Modification of Water Sorption Capacity of Polydimethylsiloxane based Composites by Incorporation of Lignin

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Lignin, a natural renewable material, was incorporated in a series of polydimethylsiloxane/silica composites. Besides the effect as bulk filler, the presence of lignin determines the change of some properties among them being surface properties that were evaluated by contact angle and water sorption measurements. The contact angles were determined in static regime by using the sessile drop technique. Dynamic water vapour sorption was applied to register the sorption/desorption isotherms and kinetic curves. The sorption type and maximum vapour sorption capacity were evaluated based on these data. The results were correlated with the composition of the prepared materials.

Keywords: surface properties; siloxanes; composites; lignin

Lignin is the second most abundant natural polymer and has a three-dimensional amorphous aromatic structure and is relatively inexpensive [1,2]. This biopolymer is obtained as a byproduct of the pulp and paper industry and has been used as an energy source [3]. Lignin has low-density and low abrasiveness. It can be used for a variety of technical purposes [1]: can provide a chemical system with stability against UV light and thermo-oxidative stress such as for polystyrene, low-density polyethylene and linear low-density polyethylene materials [4] and at high temperature in an inert atmosphere lignin gives a large amount of char making it usable as flame retardant additive [1] for isotactic polypropylene [5] and for carbon black filled natural rubbers [2].

Another application for lignin is the use as filler in polymeric materials with the purpose of increasing their content of renewable resources [3]. However, lignin possesses extensive cross-linking and also intermolecular interactions and these characteristics hinder its incorporation in solid polymeric material system. Therefore, miscible blends of such biopolymer with other systems are rare [6]. In polymer blends, miscibility is dependent on the occurrence of exothermic reactions such as hydrogen-bonding or acid–base interactions. Only in the last years, the effects of polymer-polymer interactions, specifically hydrogen-bonding, on lignin-based thermoplastics were studied in a series of lignin/synthetic polymer blends where lignin was incorporated into different polymer materials: poly(ethylene terephthalate) [1,7], poly(vinyl alcohol) and polypropylene [5,7], poly(vinyl chloride) [6,8], polyethylene and polystyrene [4] or natural rubber [2]. With certain polymers, it can give partially or completely biodegradable composites [4]. One class of polymers with interesting properties and which was not tested so far for obtaining new materials with lignin is polydimethylsiloxane. Polysiloxanes, also known as silicones, are among the most used polymers in the modern world: this class of polymers exhibits a combination of a set of properties not common to other macromolecules: small dielectrical constant, highly flexible backbone, stability towards atomic oxygen, high permeability for different gases, hydrophobicity, anti-adhesive behaviour, chemical and physiological inertness. Surface tension reduction is one of the most important properties provided by silicones.

For all their useful properties, polysiloxanes have as drawbacks: poor mechanical properties and high costs. In order to surpass these disadvantages were prepared a series of composite silicone-based materials, using lignin in the form of hydrophobized powder as cheap renewable resource-based bulk filler for silicones. The surface properties of the prepared materials were investigated and the results were compared with those of silicones reinforced with commercial silica and diatomite as classic fillers. The determination of surface properties leads to the way for the possible use of these composites as biodegradable materials and medical implants.

Experimental part

Materials

Polydimethylsiloxane-α,ω-diols having molecular masses presented in table 1 were prepared by heterogeneous cationic ring-opening polymerization of octamethyl-cyclotetrasiloxane, according to procedure described in [9].

Tetraethyl-orthosilicate (TEOS), purchased from Fluka (purity > 98 %, b.p.=163-167 °C, d_4^{20} = 0.933) was used as received.

Methyltriacetoxysilane (MTA) was prepared and purified in house using a proprietary technique (purity > 98 %, b.p.=94-95°C, d_4^{20} = 1.20).

Table 1
MOLECULAR MASS OF POLYDIMETHYLSILOXANE-α, α DIOLS

Code	Average viscometric molecular mass, Mv
S1	49000
S2	54000
S3	58000
S4	60000
S5	120000

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Dibuthyltin dilaurate was received from Merck-Schuchardt, d_4^{20} = 1.055 and was used as received.

