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Room Temperature Synthesis and Characterization of Hybrid Materials of Polymethylhydrosiloxane Modified by Hydroxide Organic Compounds

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Abstract. New monolithic and transparent hybrid gels were obtained by reaction at room temperature of polymethylhydrosiloxane (PMHS) with 1,3,5-trihydroxybenzene ($DO_{1,3,5}$) and 2-hydroxybenzoic acid (DO_2), in tetrahydrofuran, using hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) as catalyst. The products have been characterized by infrared and ^{29}Si MAS-NMR spectroscopy. The results show that the organic compounds have reacted with the PMHS, leading to monolithic and transparent gels in which organic-inorganic bridges were formed. An appropriate thermal treatment procedure was determined from TGA and DTA curves recorded on the hybrid gel powder after drying at 70°C. The morphology and structure of the materials obtained were studied by scanning electronic microscopy (SEM) and X-ray powder diffraction (XRD).

Keywords: hybrid materials, plymethylhydrosiloxane, organic hydroxide, ^{29}Si MAS-NMR

1. Introduction

Silicon oxycarbide glasses have received increasing attention over the past few years due to their high-temperature stability, good crystallization, oxidation resistance and high mechanical strength [1–4]. Introduction of carbon into a silica network by direct solid-state reaction [5] is very difficult, but it is quite easy by pyrolysing appropriate polysiloxanes [6]. The use of such polymers has also allowed the development of shaped objects such as silicon oxycarbide fibers [7–9] and composites [10, 11].

In an extension of our previous studies on hybrid organic-inorganic materials prepared from $Si(OMe)_4$-butane-1,4-diol mixtures [12] and from the reticulation of the polymethylhydrosiloxane (PMHS) using linear diamines, olefins or diols [13–15], we report the results of a study of the chemical modification of PMHS with bi-and tri-functional aromatic rings. The reaction leads to the formation of polymeric, transparent and colored networks that have been characterized by ^{29}Si-MAS NMR, IR, DTA, TGA, SEM and XRD. The presence of aromatic rings can apparently increase the pore size of the materials. In addition, this work is part of a more extensive study on the synthesis of organic-inorganic materials, carried out by chemical modification of PMHS by hydroxybenzene and 1,4-dihydroxybenzene that will be reported in a future paper.

2. Experimental

Samples were prepared by mixing PMHS and 1,3,5-trihydroxybenzene or 2-hydroxybenzoic acid in

Table 1. Experimental conditions and nature of products obtained.

Reagents	Molar ratio: reagent/(Si—H)	Gelation time	Nature of products
1,3,5-trihydroxybenzene	0.33	7 days	Yellow gel: $DO_{1,3,5}$
2-hydroxybenzoic acid	0.5	11 days	Greenness gel: DO_2

stoichiometric proportions in tetrahydrofuran (THF). Hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was used as a catalyst ($4 \cdot 10^{-7}$ mol/g PMHS). The mixture was stirred at room temperature in a closed vessel for 1 h. Gaseous bubbles were observed in the reaction medium during the synthesis due to the evolution of hydrogen [16]. Transparent and monolithic gels were formed within several days, depending on the nature of the reagent (Table 1). The gels obtained were placed in a drying oven to remove the solvent.

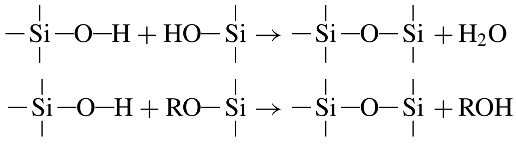
^{29}Si MAS-NMR spectra were obtained with a Bruker MSL 400 Spectrometer, using a sample spinning speed of 4 kHz. Infrared spectra were recorded on a Nicolet Magna 550 Spectrometer, with samples in the form of KBr pellets. Thermal treatment was performed under an air atmosphere from 20 to 1500°C with a heating rate of 10°C min^{-1}, using a Netzsh STA 409 thermal analyzer. X-ray powder diffraction data were collected on a CAD4 diffractometer using CuKα radiation ($\lambda = 1.54056$ Å) and graphite monochromator. Scanning Electron Microscopy was performed with a Cambridge Instruments Stereoscan 120 to investigate the morphology of the samples.

3. Results and Discussion

$DO_{1,3,5}$, and DO_2 samples were obtained by coupling PMHS with 1,3,5-trihydroxybenzene or 2-hydroxybenzoic acid, respectively, through substitution reactions. The bi or trifunctional organic rings between the siloxane chains ensured the reticulation and the formation of tridimentional networks. After drying the gels at 70°C for 24 h under air, colored xerogels were obtained. The gel-to-xerogel transformation was accomplished by evaporation of the solvent. The xerogels were ground and the resulting powders were characterized by the different techniques mentioned above. Aromatic rings, functionalized with hydroxyl groups, were used as crosslinking agents.

