Polysiloxane-Lignin Composites

George Stiubianu, Maria Cazacu, Mariana Cristea, Angelica Vlad

"Petru Poni", Institute of Macromolecular Chemistry, Inorganic Polymers Department, Aleea Gr. Ghica Voda 41A, Iasi 700487, Romania

ABSTRACT: A series of composites based on polydimethylsiloxane-α,ω-diol (PDMS) as polymeric matrix, silica aerogel as reinforcing filler, and the lignin powder—a biomass derivative, as bulking filler, have been prepared. Different weight ratios between components were used. The composites were investigated by scanning electron microscopy, dynamic mechanical analysis, tensile strength tests, X-ray diffraction analysis, thermogravimetric analysis, and differential scanning calorimetry. The results were compared with those obtained on a reference sample prepared by using a classical material—diatomite and a pure crosslinked PDMS. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2313–2321, 2009

Key words: composites; polysiloxanes; fillers; crosslinking; silicones

INTRODUCTION

The use of biologically derived polymers is an important component for economic development.[1] Such a compound is lignin, a three-dimensional amorphous aromatic natural biopolymer that is easily available and relatively inexpensive.[2,3]

A wide amount of lignin is obtained as a byproduct of the pulp and paper industry and traditionally has been used as an energy source.[4] Otherwise, residual lignin constitutes a major environmental problem; therefore, it would be important to find new applications for it.[5] Because of its properties, lignin can be used for different technical purposes[2]; thus, lignin gives a large amount of char by heating at high temperature in an inert atmosphere, this feature being a basic aspect of flame retardant additives, because char reduces the combustion rate of polymeric materials.[2] Moreover, the presence of the phenolic groups in lignin can provide thermooxidative and light stability to a chemical system in which it is incorporated. Lignin is a low-density, low abrasive, and low-cost material. Although all these features are attractive from the industrial point of view, only rarely lignin has been used to obtain new materials.[5]

One of the possible applications for lignin is its use as filler in the formulation of polymeric materials to increase their content of renewable resources.[4]

With certain polymers, it can give partially or completely biodegradable composites.[5]

It is known that lignin molecules present extensive crosslinking and strong intermolecular interactions that hinders their incorporation in solid material system. Therefore, miscible blends of such biopolymer with other systems are rare.[6] However, in optimal blending conditions, these interactions could be disrupted.[1] Only in the last years, some efforts have been made to incorporate lignin into different polymer materials: poly(ethylene terephthalate),[2,7] poly(vinyl alcohol) and polypropylene,[7,8] poly(vinyl chloride),[6,9] polyethylene, and polystyrene[5] or natural rubber.[3]

One of the polymers untested in blending with lignin is polydimethylsiloxane (PDMS). Polysiloxanes (silicones) are one of the most studied and useful polymers in the modern world, as this class of polymers exhibits a variety of properties combinations not common to other macromolecules: highly flexible backbone, small dielectrically constant, stability toward atomic oxygen, high permeability for different gases, hydrophobic and antiadhesive behavior, chemical and physiological inertness.

Yet the polysiloxanes have two major drawbacks: (a) poor mechanical properties and (b) high cost. To surpass these disadvantages, two approaches are being used: (a) the crosslinking of the siloxane backbone and (b) the incorporation of powders, usually inorganic ones as reinforcing and/or bulking fillers, in the siloxane matrix.

Silica is the usual additive used as reinforcing material for the improvement of the characteristics of the polysiloxanes: mechanical strength, insulating properties, and thermal stability. Other materials, such as diatomite, calcium carbonate, have a lower hardening effect, and are used as bulking filler.

The purpose of our research was to try to use lignin powder as filler for the polysiloxane matrix, the motivation for this being the use of cheap renewable materials from biomass for obtaining new materials. The incorporation of the lignin in silicone matrix and study of the effect of its presence on the properties of the resulted materials is what we aimed for. In our knowledge, there are no reports in literature regarding the use of these materials together in a single system. Using lignin as filler could be useful for room temperature applications of polysiloxane rubber such as medical applications, construction restoration, flexible seals, and gaskets. Because all the materials added to polysiloxane are hydrophobized powders, the resulted materials will be considered composites.

MATERIALS AND METHODS

Materials

Octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, (D$_4$), supplied by Fluka AG, with the following characteristics: b.p. = 175°C; n_D^{20} = 1.396; d_4^{20} = 0.955, purity >99% (GC), was dried over Na wire and freshly distilled before use.

Purolite CT-175, a styrene-divinylbenzene ion exchanger with —SO$_3$H groups (4.1 mequiv/g) was dehydrated by azeotrope distillation with toluene and vacuumation at 110 °C/10 mmHg.

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

Fumed silica, Aerosil 380 (Degussa), 100% purity, specific surface 380 m^2/g, particle diameter 0.003–0.015 μm , was used after hydrophobization by treatment with D$_4$ for 3 h at 180°C.

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

Diatomite Filia (SiO$_2$ max. 90%, Fe$_2$O$_3$ max. 1%, CaO max. 1%, granulation 85% <20 μ).

