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REINFORCEMENT OF EPOXY POLYMERS WITH HYDRIDE-SILYLATED FUMED SILICA

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Fumed silica (FS) is widely used in numerous fields of application, the plastics industry being one of the most significance, where FS has proved to be successful as an efficient thickening, thixotropic, and anti-settling agent, as well as reinforcing filler. Chemical modification of silica surface enlarges its functional capabilities. In particular, silica with grafted silicon hydride groups was found to be active in the processes of hydrosilylation of alkene and alkyne bonds in monomers during their polymerization, resulting in the formation of reinforced polymeric composites. Recently, specific epoxy resins have gained significance, and FS was found to be useful, particularly as rheological additive. The aim of this study was to evaluate the efficiency of hydride-silylated FS (HFS) as a potentially active reinforcing component for epoxy-based polymers. The activation energy for hydrosilylation of olefins is higher than that for ring-opening polymerization of epoxides, therefore, one may expect the latter process with participation of $\equiv\text{SiH}$ groups to proceed more readily.

HFS was obtained via FS treatment with triethoxysilane. The presence of grafted silicon hydride groups was confirmed by means of IR spectroscopy, and their concentration measured by titrimetric and spectrophotometric analysis was found to be about 0.4 mmol/g. FS-epoxy and HFS-epoxy composites were prepared by the corresponding filler introduction (2 wt. % loading) into the mixture of epoxy monomer and amine hardener. The resulted materials after curing were subject to compression, bending, and adhesion tests.

Compression tests revealed that filling with FS and HFS reduced the compressive strength by 10%, however, HFS-epoxy composite was found to possess an increased by 20 % Young's modulus for compression as compared to that for the unfilled epoxy polymer. Upon this, 2 wt. % loading with silicas keeps the ductility of the polymer. Also, silica-containing epoxy polymers showed an improved bending strength and bending modulus, the former being two times higher for HFS-epoxy composite than that for the unfilled polymer. The adhesion to steel was found to increase by more than 2 times upon filling with silicas, HFS-epoxy composite being also superior as compared to the FS-epoxy one. Thus, preliminary results indicate that fumed silica with grafted silicon hydride groups shows promise as active reinforcing filler for epoxy polymers.

Keywords: silica, silicon hydride groups, epoxy polymers, reinforcement

INTRODUCTION

Fumed silica (FS) is widely used in numerous fields of application [1, 2], the plastics industry being one of the most significance, where FS has proved to be successful as an efficient thickening, thixotropic, and anti-settling agent, as well as reinforcing filler [3]. Chemical modification of silica surface enlarges its functional capabilities. In particular, silica with grafted silicon hydride groups was found to be active in the processes of reduction in aqueous medium [4, 5] as well as in the processes of catalytic hydrosilylation of alkene bonds in monomers during their polymerization, resulting in the formation of reinforced polymeric composites [6]. Among the variety of the polymers, epoxides represent an important class of thermosetting resins. The abundance of their applications is vast, including, for example, aircraft, train and car manufacturing, electronic

assembling, jewelry, and so on [7]. Recently, specific epoxy resins have gained significance, and FS was found to be useful, particularly as rheological additive [3, 8]. The aim of this study was to evaluate the efficiency of hydride-silylated FS (HFS) as a potentially active reinforcing component for epoxy-based polymers. The activation energy for hydrosilylation of olefins (140–160 kJ/mol) is higher than that for ring-opening polymerization of epoxides (~110 kJ/mol) [9], therefore, one may expect the latter process to proceed more readily with participation of $\equiv\text{SiH}$ groups at elevated temperature during the epoxy curing, and likely with no need to use the costly catalysts.

EXPERIMENTAL

FS with a specific surface area of 300 m²/g (A-300, Kalush, Ukraine) was used as an initial

filler. HFS was obtained via FS treatment with triethoxysilane. The procedure of hydrophobic (SiH-1) and hydrophilic-hydrophobic (SiH-2) HFS synthesis was as follows.

