

EFFECT OF SILYLATION OF CELLULOSE MICRO FIBRES ON THE MECHANICAL PROPERTIES OF POLYDIMETHYLSILOXANE COMPOSITES

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ABSTRACT

In this study, the influence of the silane treatment of cellulose microfibers (CF) on the polydimethylsiloxane (PDMS) mechanical properties was investigated. The surface modification of CF was carried out using hexamethyldisilazane (HMDS) solution or vapour treatment. The effectiveness of CF surface treatment was determined by scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), Fourier transform infrared spectroscopy (FT-IR) analyses and water contact angle measurements. The results of SEM/EDS analysis show that compared to unmodified CF, a strong Si energy peak appeared indicating that the silane moieties were bonded onto CF surface after silylation. FT-IR analysis shows the chemically bound methyl groups on the treated CF. Measurement of the water contact angle reveals the changes of CF surface from hydrophilic to hydrophobic after modification. Mechanical properties of the PDMS/CF composites such as tensile strength and elongation at break were analysed. The silane treatment of CF possess a significant increase in mechanical properties of PDMS.

1 INTRODUCTION

Silicones are synthetic and non-carbon skeleton polymer based on high molecular weight polyorganosiloxanes. The basic skeletal backbone of silicone is made up of silicon-oxygen bonds and organic groups attached directly to the silicon atom via silicon-carbon bonds [1]. For this unique structure, silicone has superior performance including biocompatibility, excellent elasticity, high temperature and chemical resistance [2]. These characteristics make the silicone widely applied in many areas. The most common member of siloxane family is poly(dimethylsiloxane) (PDMS). However, due to weak intermolecular interaction between polymer chains PDMS have poor mechanical properties [3]. For increase mechanical properties of PDMS various fillers are used [4-6].

The biodegradability, strength properties, low density, renewability, non-toxicity and easy chemical modification of the cellulose show promising results for its use as additive in the PDMS compositions [7]. However, cellulose fillers are hydrophilic and cannot be uniformly dispersed in the non-polar polymer matrices. Hence, surface modification and reduction of the hydrophilicity of cellulose is necessary.

Several different approaches are proposed for increasing the hydrophobicity of cellulose [8,9]. The use of silane coupling agents in order to improve the hydrophilicity of cellulose is well known. Silanes change the physical and chemical structure of the fiber by reacting with the OH group of the cellulose [10]. For silylation of cellulose chlorodimethyl isopropylsilane [8], dimethylchlorosilane [11], and hexamethyldisilazane (HMDS) [12-14] are used. High silanization power of HMDS on the different types of celluloses has been demonstrated in a number of studies. Mormann et al. [13] described the silylation of microcrystalline cellulose with HMDS in ammonia as reaction medium. Grunert and

Winter [14] performed of the cellulose surface silylation with HMDS in formamide. The resulting modified cellulose shows the improved hydrophobicity.

In this paper, the influence of two different silylation methods by HMDS on the structure and surface properties of cellulose microfibrils is characterized. The effect of cellulose treatment mode on the structure and mechanical properties of PDMS composites is also investigated.

2 EXPERIMENTAL

2.1 Materials

Vinyl-terminated PDMS Endeavour T-2516 (Endeavour Enterprise Co, Taiwan) was used in this study. PDMS is a room-temperature vulcanizing polymer supplied as a two parts system. Part A is prepolymer terminated with vinyl groups, and Part B contains prepolymer with Si-H groups and platinum complex. The mixing ratio of parts A and B was 1:1. Cellulose fibres of medium particles size from Sigma Aldrich were used for PDMS properties modification. Hexamethyldisilazane (HMDS), N,N – dimethylformamide (DMF), and toluene were analytical grade and purchased from Sigma Aldrich.

2.2 Silylation of cellulose fibres

Two methods of CF silylation with hexamethyldisilazane were used.

Vapour treatment. CF powder was exposed to HMDS vapour at temperature of 120°C for 6 h for the. The vapour silylated CF was used without further washing.

Liquid treatment. CF powder was immersed in the mixture of HMDS and organic solvents, such as N,N – dimethylformamide (DMF) and toluene. CF (10 g) was dispersed in 135 ml of HMDS:DMF: toluene =6:1:20 mixture by magnetic stirring at temperature of 175°C for 6 h. After immersion the silylated CF were dried in ventilated oven at 150°C for 3 h.