Protobind 100SA-140 a lower molecular weight (average M_W 1500) commercial lignin from India obtained from Sarkanda grass, was supplied by Granit Recherché Development SA Lausanne, having the following characteristics: 93.59% solids; softening temperature (°C) >200; pH = 2.11; aromatic OH = 1.75 mmol/g; carboxyl = 2.12 mmol/g and was used after drying and hydrophobization. The particles' size evaluated by SEM range between 0.5-8μm.

Methods

Equipments

FTIR spectra of the ground samples were recorded from KBr pellets on a Bruker Vertex 70 FTIR spectrometer.

The average viscometric molecular mass of the siloxane polymer was determined based on flowing time in the Ubbelohde viscometer.

Dynamic mechanical analysis (DMA) was run on a dynamic mechanical analyzer Diamond Perkin Elmer apparatus, in tension mode, at a frequency of 1 Hz. The temperature scans were performed between −150°C and 300°C at 4°C/min, in a nitrogen atmosphere. The films were longitudinally deformed by small sinusoidal stress and the resulting strain was measured. The force amplitude used was well within the linear viscoelastic range for all investigated samples. The behavior of all samples was measured in identical testing conditions. Moreover, the rate of cooling was maintained constant.

Differential scanning calorimetry (DSC) analysis was performed on Diamond Perkin Elmer equipment between −150°C and −25°C with a heating rate of 20°C/min, in nitrogen. The glass transition temperature was determined as the midpoint of the heat capacity change in the heating scan.

Scanning electron microscopy (SEM) was performed on a TESLA BS 301 SEM at 25 kV with a magnification of 300–15,000. The images were recorded on freeze-fractured surfaces deposed on Al supports and coated by sputtering with Au thin films using an EK 3135 EMITECH device.

Tensile strength tests. Specimens for tensile measurements were cut out from the thick films using a V cutter. The tests were performed at room temperature using an Instron Single Column Systems tensile testing machine (model 3345) equipped with a 5k N load cell and activated grips, which prevented slippage of the sample before break. The used crosshead speed was 50 mm/min. At least five identical dumbbell-shaped specimens for each sample were tested, and their average mechanical properties are reported. The reported errors are the subsequent standard deviations.

X-ray diffraction of the thin film obtained by spin coating was performed by using a DRON-2 diffractometer with CoK$_\alpha$, λ = 0.1789 nm and CuK$_\alpha$, λ = 0.154 nm radiation.

Thermogravimetric measurements (TGA) were performed in the temperature range 25°C–750°C at a heating rate of 10°C/min in air using a Q-1500D System.

Procedure

Synthesis of Polydimethylsiloxane-α,ω-diol. The mixture consisting in D$_4$ with 2.5 wt % Purolite CT-175 and 0.8% water was stirred at 80°C for 4 h in a thermostated reaction vessel equipped with reflux condenser, thermometer, and mechanical stirrer. Then, the reaction was stopped by removing the catalyst through filtration. The filtrate was devolatilized in a

Sample	Composition, weight parts					
	PDMS	Silica aerogel	Diatomite	Lignin	TEOS	DBDTL
S1	100	6	–	20	5	1
S2	100	6	20	–	5	1
S3	100	–	–	20	5	1
S4	100	6	–	10	5	1
S5	100	6	–	30	5	1
S6	100	–	–	–	5	1

rotavap at 150°C/10 mmHg to remove the cyclic and linear low-molecular weight compounds.[10] The molar mass of the remained polymer was evaluated by viscometric measurement using an Ubbelohde viscometer.

The hydrophobization of the fillers. The powder is charged in a three-neck flask equipped with dropping funnel, thermometer, and mechanical stirrer. The installation is heated in an electric mantle at 110°C. A vacuum (20 mmHg) is applied about 1 h to remove the water traces. Then, from dropping funnel D_4 (20% wt. reported to powder weight) is added to powder after which the dropping funnel is replaced by a reflux condenser. The temperature is increased to 180°C, and the mixture is maintained in these conditions under stirring about 3 h.

Preparation of the composites. PDMS was mixed with preestablished amounts of fumed silica, lignin or diatomite, and TEOS, according to Table I and stirred thoroughly with a glass rod to achieve a homogenous mixture of reagents. After that, the resulted mixture was kept under vacuum for 30 min to remove all the air bubbles trapped in the mixture, after that the catalyst (DBTDL) was added (0.2 mL), quickly stirred, and again shortly vacuumed.

The resulted mixture was used to obtain thick films (of about 3 mm thickness) by pouring in an iron mold 10 × 10 cm, pressed with a 250 g weight. The samples were maintained in such conditions at room temperature for 24 h after that, the formed films (colored brown and dark brown for those prepared with lignin, vivid orange for that prepared with diatomite and colorless and transparent for the reference sample) were easily peeled off from the substrate.

The films were then kept in the laboratory environment about 2 months before investigations by different techniques (FTIR, SEM, DMA, DSC, X-ray diffraction analysis, TGA, and mechanical testing).

RESULTS AND DISCUSSIONS

The PDMS with $M_v = 49,000$ was synthesized by cationic ring-opening polymerization of D_4 in the presence of Purolite CT-175 as catalyst (Scheme 1). A certain amount of water was added as chain-transfer agent (and chain blocker) to provide the terminal —OH functional groups and to regulate in a certain degree the molecular mass of the polymer.