Fumed silica, Aerosil 380 (Degussa), 100% purity, specific surface 380 m^2/g, particle diameter 0.003 – 0.015 μm.

Diatomite Filia (SiO_2 max. 90%, Fe_2O_3 max. 1%, CaO max. 1%, granulation 85% <20μ).

Lignin Protobing 100SA-140 was received from Granit Recherché Development SA Lausanne and was used after drying and hydrophobization having the following characteristics: lignin insoluble in acids 87%, uronic acid 0%, nitrogen 1.2%, carboxyl groups 3.3%, p-OH 1.7%, *p*H in water 3.2, manganese 690 ppm, polydispersity 10.8. It was used after hydrophobization by treatment with D_4 for 3 h at 180 °C.

Equipment

Contact angles were measured by the sessile drop technique at room temperature, using a KSV CAM 101 goniometer, equipped with a special optical system and a CCD camera connected to a computer to capture and analyze the contact angle (five measurements for each surface). A drop of liquid (~1μL) was placed on a specially prepared plate of substratum and the image was immediately sent via the CCD camera to the computer for analysis. The angle formed between the liquid/solid interface and the liquid/vapor interface is the contact angle. Temperature and moisture were kept constant during the experiment (23°C and 68 % respectively).

The measurements for dynamic vapour sorption (DVS) and sorption hysteresis were performed with an IGAsorp Dynamic Vapour Sorption apparatus, with the characteristics: minimum gas pressure: 2 bar; resolution of 0.1 μg for 100 mg and with sample containers made out of stainless steel micron size mesh. The drying of the samples before sorption measurements was carried out at 25°C in flowing nitrogen (250 mL/min) until the weight of the sample was in equilibrium at RH<1%.

Procedure

Preparation of the composites crosslinked with methyltriacetoxysilane

Polydimethylsiloxane-α,ω-diol was mixed in a laboratory mixer with pre-established amounts of fumed silica, lignin and/or diatomite, (table 2, Samples PDMS1, D1, L1-1 ÷ L1-3, PDMS2, D2, L2-1 ÷ L2-3, PDMS3, D3, L3-1 ÷ L3-3, PDMS4, D4, L4-1 ÷ L4-3). The mixture was kept under vacuum for 10-20 min in order to remove all trapped air bubbles, and then methyltriacetoxysilane was incorporated by mechanical mixing. The resulted formulation was used to obtain thick films (3 mm thick) by pouring in an iron mold 10x10 cm, and pressed between

Sample	PDMS	Composition, weight parts						
		PDMS	Silica	Diatomite	Lignin	TEOS	MTAS	DBTDL
PDMS1	S2	100	-	-	-	-	8	
D1		100	7	20	-	-	8	
L1-1		100	4	-	20	-	8	
L1-2		100	7	-	20	-	8	
L1-3		100	10	-	20	-	8	
PDMS2	S3	100	-	-	-	-	8	-
D2		100	7	20	-	-	8	-
L2-1		100	4	-	20	-	8	-
L2-2		100	7	-	20	-	8	-
L2-3		100	10	-	20	-	8	-
PDMS3	S4	100	-	-	-	-	8	-
D3		100	7	20	-	-	8	-
L3-1		100	4	-	20	-	8	-
L3-2		100	7	-	20	-	8	-
L3-3		100	10	-	20	-	8	-
PDMS4	S5	100	-	-	-	-	8	-
D4		100	7	20	-	-	8	-
L4-1		100	4	-	20	-	8	-
L4-2		100	7	-	20	-	8	-
L4-3		100	10	-	20	-	8	-
PDMS0	S1	100	-	-	-	5	-	1
D0		100	6	20	-	5	-	1
P1		100	6	-	10	5	-	1
P2		100	-	-	20	5	-	1
P3		100	6	-	20	5	-	1
P4		100	6	-	30	5	-	1

Table 2
THE FORMULATION OF PREPARED SILOXANE-BASED COMPOSITES

two Teflon plates. The samples were thus maintained at room temperature and environmental humidity for 24 h. The formed films were easily peeled off from the substrate.