SiH-1 synthesis: 20 g of silica A-300 were placed into the 3-necked glass reactor and 4 mL of triethoxysilane (95 % purity, Acros Organics) were added dropwise at high agitation speed. Then the mixture was agitated at the same speed for additional hour at room temperature. After that 10 g of the resulted powder were taken out for the SiH-2 synthesis, and the residual material was heated for two hours at 90 °C (to remove the reaction product – ethanol) and then at 140 °C for another hour (to remove the residual modifying agent).

SiH-2 synthesis: 10 g of silica obtained in the first part of the SiH-1 sample synthesis were placed into the 3-necked glass reactor and 1 mL of distilled water was added dropwise at high agitation speed. Then the mixture was agitated at the same speed for additional hour at room temperature. After that the resulted material was heated for two hours at 90 °C and then at 140 °C for another hour.

The presence of grafted silicon hydride groups in SiH-1 and SiH-2 samples was confirmed by means of IR spectroscopy, and their concentration measured by spectrophotometric analysis (the procedure is described elsewhere [10]) was found to be about 0.4 mmol/g. IR spectra were recorded using a Thermo Nicolet Nexus spectrophotometer within the region of wavenumbers 4000–400 cm^{-1} . For the spectra registration, the silica powders were mixed with KBr in a ratio of 1:10.

The morphology of initial and modified fumed silica samples was studied by means of SEM microscopy (Zeiss Gemini 500, Germany). The specific surface area of silicas was derived from the low-temperature nitrogen adsorption isotherms using the BET method (Quantachrome AUTOSORB-6B sorptometer, USA).

FS-epoxy and HFS-epoxy composites were prepared by the corresponding filler introduction (2 wt. % loading) into the mixture of epoxy monomer (Epoxy520, Czech Republic) and amine hardener (PEPA, resin:hardener ratio 5:1) at constant mechanical stirring under normal conditions, without vacuum treatment. After mixing, the compositions were treated at 60 °C for 5 min (to remove the air bubbles). After 3 days of initial curing, the resulted materials

were heat-treated at elevated temperature for 5–7 h for mechanical tests (compression, bending, and adhesion). Compression tests were performed using a L. Shopper press-machine and cylindrical samples ($D = 6.5 \text{ mm}$, $H = 11.0 \pm 0.5 \text{ mm}$) in accordance with ISO 604:2002. For bending tests (GOST 56810-2015), plates with a size of $6 \times 1 \times 0.2 \text{ cm}$ were made. Their bending fracture was carried out using a bending test machine with a length between the supports $L = 3 \text{ cm}$. The peel adhesion test was carried out according to ISO 4624:2002 and GOST 32299–2013, using steel cylinders with diameter 2.2 cm.

RESULTS AND DISCUSSION

The scheme of silica surface hydride-silylation is given in Fig. 1. The presence of three ethoxy groups in the silanizing agent molecule, although provides high reactivity, however, during chemisorption, leads to the formation of various surface structures as a result of mono-, bi-, or tridentate anchoring of the modifying agent molecules to silica surface. After the contact of modified silica surface with air moisture, some of the grafted ethoxy groups could hydrolyse to yield silanol groups. Nevertheless, at a relatively high concentration of grafted silicon hydride groups (above 0.3 mmol/g) the resulted silica for a while is poorly or not wettable at all with water. The purposeful hydrolysis of ethoxy groups via the water addition during the modification process allows one to obtain hydrophilized silica with almost complete substitution of organic groups with silanol ones, however, some part of silicon hydride groups may also hydrolyse to yield silanol groups, especially at elevated temperature.

Modification with triethoxysilane under quasi fluidised bed conditions applied only slightly decreased the specific surface of fumed silica – from 319 m^2/g (A-300) to 310 m^2/g (SiH-2). SEM images (Fig. 2) also confirm minimum influence of surface modification on the structure and morphology of silica primary particles and agglomerates.