This resulted polymer was used as a matrix for obtaining composites by filling it with the conventional fillers (silica and diatomite) and with the one used in this work, lignin. To improve their compatibility with the polymeric matrix and to avoid the hardening of the resulted composites during storage and handling, the filler powders (silica, diatomite, and lignin) were hydrophobized by treatment with D_4 in vapor state.

We verified the hydrophobization treatment efficiency by making the water wetability test for resulted powder (Fig. 1).

The IR spectra of the treated lignin [Fig. 2(b)] emphasizes the presence of the siloxane by its specific bands: $\nu CH_3 = 2959$ cm^{-1}, νSi—O—$Si = 1088$ cm^{-1}, νSi—$CH_3 = 1265$ and 807 cm^{-1}, besides those specific for lignin that are slightly shifted when compared with the original lignin [Fig. 2(a)]: $\nu(C=O)$ from 1706 cm^{-1} to 1710 cm^{-1}, and $\nu(OH)$ from 3422 cm^{-1} to 3425 cm^{-1}.
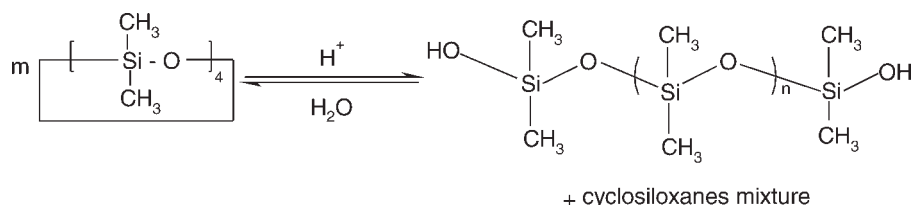
Scheme 1 Cationic ring-opening polymerization of octamethylcyclotetrasiloxane (D4).
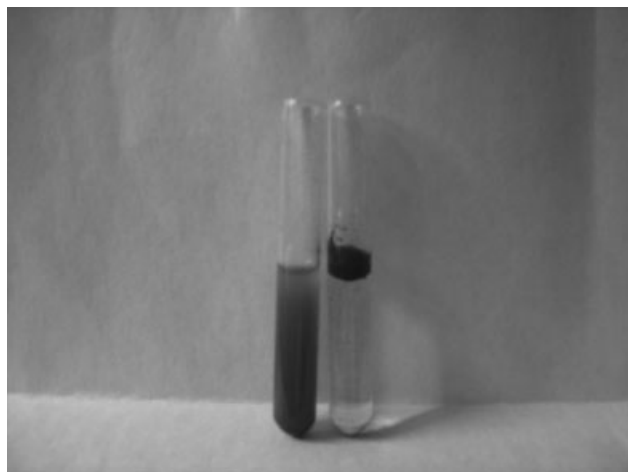
Figure 1 Wetability test for the the initial (left) and treated (right) lignin.

The treated fillers were mixed with the PDMS in the weight ratios as is presented in Table I by mechanical blending. The purpose of this research is to use lignin—a renewable material from biomass—as filler for the polysiloxane matrix for obtaining new materials.

As it is well known, TEOS and its homologues are rapidly hydrolyzed by water in the presence of acid or base as catalyst therefore it is used as the crosslinking agent for PDMS.[11] The hydrolysis of TEOS used in the process as crosslinker relied on atmosphere humidity. DBTDL was used as a catalyst for condensation. PDMS chains are crosslinked in a network by coupling of their ends through chemical bonding to the species derived from TEOS (Scheme 2).

It is presumed that the filler's particles (silica, diatomite, or lignin) are dispersed within the dimethylsiloxane network.

The post-processing of the samples, which consists in the formation and storage of the films in the laboratory environment, allows the reaction of hydrolysis and condensation of OH groups to proceed at a high degree. This procedure is based on the same principle as the room temperature vulcanization silicone preparation, when the crosslinking of the PDMS occurs by polycondensation reactions in the presence of the environmental humidity, needing a few days to process ending. Water must diffuse deep in film, whereas low-molecular condensation compounds (i.e. alcohol) migrate to the outside. Therefore, the films having the thickness of about 3 mm were kept in the laboratory environment for long time enough (about 2 months) before investigations, when the weighting revealed the mass stabilization.

By comparing FTIR spectrum of free lignin with that of the samples containing lignin incorporated in a crosslinked polysiloxane matrix [Fig. 2(c)], only a slight shifting of the bands specific for lignin can be seen. Thus, $\nu(C{=}O)$ is shifted from 1706 cm^{-1} in lignin to 1716 cm^{-1} in S3 sample and $\nu(OH)$ is shifted from 3422 cm^{-1} in lignin to 3431 cm^{-1} in S3 sample indicating the polysiloxane-lignin interaction.[6] Such an interaction can occur between carbonyl and hydroxyl groups from lignin with hydroxyl groups from the surface of the other fillers or between lignin hydroxyl group and Si—O—Si bond.

SEM was employed to study the cryofractured surfaces of the samples (Fig. 3).