3.1. ^{29}Si MAS NMR Spectroscopy

^{29}Si-MAS NMR is a convenient tool to probe the different Si sites existing in the material. The ^{29}Si solid-state NMR spectrum of $D_{1,3,5}$ (Fig. 1) shows two main peaks at −56.4 and −65.4 ppm, together with an additional weak peak at 10 ppm. The first is attributed to T_2 units [17, 18], resulting from the substitution of Si—H by Si—O—C linkage [15, 19] (and possible subsequent formation of Si—OH species). The second one is assigned to T_3 units. T_3 units might result from (1) partial hydrolysis of the silicon-hydrogen bond followed by intra or intermolecular cross-linking of PMHS [17]; or (2) from a condensation between silanols or between silanols and alkoxo groups, leading to the formation of siloxanes bonds [20] according to the following reactions:



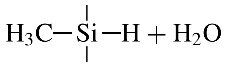
$$-\overset{|}{\underset{|}{Si}}-O-H + HO-\overset{|}{\underset{|}{Si}} \rightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}} + H_2O$$

$$-\overset{|}{\underset{|}{Si}}-O-H + RO-\overset{|}{\underset{|}{Si}} \rightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}} + ROH$$

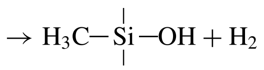
The small peak at 10 ppm is assigned to M units corresponding to $(CH_3)_3Si$—O— end chains groups [13, 15], although a contribution from spinning side bands cannot be completely excluded (note that the peak at −130 ppm is attributed to a spinning side band).

3.2. Infrared Spectroscopy

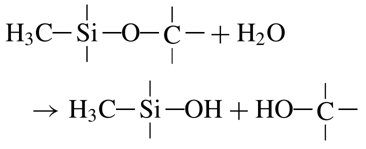
Figure 2 illustrates the IR spectra of $DO_{1,3,5}$ and DO_2. These spectra show the complete disappearance of the band associated with Si—H species at 2160 cm^{-1} (ν_{Si-H}), reflecting essentially complete reaction of the hydrides. The IR spectrum of $DO_{1,3,5}$ (Fig. 2(a)) exhibits a broad band profile assigned to ν_{OH} at 3200–3500 cm^{-1}. In the case of DO_2 (Fig. 2(b)), the corresponding profile extends from 2500 to 3400 cm^{-1}, due to the contribution of COOH groups which typically exhibit significantly different spectral profiles in this region to those of OH groups in Si—OH and Ph—OH. The observed OH groups are attributed to aromatic hydroxyls species that remain unreacted, and to Si—OH groups resulting from possible hydrolysis of the hydrides [reaction (1)] [21] and Si—O—C linkages [reaction (2)]:



$$H_3C-\overset{|}{\underset{|}{Si}}-H + H_2O$$



$$\rightarrow H_3C{-}\overset{|}{\underset{|}{Si}}{-}OH + H_2 \qquad (1)$$



$$H_3C{-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{C}}{-} + H_2O$$

$$\rightarrow H_3C{-}\overset{|}{\underset{|}{Si}}{-}OH + HO{-}\overset{|}{\underset{|}{C}}{-} \qquad (2)$$

Furthermore, the acidic —COOH species can enhance the hydrolysis reaction, which might explain the higher abundance of T_3 sites in DO_2 compared with $DO_{1,3,5}$.

The IR spectra exhibit additional sharp bands corresponding to C-H species (ν_{C-H}, 2800–3020 cm^{-1}) and organometallic groups (Si—CH_3; ν_{Si-CH_3}, 1300 cm^{-1}; ν_{Si-C}, 770 cm^{-1}). A broad band observed around 1150 cm^{-1} is attributed to $\nu_{Si-O-Si}$ [22].