Fig 3 shows IR spectra of the samples under study. The distinct narrow absorption band at 3750 cm^{-1} in the FS spectrum (A-300) is due to stretching vibrations of O–H in free silanol groups. This band is also registered in the IR spectra of SiH-1 and SiH-2. Its reduced intensity is a consequence of partial substitution of OH

groups as a result of hydride-silylation. In the case of SiH-1 (very low intensity) it indicates the presence of residual free silanol groups, and in the case of SiH-2 (higher intensity) it confirms the presence of additional $\equiv\text{SiOH}$ groups formed mainly due to ethoxy groups hydrolysis. The presence of absorption bands at about 2250 cm^{-1} (intense, stretching vibrations of Si-H bonds), and those in the region of $2900\text{--}2985\text{ cm}^{-1}$ (lower intensity, stretching vibrations of C-H

bonds) indicates the presence of grafted silicon hydride and ethoxy-silyl groups, respectively, at the surface layer of HFS. And again, less intensity of absorption bands attributed to the presence of ethoxy groups in SiH-2 sample as compared to those for the SiH-1 sample confirms, though not complete, hydrolysis of grafted ethoxy groups after hydrophilization of SiH-1 sample via its treatment with water.

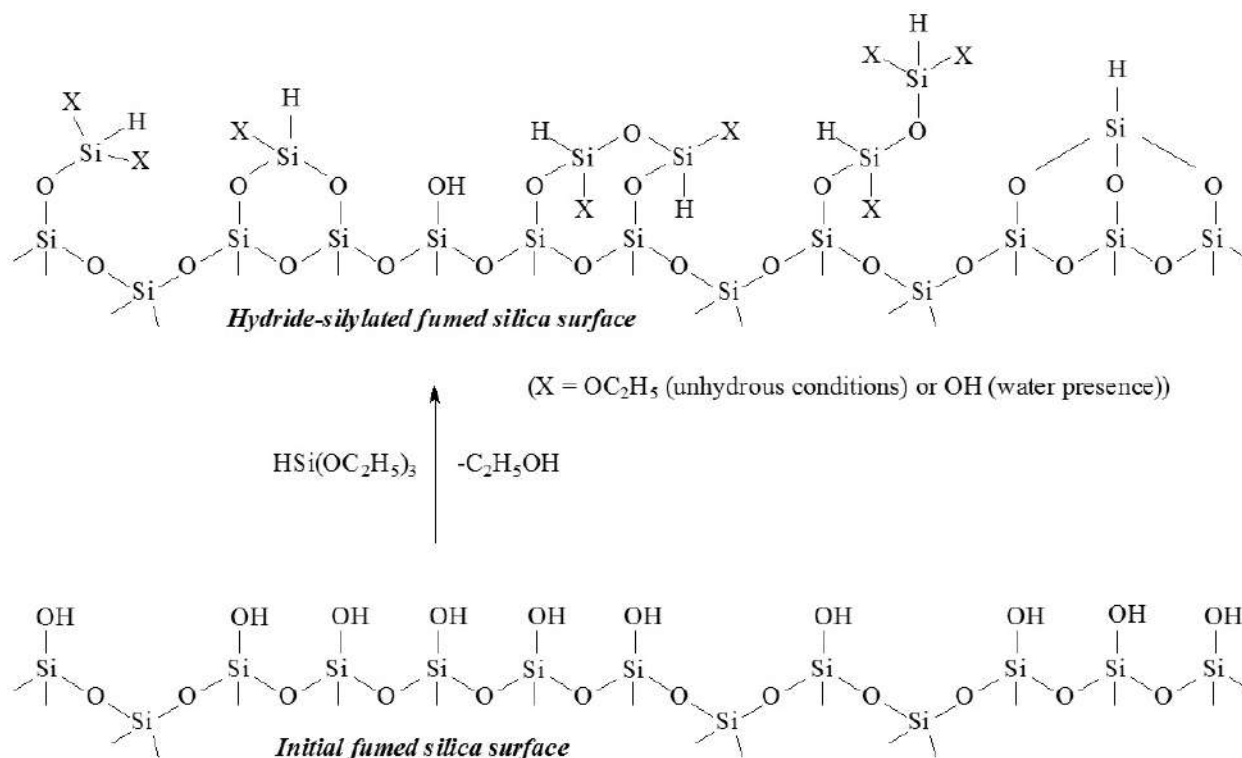


Fig. 1. A scheme of silica surface hydride-silylation with triethoxysilane. Some functional groups hydrolyze in air or during water addition to produce silanols (X = OH)

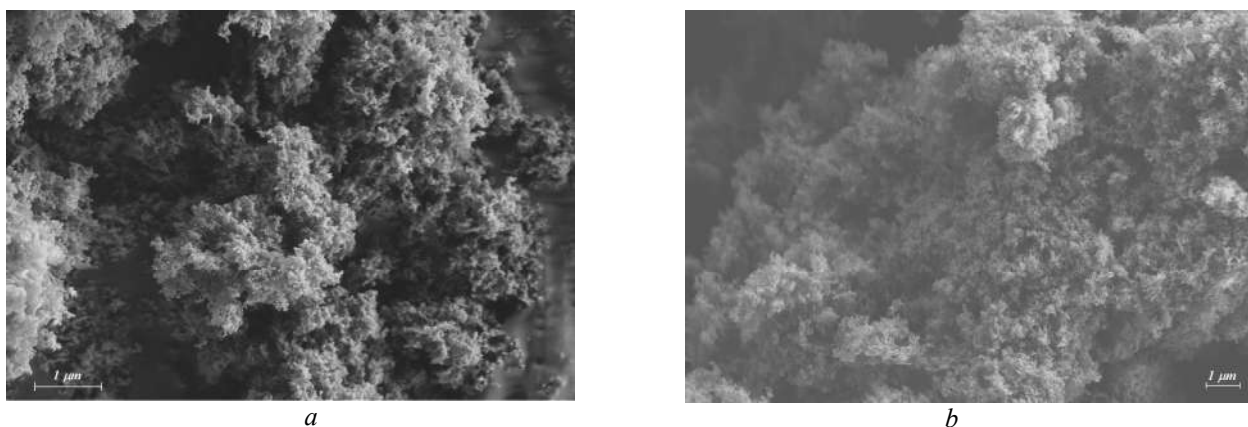


Fig. 2. SEM images of the initial fumed silica A-300 (a) and after modification with triethoxysilane and then with water (SiH-2 silica) (b)

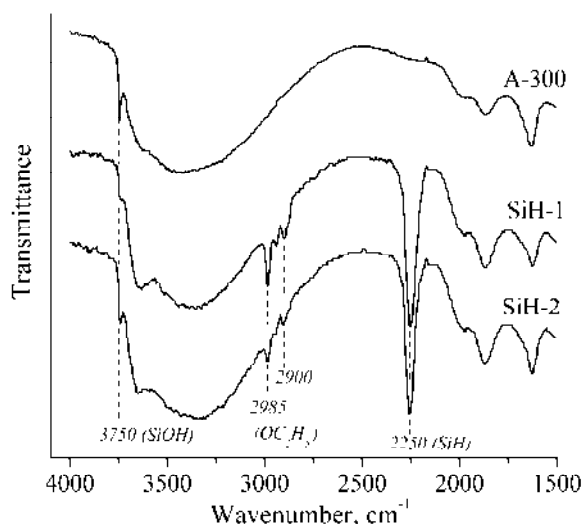


Fig. 3. IR spectra of initial (A-300) and hydride-silylated silicas before (SiH-1) and after water addition (SiH-2)