2.3 Preparation of composites

PDMS/CF composites preparation steps depend on CF treatment method. Vapour silylated CF powder was added directly into PDMS base and curing agent blend under sonification for 10 min. Liquid silylated CF firstly was dispersed in chloroform for 10 min and added in PDMS base under mechanical stirring. After treatment under vacuum for 60 min solvent was removed and curing agent was added under stirring. After cellulose fibre dispersing both PDMS/CF composites were degassed under vacuum for 60 min and further cured for 25 min at temperature of 70 °C.

2.4 Characterization

Topography of the CF and fracture morphologies of PDMS/CF composites were carried out using a scanning electron microscope Quanta 200 FEG (FEI, Netherlands). The samples were examined in low vacuum mode operating at 20.0 kV using an LDF detector. The elemental composition (Si) was determined with an energy dispersive spectrometer (EDS) with a Bruker XFlash 4030 detector (accelerating voltage 10 kV, distance between the bottom of the objective lens and the object 10 mm).

Fourier transform infrared (FT-IR) analysis was performed using Spectrum GX Perkin-Elmer FT-IR spectrometer. The CF was mixed with analytical grade KBr at a weight ratio of 1/200.

Contact angle measurements were performed using goniometer. For wettability investigation CF tablets were prepared by powder compressing at 3 MPa for 3 min. Digital images of a (ca. 5 µl) deionized water droplet on tablets surface were captured and analysed using the software.

Tensile tests were carried out at ambient temperature using universal testing machine H25KT (Tinius Olsen, England) with load cell of 1 kN and a cross-head speed of 50 mm/min. Measurements were performed with dumbbell shape specimens having gage area of 25 mm × 4 mm and thickness of 4 mm. Ten test pieces were tested for each set of samples and the mean values were calculated.

3 RESULTS AND DISCUSSION

The changes of CF morphology after HMDS treatment were investigated by SEM analysis. The CF

without HMDS treatment exhibited the rod-like particles, which were about 47 μm and 16 μm in length and width, respectively, corresponding to an aspect ratio of 3 (Fig. 1 a). Their compact agglomeration shows that cellulose chains have an intermolecular hydrogen bonding and a strong interaction between the cellulosic chains.

HMDS vapour and solution treatment facilitates the fibrillation of the fibres into individualized fibrils (Fig. 1 b, c). The treated CF particles exhibited higher polydispersity than that of unmodified ones with an increased particles aspect ratio to 4 (40 μm /10 μm).

Figure 2 shows the SEM/EDS of unmodified and modified CF. Compared to unmodified CF, a strong Si energy peak appears indicating that the silane moieties are bonded onto CF surface. Moreover, the intensity of Si peak is higher in the case of vapour treated CF.

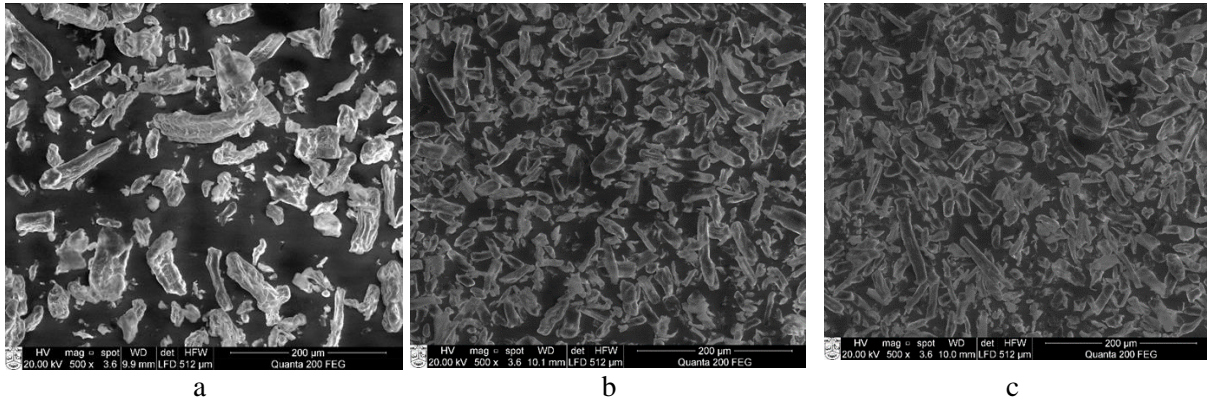


Figure 1. SEM images of CF: untreated (a), HMDS solution treated (b) and HMDS vapour treated (c). Magnification 500 \times

