

THE EFFECT OF THE STORAGE TIME OF THE MATRIX PRECURSOR ON THE MECHANICAL PROPERTIES OF THE FIBER COMPOSITE

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Submitted October 10, 2006; accepted March 13, 2007

Keywords: Matrix precursor, Fiber composite, Mechanical Properties, Storage time

The aim of this paper was to study the effect of temperature and storage time of polysiloxane resins M130 and 901 used in the preparation of fiber composites on the resulting mechanical properties of the composites. Composites, prepared by pressing the glass fiber impregnated with polysiloxane stored for the period of up to one year, were studied. The results of mechanical tests showed that the applied storage of the studied polysiloxanes has no substantial effect on the mechanical properties of the composites.

INTRODUCTION

Polysiloxane resins are typical amorphous branched polymers. In comparison with other polymers, they are relatively inexpensive and have excellent thermal, fire-resistant and corrosion-resistant properties.

Polycondensation networking reactions, taking place during the preparation of the composites, enable us to obtain products highly suitable for applications in medicine. The resins may be also used as biomaterials in orthopaedics [2, 3, 8]. An advantage represents also the light color of such composites, which makes them usable e.g. in facial surgery [3].

Besides that, polysiloxanes are applied as polymer precursors of ceramic composites, where the polymer matrix is transformed to an inorganic form under relatively easily achieved thermal conditions. The materials thus produced display good mechanical properties and exhibit outstanding heat resistance in an oxidizing medium. These properties and technological possibilities of preparation earmark them for use in such demanding fields as aviation and space research.

For example, oxide or siliconcarbide fibers and a ceramic (or quasiceramic) matrix, e.g. a polysiloxane precursor [1] may be used in high-temperature applications. They are widely used in coating and painting. If pyrolyzed in an inert atmosphere, they yield vitreous materials resistant to some extent to oxidation at higher temperatures. For example, Blackglass™, which is prepared from siloxane monomer and a catalyst by pyrolysis at 900°C, was developed as the matrix material for

composites resistant to such higher temperatures. Recent papers [9-11] indicate the increasing interest in using Blackglass™ as an accessible matrix with Nextel fiber reinforcement.

Apart from special applications, polysiloxane composites may be used also in more common fields such as mechanical engineering, in which mechanical stress is combined with the demand for temperature- and fire-resistance.

In the thesis [4] it was stated that the viscosity of siloxane resins is, on the whole, unstable when they are stored and that condensation of the silanol groups or the rearrangement of polymer chains takes place at laboratory temperature. This phenomenon may be slowed down by adding cyclohexanone.

The resultant mechanical properties of the cured siloxane resins depend on the degree of curing and pyrolysis [5]. Hydroxyl or alkoxy groups condensate during curing whereby the networking occurs. The rate and degree of curing may be affected by adding a catalyst. The cured resin contains a small percentage of free hydroxyl groups which have no substantial influence on its properties. The curing can be monitored by infrared spectroscopy and NMR spectroscopy. The possibility of following the curing of polysiloxanes by dielectric analysis [12] was studied. Experiments with epoxide and polyamide resins, modified by polysiloxane, have been described [6]. With polysiloxane resin itself the research of curing by using dielectric analysis is in an initial stage because in general with polysiloxanes there is the problem of weak response to the action of the electric field.

The purpose of this study was to establish the effect of the duration and of the temperature of storage of polysiloxane precursors, used as a matrix, on the resultant mechanical properties of the cured composites.

Polysiloxanes (trademark Lukosil 901 or Lukosil M130, produced in September 2000, both in Lučební závody Kolín, Czech Republic) were used as matrix precursors. Table 3 summarizes selected properties of these materials.

EXPERIMENTAL

Materials

The composites were prepared from E-type glass fiber cloth (trademark V240 with lubrication L706, manufacturer VERTEX, Litomyšl, Czech Republic), with the fabric surface density of 240g/m² and thickness of 0.3 mm. The composition of E-glass is given in Table 1. Table 2 shows its mechanical properties.