3.3. Thermal Analysis

The TGA and DTA curves for $DO_{1,3,5}$ and DO_2 are illustrated in Figs. 3(a) and (b), respectively. Figure 3(a)

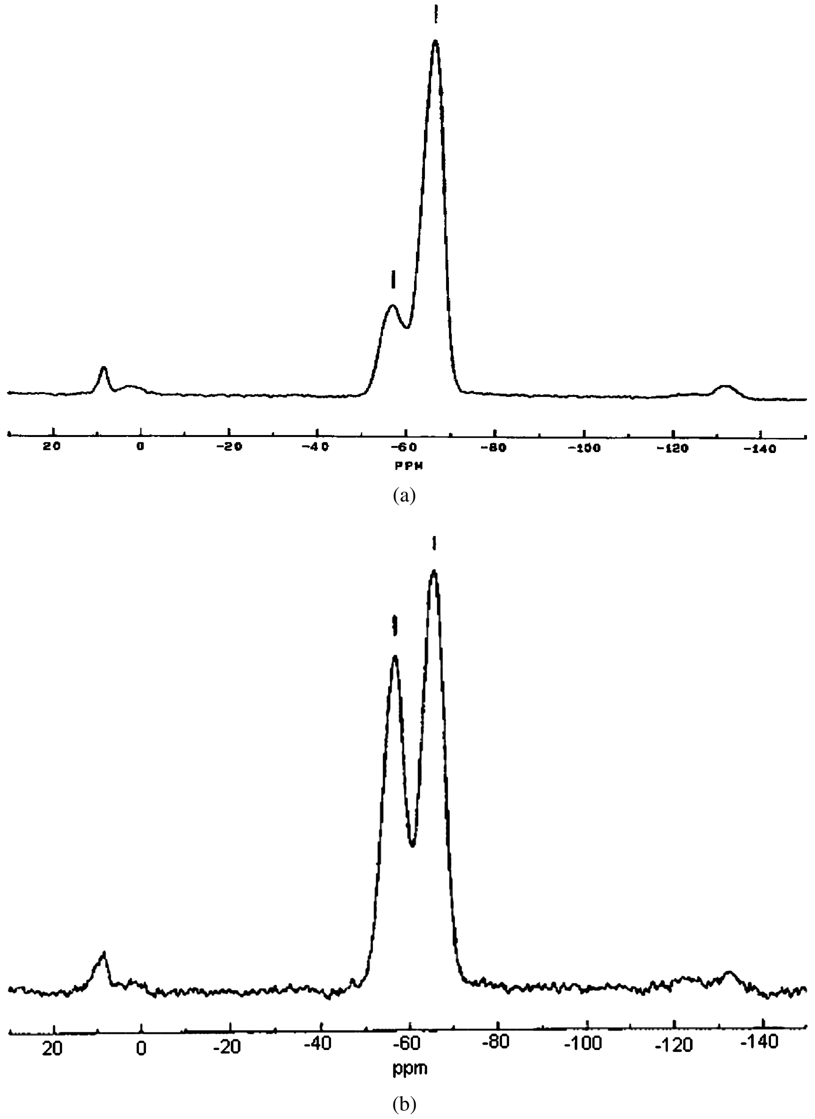
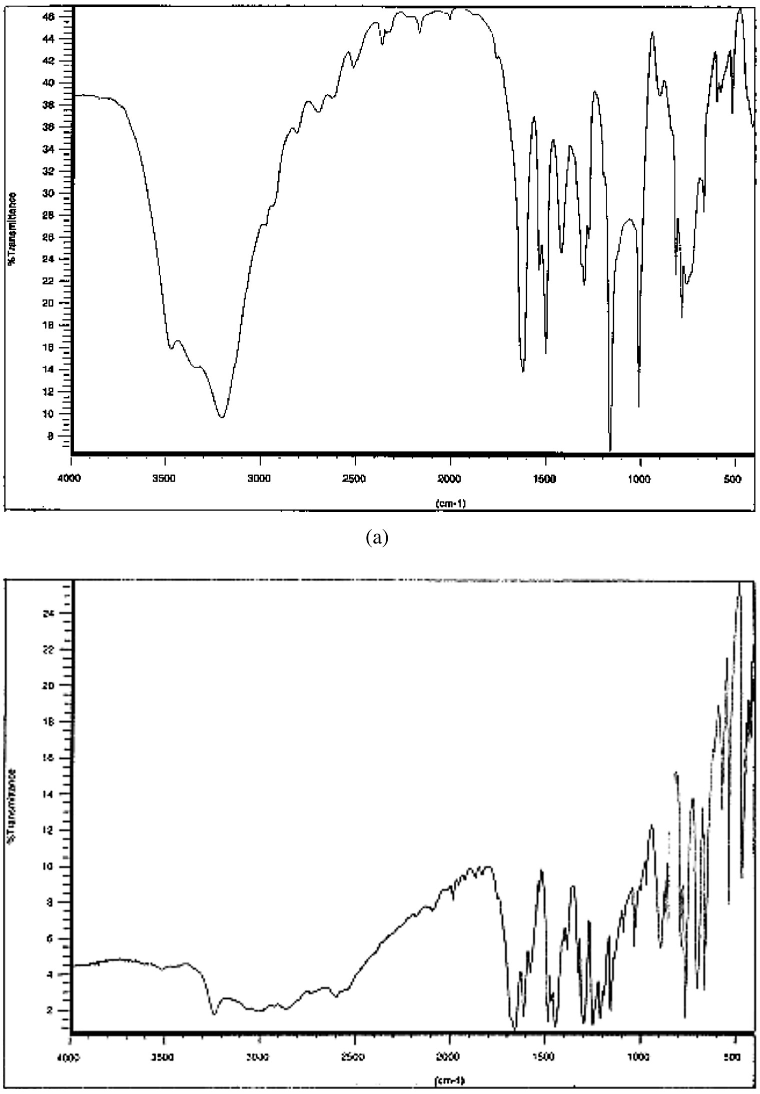