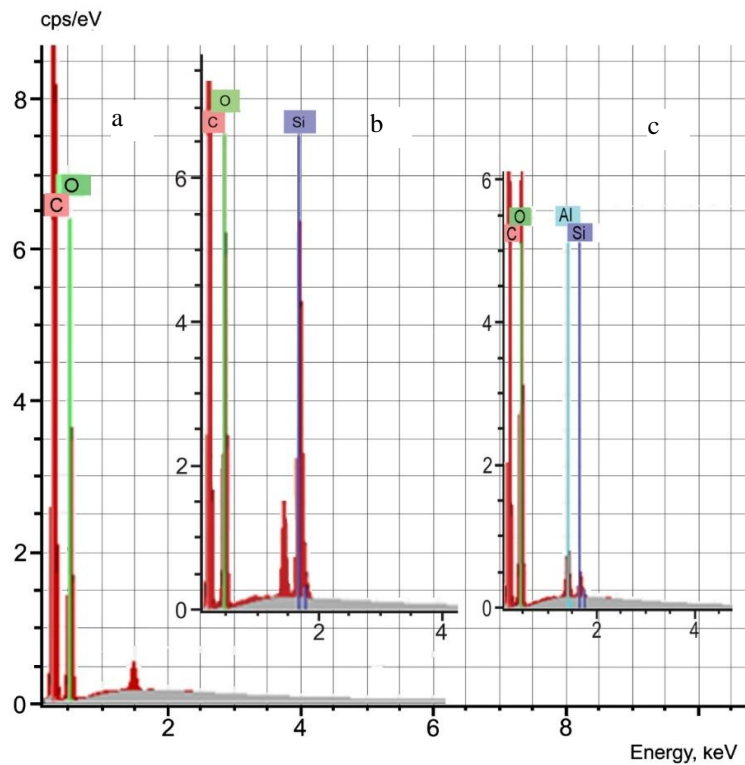


Figure 2. SEM/EDS of CF: untreated (a), HMDS solution treated (b) and HMDS vapour treated (c)

Figure 3 shows a typical FTIR spectrum of cellulose. The characteristic bands for CF are OH stretching vibration at $3700\text{--}3000\text{ cm}^{-1}$, the C-H stretching vibration at 2850 cm^{-1} , the CH_2 symmetric bending vibration at 1430 cm^{-1} , the CH bending at 1380 cm^{-1} , the CH bending or CH_2 stretching at 900 cm^{-1} and C-O-C stretching at 898 cm^{-1} [15]. After chemical treatment with HMDS the new peak observed at 1259 cm^{-1} can be referred to Si- CH_3 symmetric deformation [8]. Appearance of Si- CH_3 peaks at the assigned spectral position confirms that HMDS react with cellulose surface $-\text{OH}$ groups.

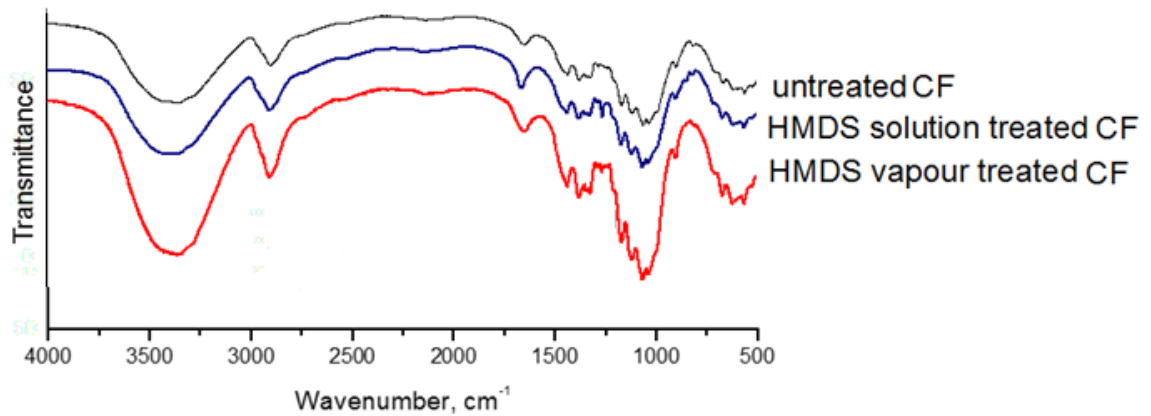


Figure 3. FT-IR spectra of untreated and treated CF

Changes of surface free energy due to the silylation were determined using contact angle (CA) measurements. The unmodified CF was found to be hydrophilic ($\text{CA} = 15^\circ \pm 1^\circ$). The water contact angle of the CF surface increased with treatment independently on the used method. As expected, the water contact angle values increase up to 94° and 92° after vapour and solution treatment for 6 h, respectively.