A pure crosslinked PDMS (sample S6) serves as reference sample. The SEM images of the three used fillers were also taken. From the analysis of the images, one can draw the next observations: although the treated lignin appears to be in the form of particle aggregates with dimensions in the range of up to 8 μm, by incorporating them in the PDMS matrix these aggregates break-up such that they can be found very rarely and only in the samples where there is a higher content in lignin. Thus, the S3 sample that contains only lignin as filler and the S5 sample, that has the highest content of lignin, appear as more homogenous in comparison with the samples without lignin (S2) and the ones with a small content of lignin (S4). In the latter samples, a higher density of spherical or other geometrical shapes domains can be seen that can be ascribed to the silica and diatomite particles, respectively. This suggests that although it was not expected due to the difference in polarity yet there is a good dispersal of the lignin in the polysiloxane matrix. Even more it seems the presence of polar lignin induces a degree of ordering in the polysiloxane matrix (lamellar domains). However, from the DMA curves (Fig. 4) we can ascertain that the samples present two transition temperatures corresponding to the two components: one in the negative domain, corresponding for the polysiloxane component and one in the positive domain, around 220°C corresponding to lignin. Values close to that were obtained through DSC (Fig. 5).

DSC experiments in general evidence the step of heat capacity (ΔC_p), associated with the glass transition in the range $-121/-124$°C, an exothermic peak at about -100°C and an endothermic peak (at $-43/-46$°C) assigned to the cold crystallization phenomenon and to the melting of the crystalline phase, respectively. The fact that the melting peak is much more prominent than the crystallization one which is simply missing in most cases evidences that an important amount of crystalline phase is developed during cooling scan. This is an outcome of the great mobility of PDMS chains that make possible a three-dimensional chain arrangement required for crystalline phase development. It can be noticed that the DSC curves of S3 and S6 samples are almost
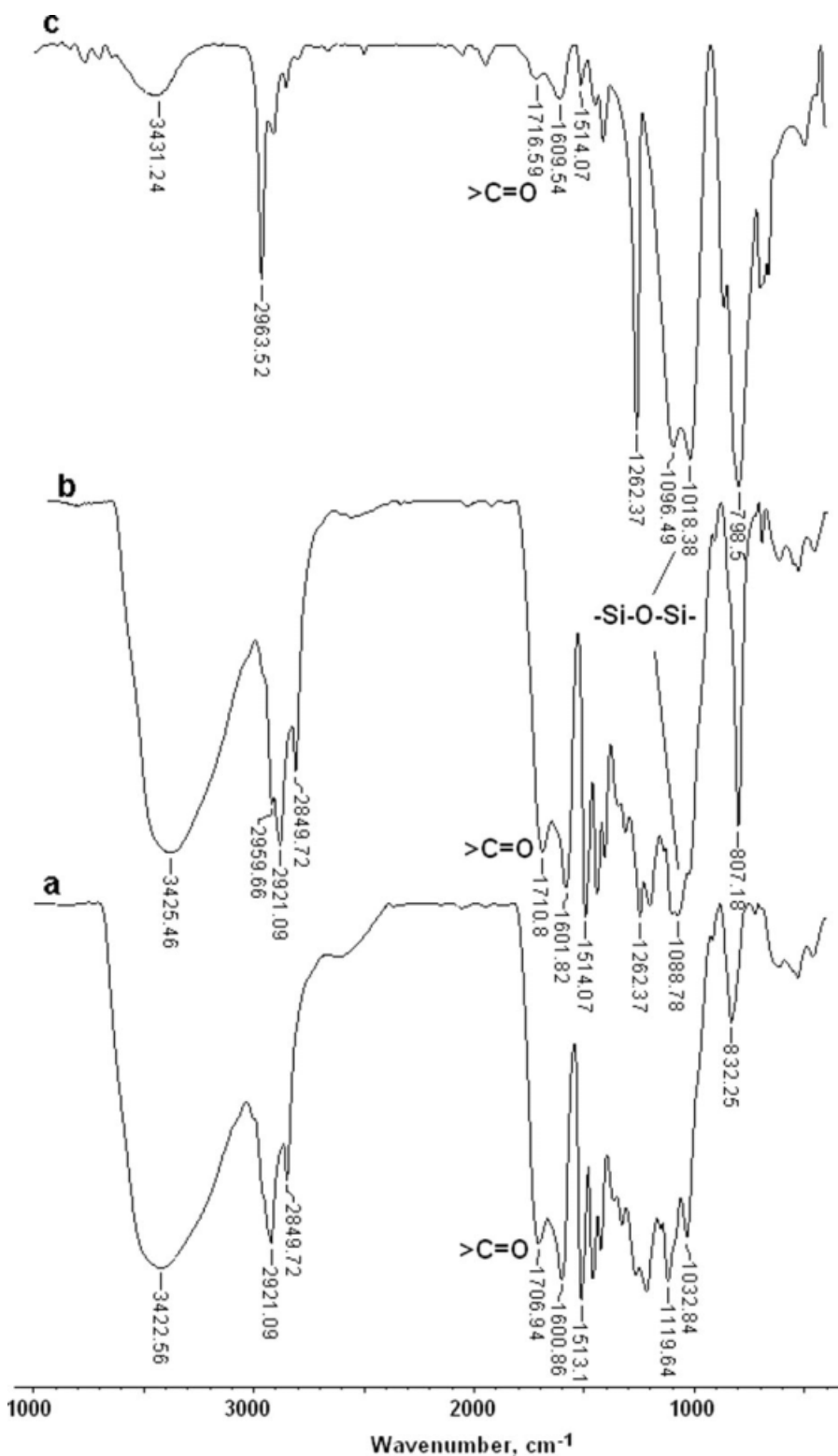
Figure 2 IR spectra of the initial (a) and treated (b) lignin as well as for the polydimethylsiloxane/lignin composite, S3 (C).

identically this suggesting that the lignin has a negligible influence on the thermal behavior of the samples.