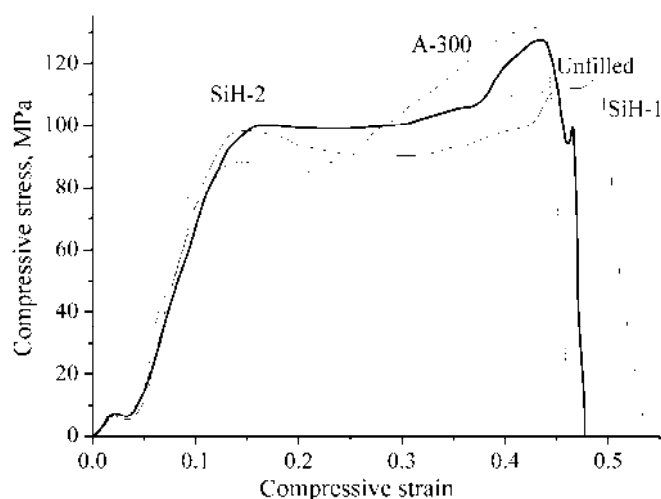


Fig. 4. Typical compressive stress-strain curves for the unfilled epoxy resin and filled with initial (A-300) and hydride-silylated (SiH-1, SiH-2) silicas at 2 wt% loading

The typical compressive stress-strain curves for neat epoxy and epoxy filled with pristine or hydride-silylated silicas are shown in Fig. 4. As one can see, 2 wt. % introduction of silica, whether it is surface-modified or not, does not change drastically the shape of the stress-strain

curve, thus keeping relatively high strength and ductility of epoxy polymer. More detailed results on the investigation of some mechanical properties of silica-containing epoxy composites are given in Table.

Table. Some mechanical properties (in MPa) of epoxy polymer filled with initial or hydride-silylated fumed silica

Parameter* \ Sample	Neat epoxy	A-300/epoxy	SiH-1/epoxy	SiH-2/epoxy
Yield compressive strength	100±5	91±3	88±10	92±6
Ultimate compressive strength	130±12	129±6	94±19	97±10
Young's modulus for compression	1070±45	1218±43	1120±142	1302±43
Bending strength	56±3	82±22	64±5	109±5
Young's modulus for bending	1275±98	1765±105	1570±96	1470±83
Adhesive strength	15±4	28±9	41±10	36±14

* – each value is an average of at least three independent tests

The data from this Table show that 2 wt. % silica loading increases the Young's modulus for compression and bending generally by 20–30 %, and even more this influence is observed for an increase in adhesion to steel – from about twice as much for unmodified fumed silica to about twice and a half for hydrophilic-hydrophobic and to approximately triple for hydrophobic hydride-silylated silica. Also, the bending strength grows upon epoxy filling with silica, the effect being the most pronounced for hydrophilic hydride-silylated silica. Besides, filling with silica generally decreased the compressive strength of

epoxy resin, the influence was generally more pronounced for modified silica.

As for the role of the specific surface groups, it appears that $\equiv\text{SiOH}$ groups are important for the bending strength improvement as well as for the increase in Young's modulus and adhesive strength (adhesion to steel), while surface $\equiv\text{SiH}$ groups are also responsible for an increase in Young's modulus and adhesive strength. The latter parameter increases in higher extend when hydrophobic hydride-silylated silica is used instead of the hydrophilic-hydrophobic one. All of these findings suggest that, beside the stiffing

function of rigid silica nanoparticles [11], the structuring role of surface $\equiv\text{SiOH}$ and $\equiv\text{SiH}$ groups may be an important factor for epoxy polymer reinforcement. A scheme of possible

interaction of these groups with the polymer matrix during the curing process at elevated temperature is shown in Fig. 5.