Table 1. The composition of E-glass (wt.%).

SiO ₂	53-57
Al ₂ O ₃	12-15
CaO, MgO	22-26
B ₂ O ₃	5-8
F ₂	0-0.6
Na ₂ O + K ₂ O	<1
Fe ₂ O ₃	0.5

Table 2. Mechanical properties of E-glass.

Tensile strength (Virgin filament tensile test)	3400 Mpa
Tensile strength (Impregnated strand tensile test - related to the fiber cross section)	2400 Mpa
Tensile modulus	73 GPa
Tenacity (sized yarns)	min. 50 cN/tex.
Elastic recovery	100 %

Table 3. Selected properties of polysiloxanes [7].

	Lukosil 901		Lukosil M130	
Chemical composition	methylphenylsiloxane resin		dimethylsiloxane resin	
Solvent	toluene		xylene	
Viscosity (23.1 °C), (MPas)	0.0286*		0.0581*	
Dry mass (%)	69*	70±2	54.4*	50±2
Consistency, Ø 4mm, 23°C (s)	18*	14-18	23*	15-21
Coloring	colorless to brownish		colorless to yellowish	

Table 4. Summarized values of the consistency of polysiloxanes during storage time (s).

Lukosil	new	after 6 months*	8 months*	10 months*	14 months*
901, lab.temp.	16.5	17.5	17.5	17.5	
901, refrigerator	16.5	16.5	17	17	17
M130, lab.temp.	21	22.5	23.5	23.5	
M130, refrigerator	21	21	23	23	23

*The storage time indicates the age of the polysiloxane as referred to the beginning of the composite preparation. The consistency was measured at laboratory temperature, i.e. at about 24.5°C, the flow time in seconds from the cup teeming hole with the diameter of 4 mm was measured. The polysiloxanes stored in the refrigerator were slowly warmed up to laboratory temperature for about 2 days prior to the measurement itself.

The fiber volume fractions (V_f) were calculated from the dimensions and weights of the composites and the surface density of the cloth and density of the fibers. Two samples of cured Lukosil M130, one new and one aged 14 months, were analyzed by infrared spectroscopy using a Nicolet 740 spectrometer with Fourier transformation using 512 spectrum accumulations with a resolution of 2 cm^{-1} . The samples were analyzed using the KBr pellet technique, as well as by diffusive reflection infrared spectroscopy (DRIFT) using an undiluted powder sample.

RESULTS

The mechanical tests were run with 7 samples from each series. Figures 1-2 present values of the respective mechanical properties of composites prepared from resins Lukosil M130 and Lukosil 901. The figures show the values of the individual quantities of the mechanical tests related to the volume fraction V_f (with E_{dyn} and R_m), the absolute values of G versus resin storage time preceding the beginning of preparing the composite.