Figure 1. ^{29}Si-MAS NMR spectra of (a) DO_2 and (b) $DO_{1,3,5}$.



(a)

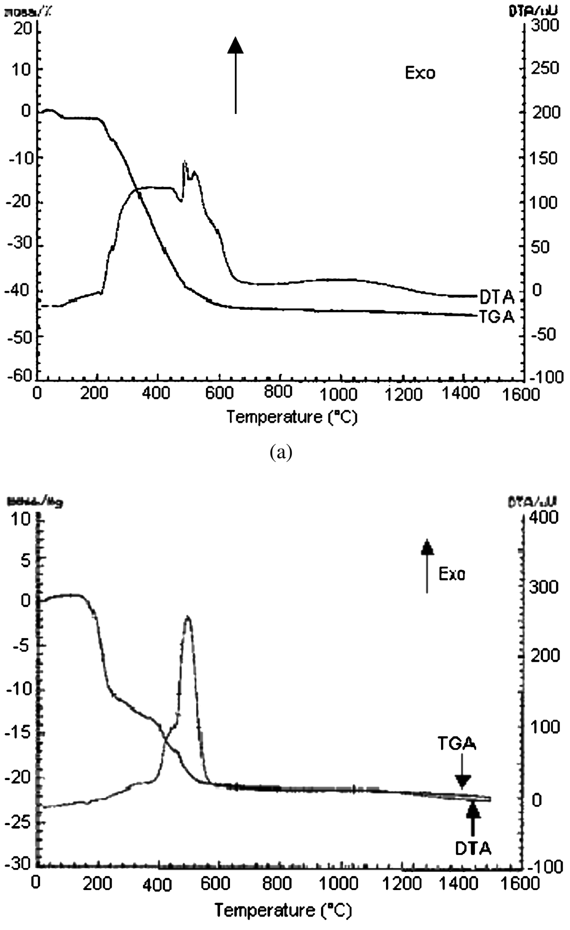
(b)

Figure 2. Infrared spectra of (a) $DO_{1,3,5}$ and (b) DO_2.

($DO_{1,3,5}$) exhibits a broad exothermic peak (DTA) at 240–400°C, which is attributed to the combustion of organic groups linked to the network through a single bond. The two sharp exothermic peaks (DTA) that occur at 490 and 516°C are attributed to the combustion of organic groups linked through two or more bonds to the PMHS backbone.

The thermal response of DO_2 (Fig. 3(b)) is somewhat different to that of $DO_{1,3,5}$, and exhibits a well-defined DTA peak at 492°C, together with a shoulder at 420°C. Both peaks are associated with weight losses, and again, are attributed to combustion of aromatic groups linked to the siloxane network.

The thermal analyses of all products clearly show retention of the siloxane backbone until 600°C. No significant weight losses (TGA) are observed between 600 and 1500°C. However the DTA curves show a broad exothermic peak in the range 900 to 1200°C. The X-ray diffraction patterns of the materials (Fig. 4) are consistent with the formation of tetragonal SiO_2 [23] after thermal analysis to 1500°C, and hence, the broad exothermic peak is attributed to crystallization of this phase.



(a)

(b)

Figure 3. Thermal analysis of (a) $DO_{1,3,5}$ and (b) DO_2.

3.4. *Scanning Electronic Microscopy*

The scanning electron micrographs of $DO_{1,3,5}$ and DO_2 are shown in Figs. 5(a) and (b), respectively. $DO_{1,3,5}$ exhibits a surface decorated with small aggregates with dimensions of ca. 100 nm. In contrast, DO_2 appears to be more homogeneous, with a relatively smooth surface.