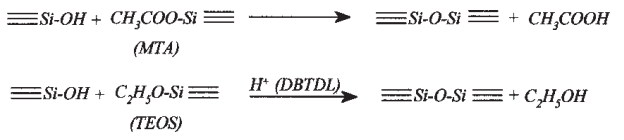
Preparation of the composites crosslinked with tetraethyl-orthosilicate

Polydimethylsiloxane-α,ω-diol was mixed in a laboratory mixer with pre-established amounts of fumed silica, lignin and/or diatomite, and tetraethyl-orthosilicate (table 2, Samples PDMS0, D0, P1, P2, P3, P4). The mixture was kept under vacuum for 10-20 min in order to remove all trapped air bubbles, then dibuthyltin dilaurate was incorporated and after that was stirred and again shortly vacuumed, poured in rectangular moulds and allowed to cross-link at room temperature in the environmental humidity for one week.

All films were kept for curing in the laboratory environment about two months before investigations.

Results and discussions

Polydimethylsiloxane-α,ω-diols of different molecular masses (table 1) were used as a matrix for preparing composites. The hidrophobized fillers (commercial ones as silica and diatomite, and the new filler – lignin) were incorporated in this matrix in different ratios according to table 2. Two crosslinking agents were used to stabilize the resulted composites: tetraethyl-orthosilicate and methyltriacetoxysilane. It is known that silanes as tetraethyl-orthosilicate and methyltriacetoxysilane are easily hydrolyzed by water and this characteristic makes them convenient crosslinking agents for polydimethyl-siloxane-α,ω-diols [10] in the presence of water vapors from atmosphere. Polydimethylsiloxane-α,ω-diol chains are crosslinked in a network by coupling of their ends through chemical bonding to the species derived from methyltriacetoxysilane and tetraethyl-orthosilicate, respectively (scheme 1). Acid or base catalysts can be used to accelerate the hydrolysis/condensation reactions. We used a catalyst, dibuthyltin dilaurate, only in the cases of crosslinking by tetraethyl-orthosilicate.



Scheme 1

The main aim of this approach was to use lignin – a renewable material – as extender for silicone material and eventually to improve the mechanical properties of the polydimethylsiloxanes [11]. However, other properties (thermal, surface) could also be changed. In this paper we investigate the modification of the surface properties of the silicones by introduction of the lignin in their composition. Two parameters that are significant for the surface properties were measured: contact angle and water vapor sorption.

The obtained values for static contact angles, measured by the sessile drop technique are presented in a graphical form in figure 1. Contrary to expectations, no significant variation in the contact angle values was obtained by introduction of the lignin. More, in some cases the water contact angle values seem to be slightly higher in the case of the composites containing lignin when compared with pure polydimethylsiloxane-α,ω-diol reference samples or those prepared with diatomite. However, all samples have values of the contact angle over 90° and this indicates that the hydrophobic character of the silicone rubber is preserved whatever filler is used.

When comparing the values of the contact angle for the sample with a larger percentage of lignin filler (30% – P4) with the other samples with lignin (20%), the contact angle values are slightly smaller for the sample with more lignin.

The slightly increased values of the water contact angles in the case of the composites containing lignin as compared with those containing diatomite and/or silica can be explained by a weaker interaction between lignin and polysiloxane matrix as compared with the other fillers having structures more similar with the siloxane. Due to the difference of the nature and polarity of the two materials a separation tendency might manifest. This, combined with the known tendency of the polysiloxane to migrate at the interface material-air, will lead to a surface richer in hydrophobic siloxane component. The reference samples made with pure polydimethylsiloxane have the lower values for water contact angles when compared with the other samples. However these values are as expected in the hydrophobic domain. There is no conclusive evolution of the contact angle values relative to the type of the used crosslinker (tetraethyl-orthosilicate or methyltria-cetoxysilane). The increase of the average molecular mass of the polysiloxane matrix does also not exert a visible influence regarding the surface properties of the samples. This is determined by the fact that flexible siloxane chains, whatever their molecular mass, migrate at the interface material-air.