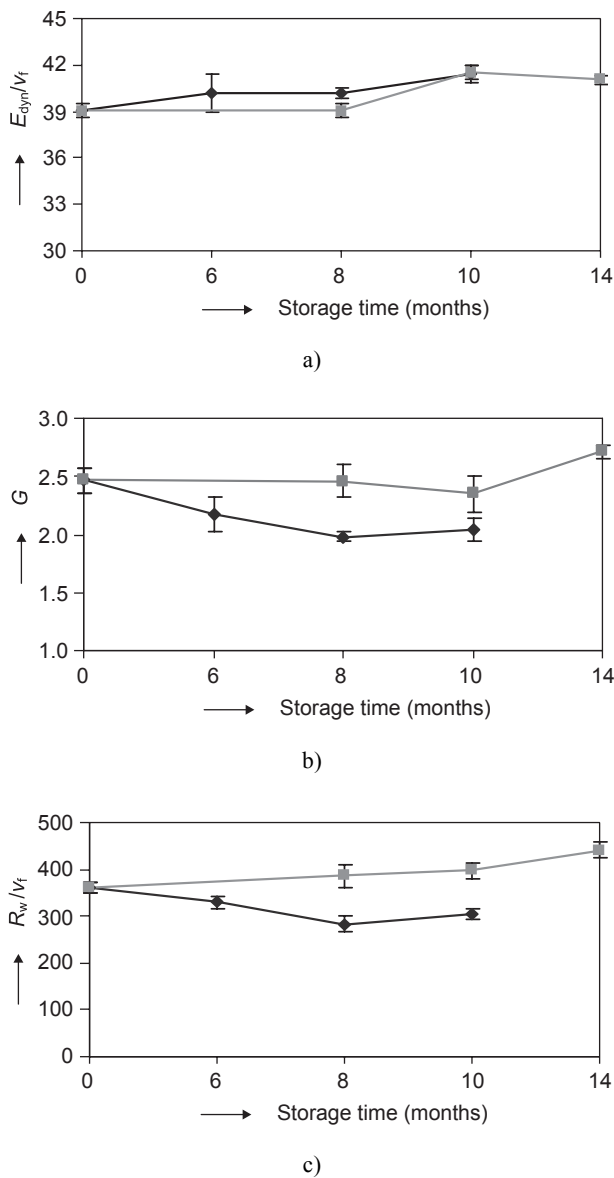


Figure 1. Mechanical properties of the composite prepared from resin Lukosil 901 in dependence on the storage time of polysiloxanes prior to composite preparation. a) E_{dyn}/V_f b) G , c) R_m/V_f , \blacklozenge - storage at laboratory temperature (24.5°C), \blacksquare - storage at refrigerator ($0\text{-}5^\circ\text{C}$).

