilica in polymer can play an essential role.

REFERENCES

- E.Lee McKague Jr., Jack D.Reynolds, John E.Halkias; Journal of Applied Polymer Science, 22(6), 1643-1654 (2003).
- [2] J.S.Zuev; M:Chemistry, 230 (in Russian), (1972).
- [3] G.Y.Vorobyova; İ:Chemistry, 400, (in Russian), (1981).
- [4] V.A.Kochetkov, R.D.Maksimov; Mechanics of Composite Materials, 32(1), 61-70 (1996).
- [5] D.L.Starokadomsky; Plastic Masses (In Rusian), 2, 33-36 (2008).
- [6] A.A.Chujko; 'Chemistry of a Surface of Silicon Dioxide', Kiev: Publishing House, ISC NASU, Part.1,2, 1300 (2004).
- [7] V.V.Guzeev, L.A.Shulatkina; 'Plastic Masses', (In Rusian), Investigation of Nanofillers Dispergation in PVC Composites,4, 23-27 (2008).
- [8] D.L.Starokadomsky; Russ.J.Applied Chemistry, 81(12), 2045-2051 (2008).