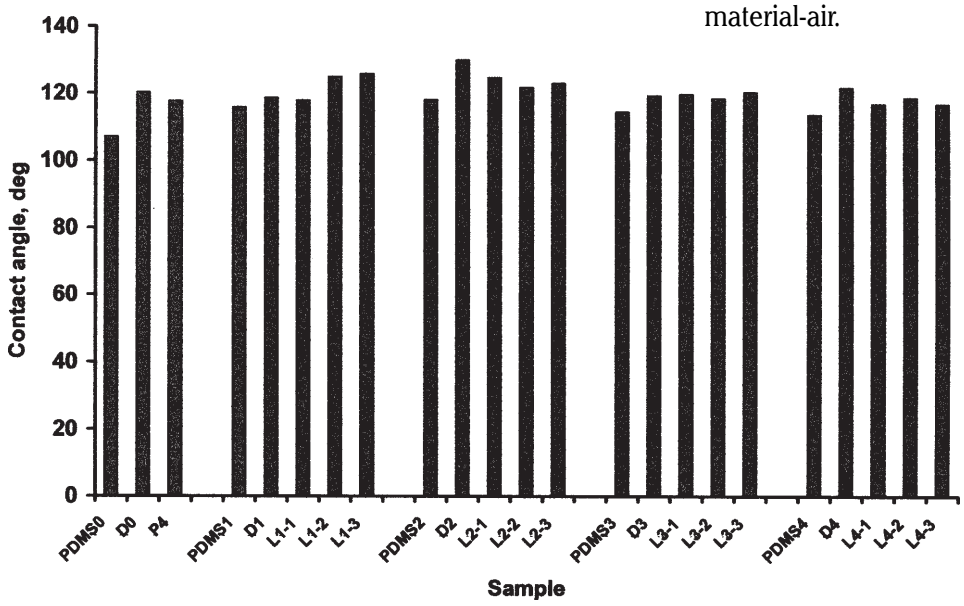
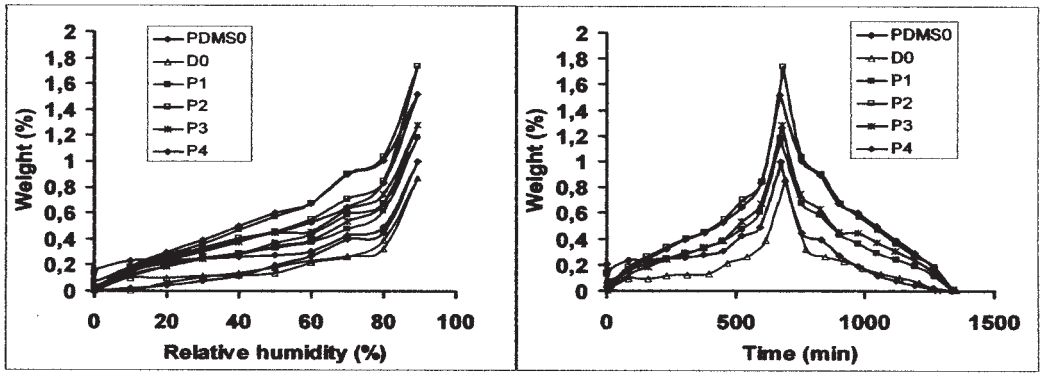
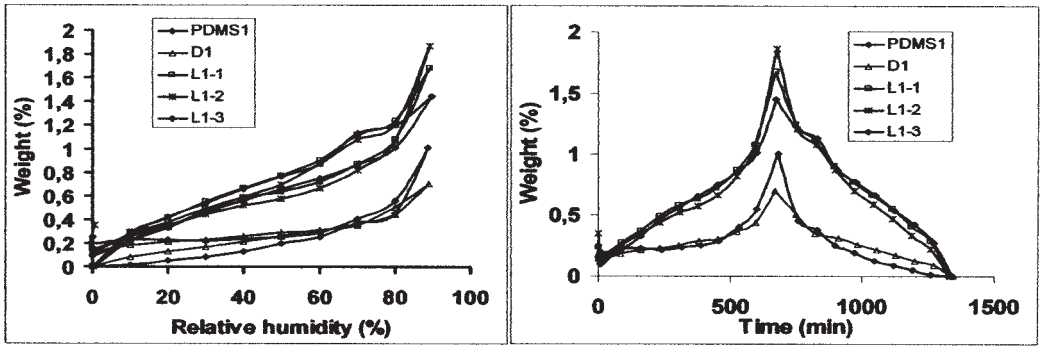