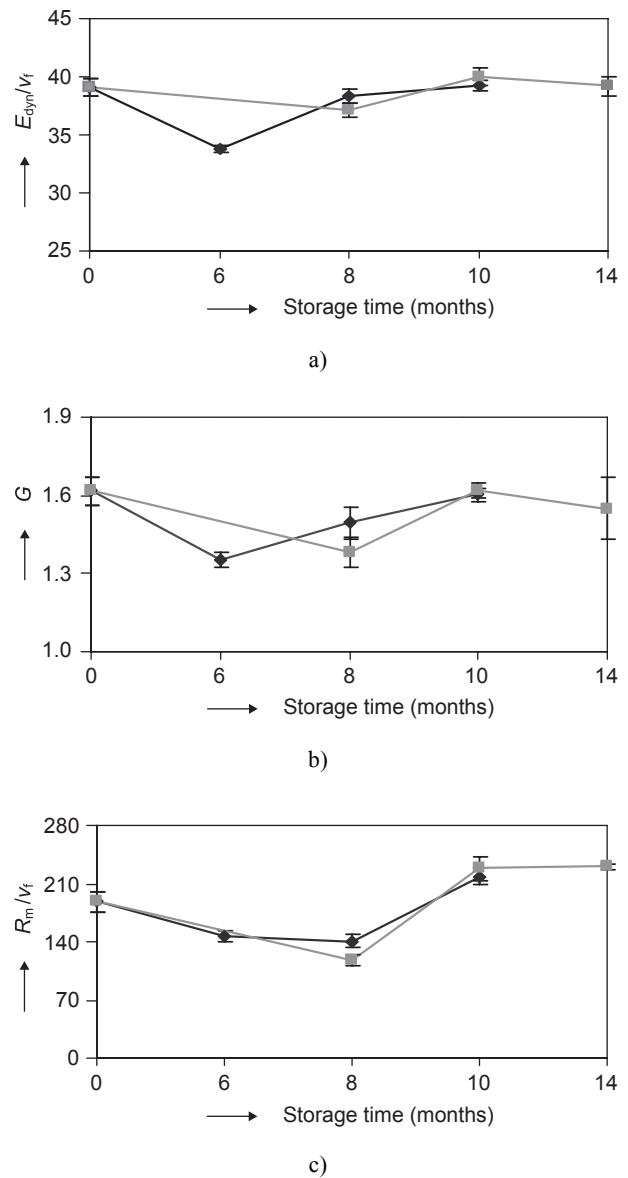


Figure 2. Mechanical properties of the composite prepared from resin Lukosil M130 in dependence on the storage time of polysiloxanes prior to composite preparation. a) E_{dyn}/V_f b) G , c) R_m/V_f , \blacklozenge - storage at laboratory temperature (24.5°C), \blacksquare - storage at refrigerator ($0\text{-}5^\circ\text{C}$).

The storage time and, hence, also the age of the Lukosils is defined as the period elapsed from the beginning of the composite preparation, i.e. in the stage of application to the fabric. The overall time of preparation and testing of one series of samples took 2-3 months. The conclusions take this fact into account. The modulus G does not depend on the volume fraction and therefore only its absolute value is given.

The volume fractions of the fibers in the composite with Lukosil M130, stored at both temperatures, and with Lukosil 901, stored in the refrigerator, differed only slightly the difference between the values did not exceed 7%. The decreasing volume fraction of Lukosil 901 at laboratory temperature was caused by less intense pressing of the sample (see Table 5).

In contrast to Table 5 (where $0 < V_f < 100\%$) in the following diagrams (Figures 1-3 for Lukosil and Figures 4-6 for Lukosil M130) the volume fraction V_f in the quantities E_{dyn}/V_f and R_m/V_f is expressed in the range of $0 < V_f < 1$.

Lukosil 901

The difference in the development of the values of E_{dyn}/V_f , G and R_m/V_f with storage time is evident when

comparing the effect of the storage temperature of the precursor. The composites with Lukosil 901, stored at laboratory temperature, generally display low values over the whole period with a rather decreasing trend with G (as much as 20 % of the initial value) as well as with R_m/V_f (by about 50 MPa), and constant values of E_{dyn}/V_f (around 40 GPa). The composites with Lukosil 901, stored in the refrigerator, displayed curves with a rather increasing trend of all quantities and values by about 10-20 % higher than those at laboratory temperature.

Lukosil M130

The time-dependent curves are similar in shape for the quantities E_{dyn}/V_f , G and R_m/V_f at one storage temperature as well as when comparing both storage temperatures. The values of E_{dyn}/V_f and G at both storage temperatures oscillate between 36 and 41 GPa (for E_{dyn}/V_f) and 1.35 to 1.6 GPa (for G). At both storage temperatures the R_m/V_f curve displays a minimum in the vicinity of 8 months, then gradually runs up to a value higher than their initial value.

Table 5. Volume fractions of fibers in samples with polysiloxane versus storage time prior to the composite preparation.

Siloxane sample	Storage time (months)				
	0 (new)	6	8	10	14
	Volume fraction (%)				
901, lab.temp.	51.63	48.31	47.49	47.19	
901, refrigerator	51.63		51.59	50.85	53.30
M130, lab.temp.	50.20	53.48	50.11	51.19	
M130, refrigerator	50.20		49.68	51.76	50.65

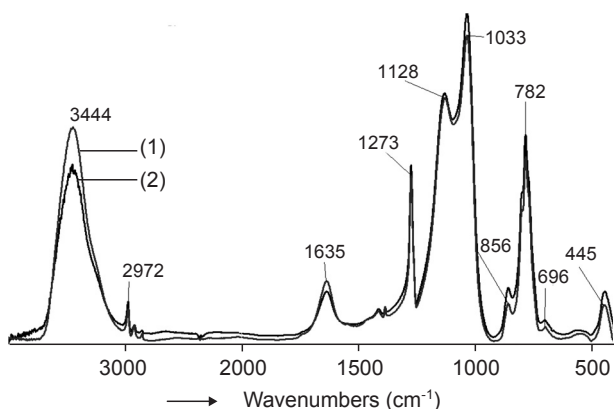


Figure 3. Infrared spectra of polysiloxane in the range of wavenumbers 4000-400 cm^{-1} measured by the technique of KBr pellets. The curve (1) refers to the "new" polysiloxane and the curve (2) to the "old" polysiloxane. The wavenumber is the reciprocal value of the wavelength.