If we analyze the viscoelastic behavior of the samples (Fig. 4), some similarities are noticeable: a glassy region ($T < -100°C$) with a storage modulus of 10^9 Pa or higher, a one or two-step descent of the storage modulus till $-40°C$ followed by an abrupt descent until a plateau characterized by a specific modulus value for each sample. A detailed
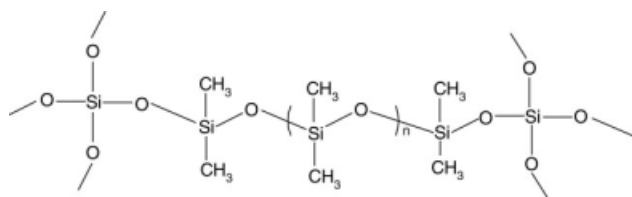
Scheme 2 Polydimethylsiloxane crosslinked network.

examination reveals peculiar features for each system. The glassy storage modulus for the S6 reference sample (1.82×10^9 Pa) (Figure 4, Curve d) decreases in one step to 2.08×10^8 Pa during the glass transition process in the interval range between $-143°C$ and $-79°C$. This fall represents almost an order of magnitude and usually suggests the absence of the constraints (physical crosslinks and/or crystalline
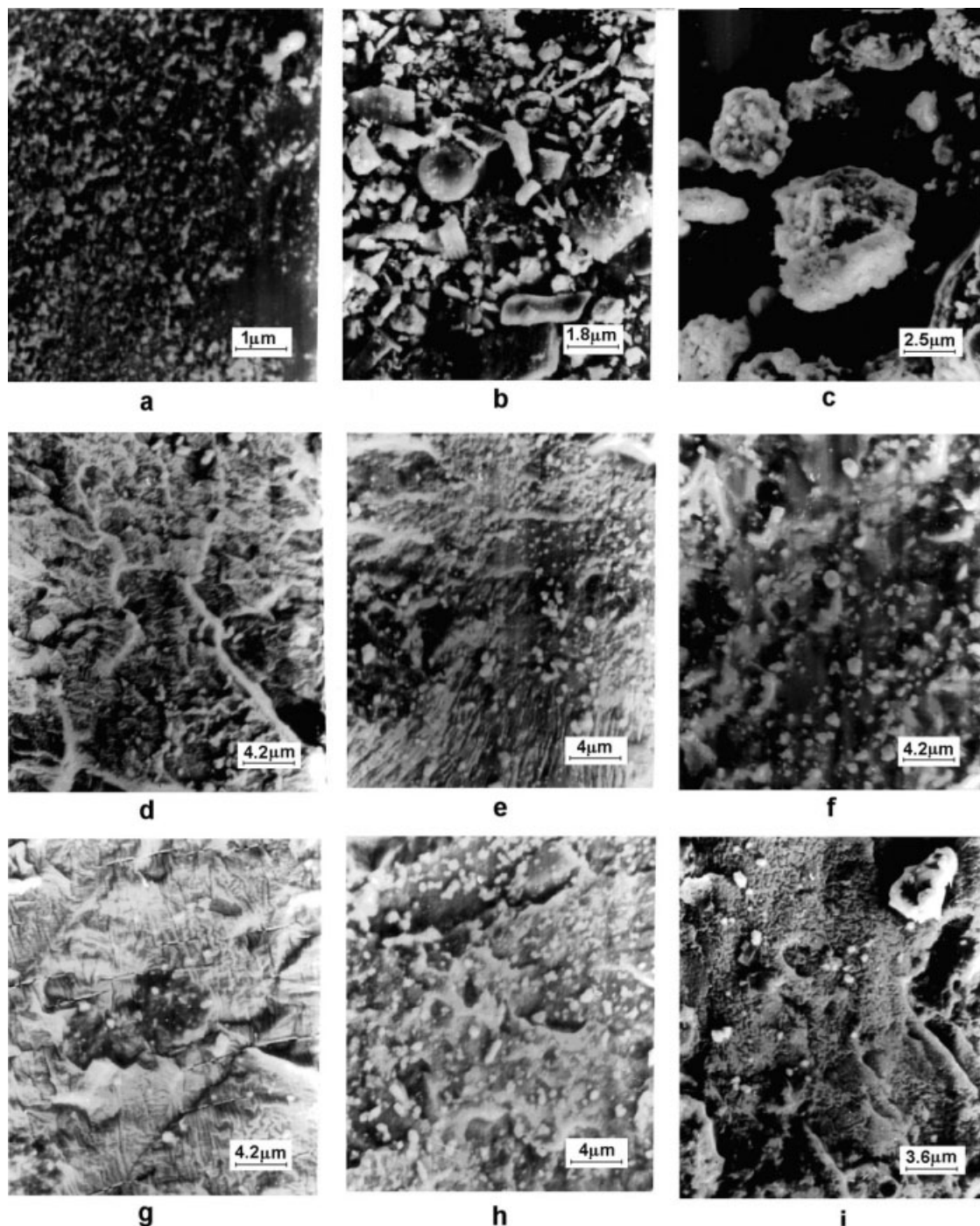
Figure 3 SEM images of (a) treated silica, (b) treated diatomite, (c) treated lignin, and the fractured surfaces for (d) reference sample S6, (e) S1, (f) S2, (g) S3, (h) S4, (i) S5.
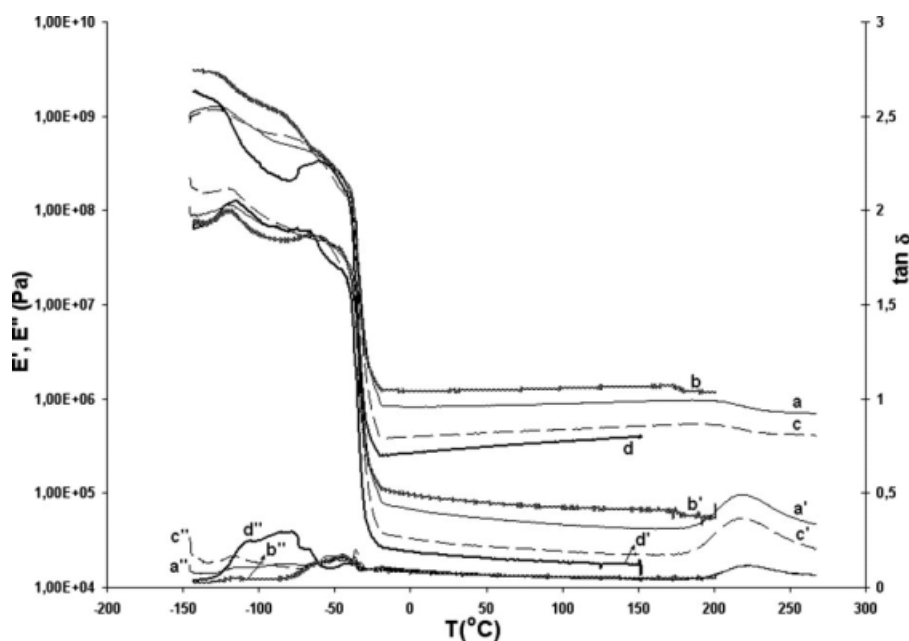
Figure 4 DMA curves of the samples: S1, S2, S3, S6. (a–d) Storage modulus vs. temperature plots; (a′–d′) loss modulus vs. temperature plots; (a″–d″) tan δ vs. temperature plots.