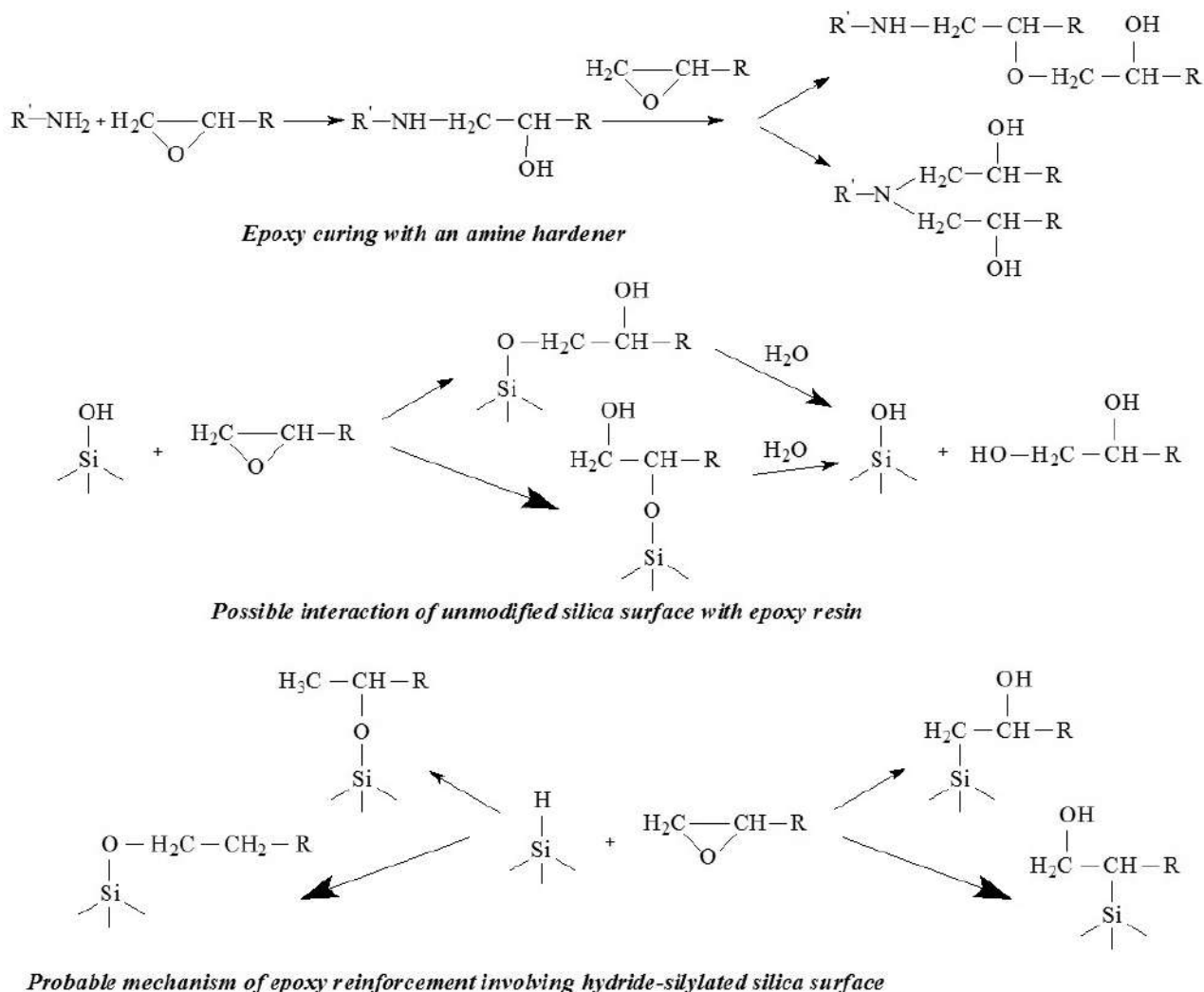


Fig. 5. The scheme of the epoxy resin polymerization in the presence of an amine hardener, and possible participation of surface silanol and/or silicon hydride groups in this process at elevated temperature