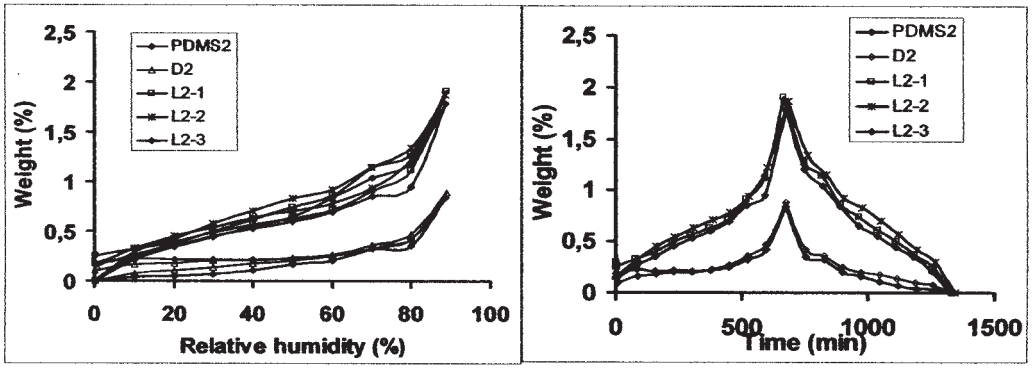
Fig. 1. Static contact angle values for the prepared samples



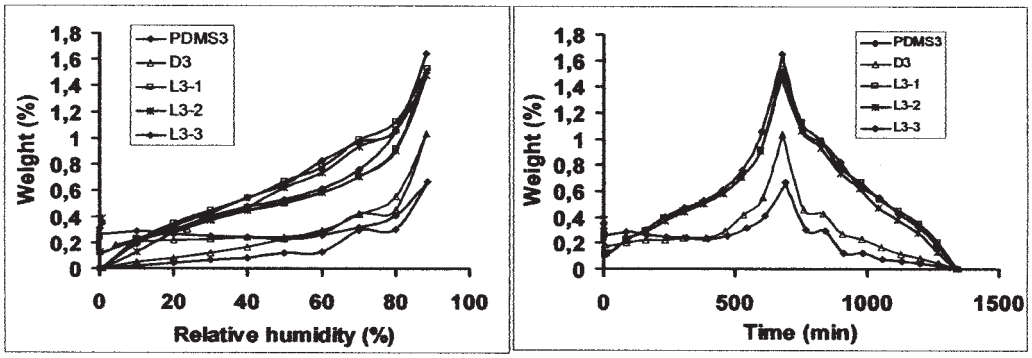
(A)



(B)



(C)



(D)

Fig. 2. Sorption/desorption isotherms (left) and kinetic curves (right) of the samples based on polymer: (A) S1; (B) S2; (C) S3; (D) S4.

The measurements for dynamic vapour sorption and sorption hysteresis were performed with an IGAsorp Dynamic Vapour Sorption apparatus. The sorption/desorption isotherms and kinetic curves are presented in figure 2.

The water vapour sorption measurements revealed notable differences in the behaviour of the samples with and without lignin. The maximum sorption capacity almost doubles in the case of the samples containing lignin (table 3). These results confirm the hypothesis used to justify the above values of the contact angles.

As can be seen in figure 2, the isotherms for samples which contain lignin have similar shape and are characteristic for hydrophobic materials with weak interactions between sorbent and sorbate. On the other hand, there is a noticeable difference between the shapes of the samples with lignin and those without lignin, the latter being more hydrophobic.