4. Conclusion

Transparent, monolithic and colored hydroxyl modified polysiloxane gels were prepared by reaction of polymethylhydrosiloxane (PMHS) with dihydroxyl (2-hydroxybenzoic acid) or trihydroxyl (1,3,5-trihydroxybenzene) species. Reactive Si—H bonds present in PMHS facilitate the easy grafting of the modifiers by condensation reaction with O—H groups in solution at room temperature, leading to the formation of Si—O—C bonds. ^{29}Si-MAS NMR revealed the grafting of organic rings onto the siloxane network of the hybrid materials, as demonstrated by the formation of *T* units. These results show that the materials obtained from chemical modification of PMHS with aromatic alcohols via the formation of Si—O—C bonds are not very stable towards hydrolysis. Thermal analysis of all products clearly shows retention of the siloxane backbone until 600°C.

These materials demonstrated excellent optoelectronic properties and might find numerous

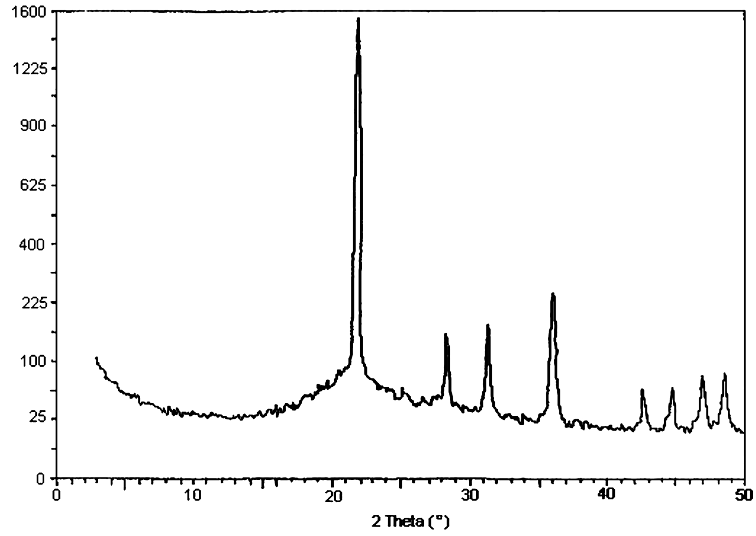
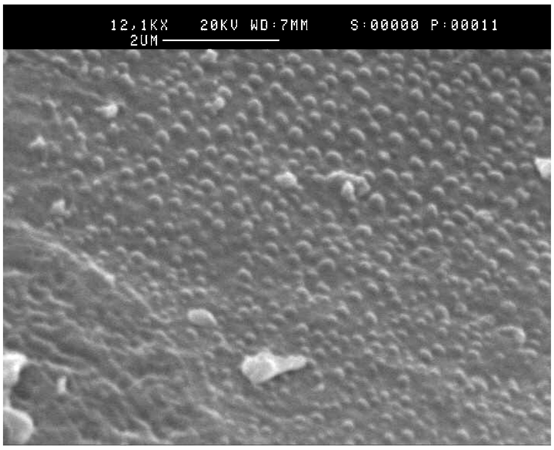
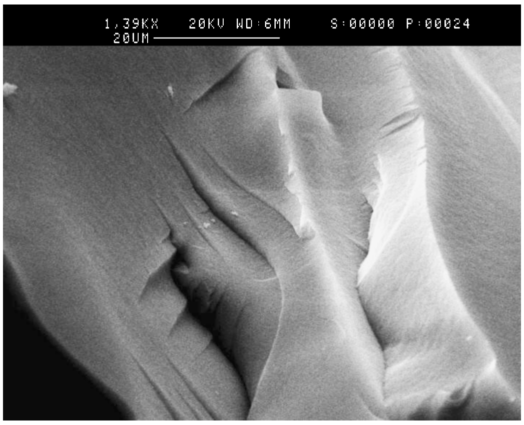


Figure 4. XRD pattern of $DO_{1,3,5}$.



(a)



(b)

Figure 5. SEM micrographs of (a) $DO_{1,3,5}$ and (b) DO_2.

applications in such areas as the manufacture of electroluminescent diodes and ion sensors. The presence of aromatic rings (π electron) allows widening the areas of application of these materials, in particular within the domain of optics. The study of the physical properties of these materials would contribute to the choice of functional organic molecules to be grafted to the siloxane background. Thus, by varying the nature of the organic chain or rings, we are able to change the composition of the precursor hybrid so that the products obtained by firing under argon contain pure Si—C or Si—O—C or Si—N—C.

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