The activation energy of silanol groups interaction with epoxides resulting in the oxirane ring opening is about 75–90 kJ/mol, and the reaction proceeds at the temperatures of 150–170 °C [12] when common curing of the epoxides is possible (up to 200 °C). Keeping in mind that the activation energy for ring-opening polymerization of epoxides (~110 kJ/mol) is close to that for silanols interaction with epoxy, it is likely that the temperature range of 150–200 °C is enough for $\equiv\text{SiH}$ groups to also chemically interact with epoxides without

catalyst. The surface $\equiv\text{SiH}$ (in comparison to $\equiv\text{SiOH}$) groups show much more promise in this respect because, aside from better compatibility and beside the possible formation of hydrolytically unstable Si–O–C bonds, the stable Si–C bonds may form during the ring-opening polymerization of epoxides in the presence of hydride-silylated silica. To reveal the role of silica filler surface $\equiv\text{SiH}$ groups in epoxy reinforcement in detail, further, more systematic studies are to be performed.

CONCLUSION

Filling of epoxy resin with pristine (FS) or hydride-silylated (HFS) fumed silica (2 wt. %) reduces the compressive strength by 10 %, however, silica-epoxy composites were found to possess an increased by 20 % Young's modulus for compression as compared to that for the unfilled epoxy polymer. Upon this, 2 wt. % loading with silicas keeps the ductility of the polymer. Silica-containing epoxy polymers also show an improved bending strength and bending modulus, the former being of up to two times higher for HFS-epoxy composite than that for the unfilled polymer. The adhesion to steel was found to increase by more than two times upon

filling with silicas, HFS-epoxy composite being also superior as compared to the FS-epoxy one. Thus, preliminary results indicate that fumed silica with grafted silicon hydride groups shows promise as active reinforcing filler for epoxy polymers, and more systematic studies are to be performed in order to elucidate the role of surface $\equiv\text{SiH}$ groups in strengthening of the epoxy polymers with hydride-silica.

ACKNOWLEDGEMENT

The authors are grateful to Dr S.V. Snegir from the University of Konstanz (Germany) for the assistance in SEM investigations of initial and modified silica samples.

Посилення епоксидних полімерів гідридсилільованим пірогенним кремнеземом

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Пірогенний кремнезем (ПК) широко використовується у багатьох галузях, причому індустрія пластмас є однією із найбільш значних, де ПК виявився ефективним як загушувач, антизлежувач і тиксотропний агент, а також посилюючий наповнювач. Хімічне модифікування поверхні кремнезему розширює його функціональні можливості. Зокрема, було виявлено, що кремнезем з прищепленими кремнійгідридними групами є активним у процесах гідросиліювання алкенових та алкінових зв'язків у мономерах під час їхньої полімеризації, внаслідок чого утворюються посилені полімерні композити. Останнім часом набули значущості специфічні епоксидні смоли, і ПК виявився ефективним, у тому числі як реологічна добавка. Метою даної роботи було оцінити ефективність гідридсилільованого ПК (ГПК) як потенційно активного посилюючого компонента у складі епоксидних полімерів. Енергія активації гідросиліювання олефінів є вищою за таку для полімеризації епоксидів з розривом циклу, отже, можна очікувати, що перебіг останнього процесу за участю $\equiv\text{SiH}$ груп відбуватиметься у більш м'яких умовах.

ГПК було одержано обробкою ПК триетоксисиланом. Наявність прищеплених кремнійгідридних груп підтверджено методом ІЧ спектроскопії, а їхня концентрація, визначена методами титриметричного і спектрофотометричного аналізу, склала близько 0.4 ммоль/г. ПК- та ГПК-епоксидні композити одержано шляхом внесення відповідного наповнювача (2 мас. %) у суміш епоксидного мономера та затверджувача на основі аміну. Утворені матеріали після затвердіння випробовували на стискання, згинання та адгезію.

