PLASMA SYNTHESIS OF POLYMERIC THIN-LAYER-NETWORKS FROM HIGH MOLECULAR WEIGHT POLYSILOXANES

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ABSTRACT

This work presents a novel approach for synthesis of three dimensional polymeric netowrks from liquid phase high molecular weight polysiloxanes. Different viscosity polydimethylsiloxanes were deposited as thin viscous layers on various substrates and converted under RF (30 kHz) oxygen-plasma conditions into uniform, solid phase transparent polymeric layers.

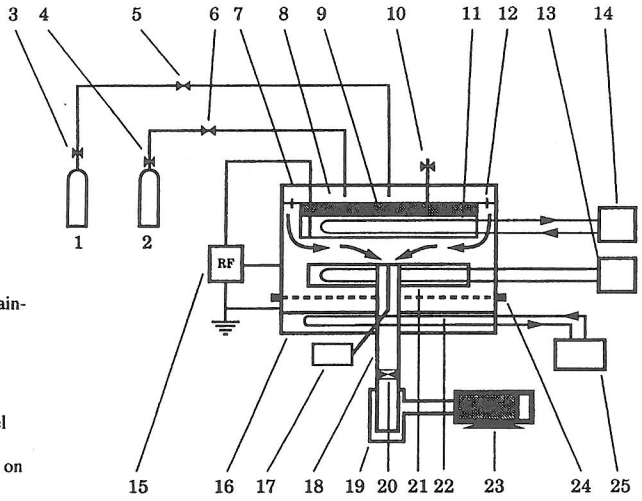
INTRODUCTION

Modern technologies like miniaturization, microelectronics, nonlinear optics, solar energy accumlation and conversion etc., have stimulated an increasing demand for ultrathin polymer film materials. The selection of a polymer thin film for a specific application is generally dictated by a combination of properties such as electrical, optical, thermal and mechanical characteristics and by the processing behaviour of these materials. During the fabrication of electronic or optical devices polymer films must survive in hostile thermal (thermal cycling), chemical (exposure to solvents and curing agents), mechanical (scratching, bending) and sometimes radiation (photo bleaching, ion beam technologies) environments, while mantaining their characteristics of modulus, thermal expansion and fluid transport within certain limits. Advanced technologies also require polymer films with specialized functions where structural precision cannot be overlooked. High tensile strength and high modulus film characteristics can only be achieved from advanced molecular symmetry (linear macromolecules) and high cohesive energies between the polymeric chains. Macromolecular structures from conventional plasma-polymer thin film deposition processes cannot generally meet these requirements. Due to the multitude of coexisting active and neutral species in plasmas, the resulting macromolecular networks do not contain a single repeat unit and usually do not retain the structural characteristics of the starting materials. The films commonly appear as colored , amorphous, brittle structures [1-5].

Active-gas plasma-induced crosslinking of liquid phase polymeric thin layers opens up new possibilities in this field through single step generation of matrices with built-in linear macromolecular chains. In this paper, oxygen-RF-plasma induced conversion of liquid phase thin-layer polydimethylsiloxane (PDMS) into a solid state network is demonstrated, and the structure and properties of the polymeric films are discussed.

EXPERIMENTAL

Methods: The plasma-induced structural modifications of polydimethylsiloxane werre followed with FT-IR, DTA, UV, ESCA, and high resolution (HR) MS techniques.



1 - Argon cylinder
2 - Oxygen Cylinder
3, 4 - Valves
5, 6 - Flowmeter
7 - Upper Part of Cylindrical Stainless Steel Reactor
8 - Gas Mixing Chamber
9 - Insulating layer
10 - Vent-valve
11 - Hollow Upper Stainless Steel Electrode
12 - Gas-Inlet Orifices Displaced on a Shower Type System
13 - Electric Heating Controller
14 - Thermostat
15 - RF generator
16 - Lower Part of Cylinderical Stainless Steel Reactor
17 - Pressure Gauge
18 - 1" Diameter Stainless Steel Connecting Tubing
19 - Liquid N_2 Trap for Vacuum Pump Protection
20 - Large Capacity Valve
21 - Lower Stainless Steel Electrode
22 - Thermostating Chamber
23 - Mechanical Pump
24 - Circular O-Ring Sealing System
25 - Thermostat