domains) in the polymer system. This is not unusual as PDMS chains have unusually low intermolecular forces and the physical crosslinks are excluded. The storage modulus of the S3 sample (1.18×10^9 Pa) decreases in one step till 6.2×10^8 Pa during the glass transition process in the interval range between $-127°C$ and $-83°C$. This fall represents less than an order of magnitude and suggests the presence of some constraints (physical crosslinks and/or crystalline domains) in the polymer system. The smaller decrease of $E′$ for S3 sample in the glassy region as

compared to S6 sample is not unusual as the storage modulus is considered a gauge of sample stiffness.

In Figure 4 curves a″–d″ we can see that the melting point comes out at the same temperature range for all the samples ($-25°C$) because the nature of the crystalline domains is alike. It is also noticeable that the T_g values emphasized by DMA differ little from those determined by DSC (Table II).

It must be mentioned that the storage modulus values reached after melting increase with the temperature (Figure 4 curves a–d). During the reaction,
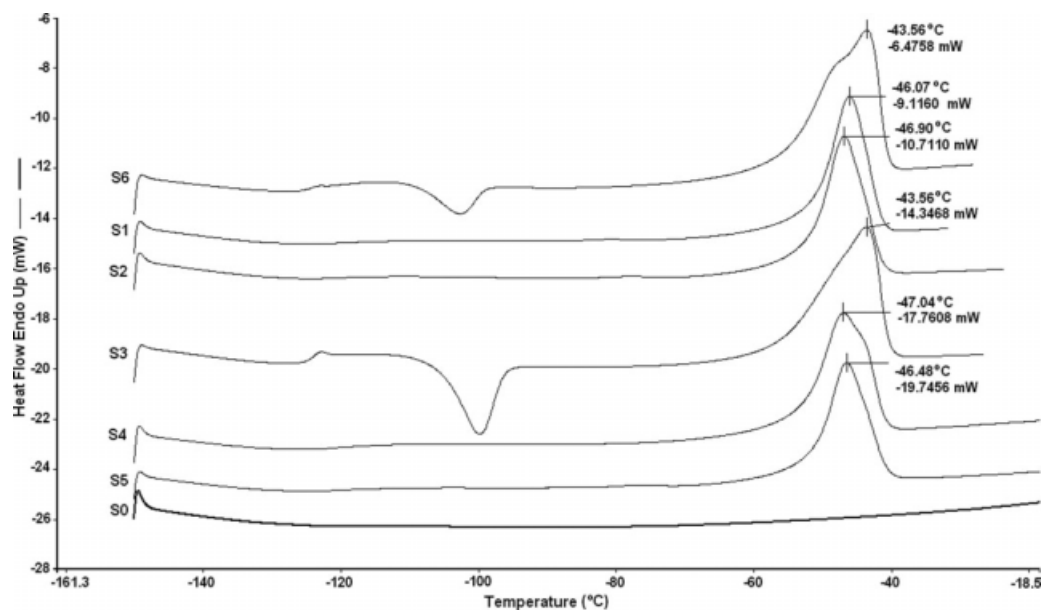