Тести показали, що наповнення епоксидної смоли ПК і ГПК на 10 % знижує міцність на стискання, проте виявлено, що ГПК-епоксидний композит має підвищений на 20 % модуль пружності на стискання у порівнянні з таким для ненаповненого полімера. При цьому, наповнення 2 мас. % кремнеземом зберігає пластичність полімера. Крім того, наповнені епоксидні полімери показали покращену міцність та модуль пружності на згин, причому міцність для ГПК-епоксидного композиту виявилась вдвічі вищою за таку для ненаповненого полімера. Також встановлено, що при наповненні кремнеземом адгезія до сталі збільшується більше ніж у 2 рази, причому ГПК-епоксидний композит також перевершує композит, що містить ПК. Таким чином, попередні результати свідчать про те, що кремнезем з прищепленими кремнійгідридними групами є перспективним посилюючим наповнювачем для епоксидних полімерів.

Ключові слова: кремнезем, кремнійгідридні групи, епоксидні полімери, посилення

Усиление эпоксидных полимеров гидридсилилированным пироженным кремнеземом

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Пироженный кремнезем (ПК) широко используется во многих отраслях, причем индустрия пластмасс является одной из наиболее значимых, где ПК оказался эффективным в качестве загустителя, антислеживателя и тиксотропного агента, а также усиливающего наполнителя. Химическое модифицирование поверхности кремнезема расширяет его функциональные возможности. В частности, было обнаружено, что кремнезем с привитыми кремнийгидридными группами активен в процессах гидросилилирования алкеновых и алкиновых связей в мономерах во время их полимеризации, вследствие чего образуются усиленные полимерные композиты. В последнее время специфические эпоксидные смолы приобрели значимость, и ПК оказался эффективен, в том числе как реологическая добавка. Целью данной работы было оценить эффективность гидридсилилированного ПК (ГПК) как потенциально активного усиливающего компонента в составе эпоксидных полимеров. Энергия активации гидросилилирования олефинов выше таковой для полимеризации эпоксидов с разрывом цикла; таким образом, можно ожидать, что последний процесс с участием $\equiv\text{SiH}$ будет протекать в более мягких условиях.

ГПК был получен обработкой ПК триэтоксисиланом. Наличие привитых кремнийгидридных групп подтверждено методом ИК спектроскопии, а их концентрация, определенная методами титриметрического и спектрофотометрического анализа, составила примерно 0.4 ммоль/г. ПК- и ГПК-эпоксидные композиты были получены путем внесения соответствующего наполнителя (2 масс. %) в смесь эпоксидного мономера и отвердителя на основе амина. Образовавшиеся материалы после отверждения испытывали на сжатие, изгиб и адгезию.

Тесты показали, что наполнение эпоксидной смолы ПК и ГПК на 10 % снижает прочность на сжатие, однако обнаружено, что ГПК-эпоксидный композит имеет повышенный на 20 % модуль упругости на сжатие по сравнению с таковым для ненаполненного полимера. При этом, наполнение 2 масс. % кремнеземом сохраняет пластичность полимера. Кроме того, наполненные эпоксидные полимеры показали улучшенную прочность и модуль упругости на изгиб, причем прочность ГПК-эпоксидного композита оказалась в два раза выше, чем в случае ненаполненного полимера. Установлено, что при наполнении кремнеземом адгезия к стальной поверхности увеличивается более чем в два раза, причем ГПК-эпоксидный композит также превосходит композит, содержащий ПК. Таким образом, предварительные результаты свидетельствуют о том, что кремнезем с привитыми кремнийгидридными группами является перспективным усиливающим наполнителем для эпоксидных полимеров.

Ключевые слова: кремнезем, кремнийгидридные группы, эпоксидные полимеры, усиление

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Received 26.08.2020, accepted 25.11.2020