SEM analysis of fractured surface of PDMS/CF composites is used for assessing the wetting of the CF by the PDMS matrix. For the PDMS composites prepared with untreated CF, the rupture was accompanied by pull out of the particles, leaving holes, which indicates low adhesion between the particles and the polymer matrix (Fig. 4 a). For composites containing treated CF particles, an improvement of the fibre and matrix interface adhesion was observed, as suggested by the absence of holes and the breaking of the particles.

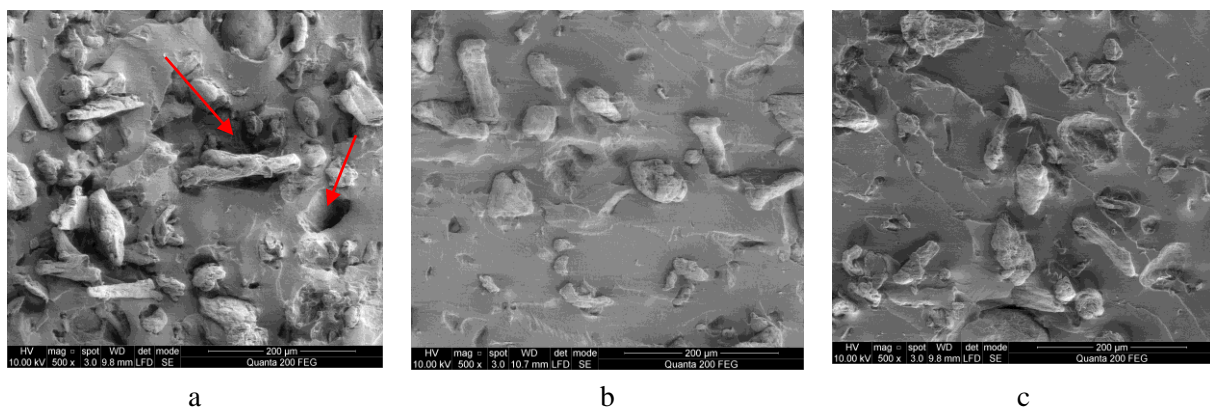


Figure 4. SEM images of fractured surface of PDMS composites with 10 wt % of: untreated CF (a), HMDS solution treated CF (c), HMDS vapour treated CF (d). Magnification $500\times$

The influence of the CF silylation method on the mechanical properties of PDMS is shown in Table 1. For composite materials filled with 10 wt.% – 20 wt.% of unmodified CF, the reinforcing effect of the PDMS matrix was found to be 40%. As expected, at the same loading levels, modified

CF had stronger reinforcing effect on the PDMS matrix than unmodified one. Compared to neat PDMS, with incorporation of 10 wt.% and 15 wt.% of treated CF, the tensile strength of the composite was improved more than 80 %. The improvement was attributed to the high dispersion of modified CF within PDMS matrix and improved interfacial interaction.

CF treatment mode	CF content, wt. %	Tensile strength, kPa	Elongation at break %
Untreated	0	420±12	743±57
	5	570±17	686±62
	10	510±23	635±41
	15	600±34	651±25
	20	610±14	611±65
Solution treated	5	750±54	950±14
	10	815±31	964±25
	15	859±27	895±57
	20	820±53	850±45
Vapour treated	5	687±18	986±15
	10	754±14	939±47
	15	768±34	941±57
	20	788±21	972±95

Table 1: Dependence of PDMS composites tensile strength (a) and elongation at break (b) upon CF content and treatment mode

As can be seen from the Table 1, elongation at break decreases with incorporating of untreated CF in the PDMS matrix. Nevertheless, addition of treated CF increases the elongation at break of PDMS composite in 30 %.

5 CONCLUSIONS

In this work, the effect of CF treatment by different silylation methods on the mechanical properties of PDMS composites was investigated. The CF surface was modified using treatment by hexamethyldisilazane solution or vapour methods. The presence Si-CH₃ groups on the cellulose surface and their surface hydrophobicity, as was verified by FTIR and water contact angle measurements, respectively, confirmed that silane moieties was held on the CF surface without degradation of the polymer chain.

PDMS composite showed a considerable improvement in the mechanical properties after surface modification of CF. At the same loading contents, treated CF showed the stronger reinforcing effect on the PDMS matrix than untreated ones. Comparing with neat PDMS, the tensile strength and elongation at break of composite increase more than 80 % and 30 %, respectively, as 10 wt.% and 15 wt.% of treated CF was incorporated.

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