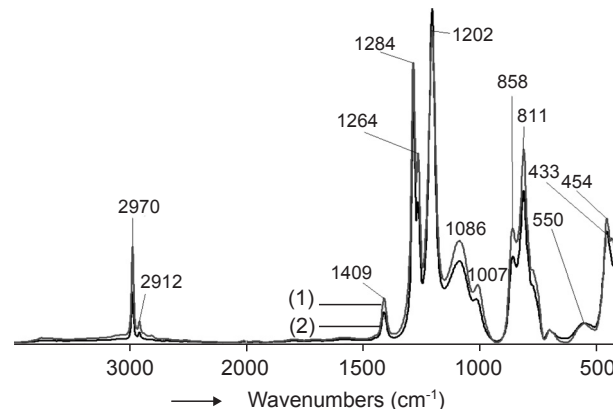


Figure 4. Infrared spectra of polysiloxane samples in the range of wavenumbers 4000-400 cm^{-1} measured by the DRIFT technique. The curve (1) refers to the "new" and the curve (2) to the "old" polysiloxane. The wavenumber is the reciprocal value of the wavelength.

DISCUSSION

It turns out that with gradual aging of the matrix precursor the values of E_{dyn}/V_f , G and R_m/V_f slightly improved, especially with samples stored for over 8 months. The effect of the storage temperature was evident only with the composites with Lukosil 901 (see the different shape of the curves). The consistency of both polysiloxanes changed only a little during storing. The measurement of the consistency did not prove to be decisive and no evident relation to the change in mechanical properties was found.

Infrared analysis

Figures 3 and 4 indicate that the spectra of the "new" (fresh) and "old" (stored in refrigerator for 14 months) samples of Lukosil M130 do not differ qualitatively. Proportional changes in the intensity of some bands can be found between the two samples. Nevertheless, these changes are not significant and cannot be attributed directly to the aging of the Lukosil M130.

CONCLUSIONS

The results show that the storage temperature of Lukosil 901 slightly affects the result mechanical properties of the composite. However, no effects were found with composites prepared with Lukosil M130. The infrared spectra of Lukosil M130 also upheld this finding.

One can conclude that if there are no strict demands on the mechanical properties of composites with Lukosil 901 or M130, their final mechanical properties exhibit on acceptable scatter, at least for the range of storage time applied in our research. If possible, it is better to store the resin at a lower temperature in spite of the fact that the temperature influence was apparent with only one of the two studied types of composites.

Acknowledgement

The measurement and interpretation of the IR spectra by V. Machovič is gratefully acknowledged. The support of the project of the Ministry of Industry and Trade of the Czech Republic No. FT-TA3/131 is also gratefully acknowledged.

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VLIV DOBY SKLADOVÁNÍ PREKURZORU MATRICE
PRO PŘÍPRAVU KOMPOZITU A JEHO MECHANICKÉ
VLASTNOSTI

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Cílem této práce bylo zjistit vliv teploty a doby skladování polysiloxanových pryskyřic M130 a 901, používaných pro přípravu vláknových kompozitů, na výsledné mechanické vlastnosti kompozitu. Byly sledovány kompozity připravené lisováním prepregu ze skleněného vlákna impregnovaného po různou dobu skladováním polysiloxanem. Výsledky mechanických zkoušek prokázaly, že skladování sledovaných polysiloxanů až přes rok nemá podstatný vliv na mechanické vlastnosti kompozitů z nich připravených.