Pasma Reactions: The experiments for synthesizing thin polymeric films were carried out in a RF (30 Kc) capacitively coupled parallel plate (20 cm diameter disc-shaped electrodes; width = 2 cm) plasma installation presented in Figure 1. The cylindrical (ID=305mm ; H=100mm) stainless steel chamber is composed of a rigid lower part [24] and a levered upper part [8] permitting easy handling of substrates and samples. Both the upper electrode and the base plate of the reactor are provided with thermostating chambers, [11] and [22], allowing the selection of proper temperatures and avoiding the transmission of caloric energy to the electronic parts of the installation located under the reaction chamber. The lower electrode is equipped with an electric heating system [13] facilitating substrate and sample pre-plasma preparations as well as post-plasma treatments. The lower electrode is also the substrate holder and is connected by means of a 1" diameter stainless steel tube [18], positioned symmetrically through the center of the electrode, to the vacuum system, composed of a high capacity valve [20], a stainless steel liquid nitrogen trap [19], a mechanical pump [23] and a vacuum gauge [17]. The gas phase components (argon and oxygen) are introduced into the reaction chamber from cylinders [1] and [2], through valves [3] and [4] and flowmeters [5] and [6]. The gas mixing chamber of the reactor [8] and the shower type orifice system [12] and the centrally positioned vacuum line [18] assure a symmetrical and uniform flow of the plasma gases (arrows) between the electrodes. The plasma state is created and sustained by the RF generator [15].

Typical experiment : A selected substrate (20 cm diameter heavy duty aluminum foil, 7.62 cm diameter silicon wafer, 2.54 x 2.54 optically smooth quartz window, 1.3 cm diameter FT-IR grade KBr pellet, or 2.4 x 3.0 cm cover glass) was positioned on the lower electrode, then the reactor was closed. The system was evacuated to base pressure level, the lower electrode heated up to 200°C, and the argon plasma was ignited to remove possible

contaminants (power: 200 W, pressure 200 mT, reaction time: 10 minutes). The RF-power was then disconnected to allow the substrate and lower electrode cool down (under vacuum conditions) to the preselected temperature for deposition. The reactor was then opened and the polysiloxane polymer (specific viscosity) was deposited as a thin film on the substrate. The chamber was closed, the base pressure level re-established, and the electrode and the polymer covered substrate were cooled down to the desired reaction temperature. Oxygen was then admitted into the reactor until the selected pressure and flow rate were established, and the plasma was ignited and sustained for the desired treatment time period. At the end of the reaction, the reactor was repressurized to atmospheric level and the sample was removed and stored for analytical porposes.

The following experimental parameters were employed during a typical plasma treatment: inert gas: argon; active gas: oxygen; RF-power dissipated to the electrodes: 100 W; base pressure: 90 mT; pressure in the absence of plasma: 185-190 mT; pressure in the presence of plasma: 195-200 mT; flow rate of oxygen: 10 sccm; plasma treatment time: 10 minutes; plymeric substrate: 100,000 centistokes PDMS; thickness of deposited PDMS: 400-800 A; temperature of the substrate holder: 25°C.

RESULTS AND DISCUSSIONS

Oxygen plasma treatment of PDMS films resulted in very uniform (smooth, mirror-like), solid phase, pale-yellow colored polymeric layers. Optical transparency estimations, carried out for networks synthesized on quartz windows, indicated that the films were transparent both in the UV and visible regions (Figure 2); however a broad, low intensity absorption was observed at around 380 nm.

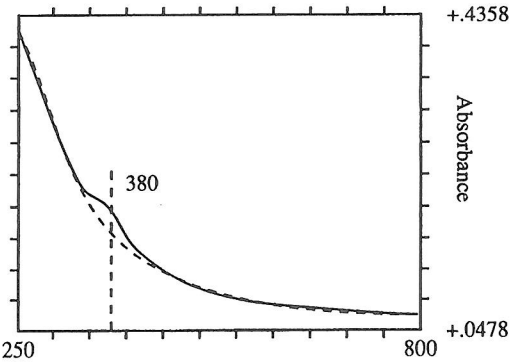


Figure 2.