Figure 5 DSC scans (second heating) for the different samples (S1–S6) and for the lignin, S0.

TABLE II
The Comparative T_g Values Evaluated from DMA and DSC curves, Respectively

Sample	T_g, °C (DSC)	T_g, °C (DMA)
S1	Not visible	−114
S2	Not visible	−82
S3	−124.51	−116
S4	−121.03	Not measured
S5	−121.72	Not measured
S6	−124.62	−120.8

TABLE III
The Main Mechanical Parameters

Sample type	Breaking stress (MPa)	Strain (%)	Young's modulus (MPa)
S1	0.424 ± 0.04	122 ± 1	0.686 ± 0.007
S2	1.249 ± 0.09	178 ± 1.1	0.836 ± 0.008
S3	0.225 ± 0.02	93 ± 0.8	0.405 ± 0.005
S4	0.448 ± 0.04	121 ± 1	0.630 ± 0.006
S5	0.400 ± 0.03	93 ± 0.7	0.822 ± 0.008
S6	0.155 ± 0.01	82 ± 0.7	0.220 ± 0.002

incomplete condensation involving TEOS or lignin and PDMS cannot be excluded. As the temperature is raised to high-positive values, the reaction between these components may be perfected, the catalyst being present in the system. The increase in storage modulus signals the completion of the reaction. The impact of raising the lignin quantity in the system on the storage modulus values is well reflected in Figure 6. On the DMA thermograms, several peaks and shoulders may be noticed until the melting. In this environment, lignin reinforces the PDMS matrix therefore inducing the largest increase of T_g. Miscellaneous morphologies prompted by the lignin/PDMS proximity indicate that lignin influences in different ways the PDMS segments, but it would be risky to draw a precise correlation of viscoelastic behavior with specific morphologies. The strength and the thermal stability of the composite throughout the positive temperature interval suggest that lignin might act as reinforcing agent.

The values of the main mechanical parameters obtained by tensile strength tests for the prepared samples are presented in Table III.

There is no significant effect of lignin on the mechanical characteristics (breaking strength and strain) of the composites. The values from Table III show only a slight increase in the strength and strain for samples with lignin by comparison with the reference sample made from crosslinked pure PDMS. The value of Young's modulus increases more significantly with the increase in the content of lignin in the samples (Table III). In fact, as literature already reported,[4] in many cases, lignins are used only as low-cost fillers and the objective is to minimize the loss of ultimate mechanical properties.

In general, the pure PDMS exhibits a peak at around $2\theta = 12.5$ assigned to the liquid-like packing in the dimethylsiloxane and a broad diffraction
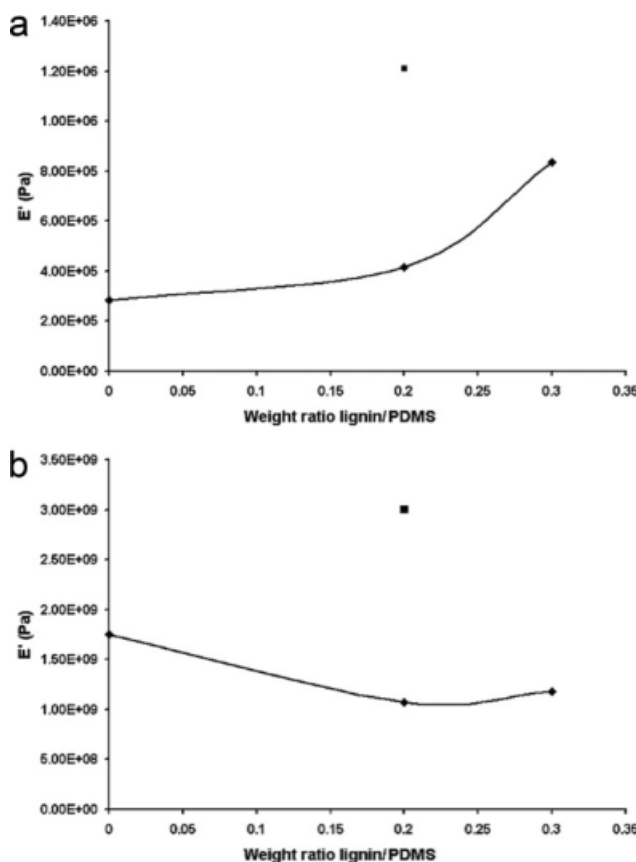