The kinetics of water vapour sorption have been also recorded and the water gain as a function of exposure time to humidity is shown in the figure 2 (right side images) for all the samples. It can be noticed that the rate of

Table 3
THE MAXIMUM WATER VAPOUR SORPTION CAPACITY FOR THE COMPOSITE MATERIALS

Sample	PDMS	The maximum water vapour sorption capacity (%d.b.)
PDMS1	S2	1.01
D1		0.70
L1-1		1.68
L1-2		1.87
L1-3		1.45
PDMS2	S3	0.84
D2		0.89
L2-1		1.91
L2-2		1.87
L2-3		1.79
PDMS3	S4	0.67
D3		1.04
L3-1		1.53
L3-2		1.48
L3-3		1.65
PDMS0	S1	0.99
D0		0.87
P1		1.18
P2		1.74
P3		1.28
P4		1.52

desorption of water vapors is generally slower than the sorption rate. The materials without lignin adsorb water more slowly in the 0 - 60 % relative humidity range and more quickly at higher relative humidity values. Another difference consists in the presence of the hysteresis for the isotherms of samples prepared with lignin. The low compatibility between polysiloxane and lignin can lead to the increasing of the porosity and therefore at the appearance of capillary phenomena. For each siloxane polymer, there is a decrease of the water vapour sorption capacity as the treated silica content added in the sample increases whereas for lignin there is an increase of water vapour sorption capacity with its content (for example, case A, fig. 2). Also as the molecular mass of polydimethylsiloxane increases (A→B→C→D) there is a decrease of the water vapour sorption capacity. The insertion of diatomite in the composites leads to a smaller capacity of water vapour sorption. Overall for samples without lignin, the isotherms correspond to a type III – specific for nonporous hydrophobic materials with weak interactions between sorbed and sorbing materials. For samples with lignin, the isotherms are type IV – specific for hydrophobic materials with pores.

Table 4
THE MAIN SURFACE PARAMETERS EVALUATED BASED ON SORPTION ISOTHERMS

Sample	Lignin content (%)	Inserted silica content (%)	The average pore size (nm)	BET data (RH: 0 - 40%)	
				Area (m^2/g)	Monolayer (g/g)
P3	20	6	2.66	9.67	0.002753
P2	20	-	2.97	11.18	0.003183
P1	10	6	3.90	6.10	0.001738
P4	30	6	2.47	12.36	0.003520
L1-1	20	4	10.78	3.13	0.000891
L1-2	20	7	2.18	17.14	0.004883
L1-3	20	10	1.88	15.41	0.004389
L2-1	20	4	2.23	17.14	0.004883
L2-2	20	7	1.94	19.30	0.005496
L2-3	20	10	2.91	12.29	0.003500
L3-1	20	4	1.70	17.99	0.005123
L3-2	20	7	2.32	12.76	0.003636
L3-3	20	10	2.45	13.46	0.003833

The average pore size for the samples having incorporated lignin in their composition was calculated from the pore volume, assuming cylindrical pore geometry using the BET specific surface area [12,13] determined from the desorption branch of sample isotherm. The obtained values are presented in table 4, beside other BET data (area and monolayer) evaluated from sorption isotherms in the relative humidity range 0-40%.

As can be observed, with the increasing in the lignin content incorporated in the samples, the average pore size is decreasing. According to the weighting measurements, it was found that the variation of lignin content from 10 to 30% leads to a decrease of the average pore size from 3.9 to 2.47 and an increase in the porosity of the material, demonstrated by the increase of sorption capacity from 1.19% (at 10% lignin), 1.28% (at 20% lignin) to 1.52 (at 30% lignin). A simple comparison of these facts suggested that the increase in the lignin content may cause the PDMS-lignin composites to have a smaller polydispersity of the pore size.

The specific BET surface area and the monolayer values increase with the increase in the lignin content.

The samples containing also silica have the values of these parameters more varied; there is not a uniform growth, probably due to the increasing in the system complexity. The predominant type of pores was found to be mesopores (2-50 nm).

Conclusions

By incorporating lignin in the polysiloxane matrix, significant changes in the water sorption capacity of the resulted materials occur. This is due to the presence of polar hydrophilic groups in the structure of lignin. Simultaneously, the low compatibility of lignin with the

siloxane matrix determines an increased porosity of the material and an increase of its specific surface. Yet the value of the contact angle does not present significant changes for the samples with different compositions, due to the preferential arrangement of siloxane chains with nonpolar CH_3 groups at the surface of the material.

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