Figure 6 Storage modulus vs. feed weight ratio plot for PDMS/Lignin and PDMS/Diatomite at: (a) 25°C and (b) −140°C: PDMS/Diatomite; PDMS/Lignin.
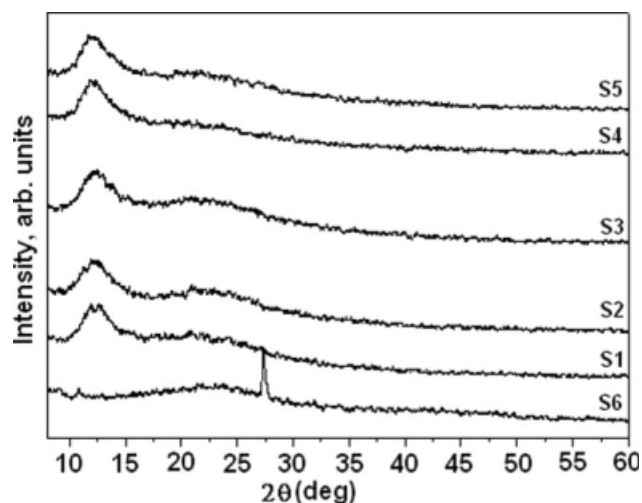

Figure 7 X-ray diffraction analysis patterns of the composites.

TABLE IV
The Main Thermogravimetric Data
for Crosslinked Structures

Sample	T_{10}[a]	T_{40}[a]	T_f[b]	% wt Residue
S1	410	503	585	33
S2	412	520	550	43
S3	410	493	585	30
S4	405	510	585	34
S5	403	498	612	29
S6	155	430	>750	13

[a] Temperature for 10 and 40% weight loss, respectively.
[b] Final decomposition temperature.

background characteristic for amorphous phase centered on $2\theta = 20$–25.[12,13] This pattern is maintained both by crosslinking and by the fillers involved as can be seen in Figure 7.

The thermooxidative stability was investigated by TGA analysis. By examining the obtained data, it can be concluded that the presence of lignin in matrix does not modify in a significant manner the thermal stability of the samples and the main data of the recorded TGA curves are presented in Table IV.

With the exception of sample S6, which begins to lose weight at about 100°C, the other samples show only thermooxidative processes beginning above 400°C in a similar way. However, between the filled samples, S3 has the lowest thermostability, but it is better in comparison with S6 reference sample. This is due to the occurrence of the lignin degradation. Although this filler would be expected to improve the thermal stability by polymer/lignin interaction, this is not happening due to the lignin degradation that, as it is known, begins at about 200°C.[5,14]

CONCLUSIONS

Lignin alone or together with silica was tested as filler for a PDMS matrix having $M_v = 49,000$. The mix-tures having different compositions and colors were processed as thick films (of about 3 mm thickness). The results of the thermomechanical, mechanical, and thermal investigations have evidenced the fact that lignin inserted in a silicon matrix does not alter its properties, and in some cases (e.g. mechanical properties), it even induces a slight improvement of these, leading to the conclusion that lignin can be used as an extender for silicones, with positive effects mainly on the material's cost. The SEM images emphasized a good phase mixing even though the T_g value specific for siloxane is visible at about the same value as in the model sample, without fillers. X-ray diffractogram is also not influenced by the filler's presence.

References

1. Canetti, M.; Bertini, F.; De Chirico, A.; Audisio, G. Polym Degrad Stabil 2006, 91, 494.
2. Canetti, M.; Bertini, F. Compos Sci Technol 2007, 67, 3151.
3. Gregorová, A.; Košíková, B.; Moravčík, R. Polym Degrad Stabil 2006, 91, 229.
4. Pouteau, C.; Baumberger, S.; Cathala, B.; Dole, P. C. R. Biologies 2004, 327, 935.
5. Pucciariello, R.; Villani, V.; Bonini, C.; D'Auria, M.; Vetere, T. Polymer 2004, 45, 4159.
6. Mishra, S. B.; Mishra, A. K.; Kaushik, N. K.; Khan, M. A. J Mater Proc Technol 2007, 183, 273.
7. Kadla, J. F.; Kubo, S. Compos Part A Appl Sci Manuf 2004, 35, 395.
8. De Chirico, A.; Armanini, M.; Chini, P.; Cioccolo, G.; Provasoli, F.; Audisio, G. Polym Degrad Stab 2003, 79, 139.
9. Raghi, S. E. l; Zahran, R. R.; Gebril, B. E. Mater Lett 2000, 46, 332.
10. Cazacu, M.; Marcu, M. Macromol Rep A 1995, 32, 1019.
11. Shirai, M.; Sumino, T.; Tsunooka, M. Eur Polym J 1993, 29, 831.
12. Diele, S.; Oelsner, S.; Kuschel, F.; Hisgen, B.; Ringsdorf, H.; Zentel, R. Makromol Chem 1987, 188, 1993.
13. Jia, Y.; Zhang, B.; Zhou, E.; Feng, Z.; Zang, B. J Appl Polym Sci 2002, 85, 1104.
14. Baumberger, S.; Aguié-Béghin, V.; Douillard, R.; Lapierre, C.; Monties, B. Ind Crop Prod 1997, 6, 259.