Figure 3 (A and B) shows the high resolution FT-IR spectra and relative peak intensities of untreated and plasma treated PDMS in the 700-1500 cm^{-1} wavenumber range. One can observe that both the vibration patterns of Si-O (backbone, 1093 and 1018 cm^{-1}, antisymmetric and symmetric stretching) and Si-C linkages (798 and 1261 cm^{-1}, stretching and deformation Si-C), and the corresponding relative ratios (6.42 and 6.12) of untreated and plasma modified polymers are practically identical. It consequently can be concluded that demethylation and main-chain scission processes were not significant during the oxygen plasma treatment reactions. The almost total disappearance of CH_3 deformation vibrations (1384 cm^{-1}), and the increased relative ratio of CH_2/ CH_3 stretching absorptions (2962 cm^{-1}

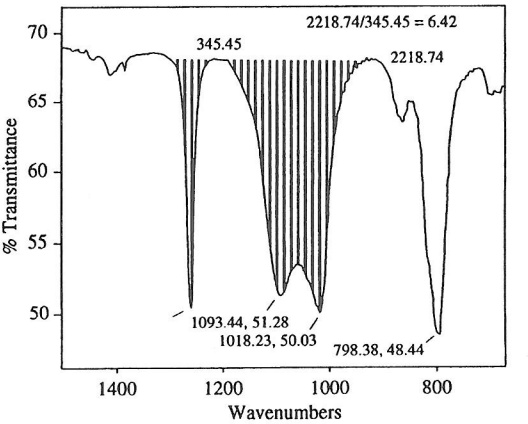


Figure 3A.

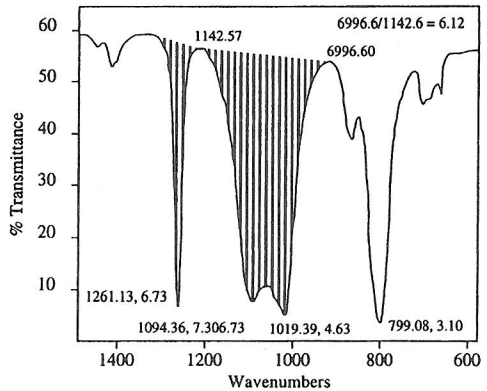


Figure 3B.

^{1} / 2907 cm^{-1}), (Figure 4, A and B, and Figure 5, A and B) for plasma modified PDMS in comparison to the starting polymer, clearly indicate the presence of plasma induced dehydrogenation reactions. The development of oxygen-plasma-induced crosslinking reactions is suggested to take place through -CH_X-O-CH_X- (x<3) ether-bond formation mechanisms. The relative ratio of Si-O-Si and C-O-C absorptions is difficult to be estimated by IR spectroscopy, because their vibrations are located in an almost identical wavenumber range.

ESCA measurements, however, indicate a significantly increased oxygen atom content of the plasma treated PDMS (Table 1). The high oxygen content can be explained by the (depth dependent) diffusion gradient of the active oxygen species (a more intense plasma induced oxydation of surface

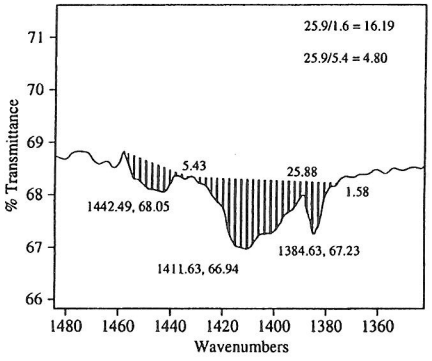


Figure 4A.

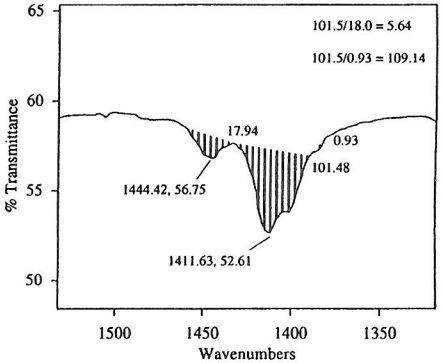


Figure 4B.

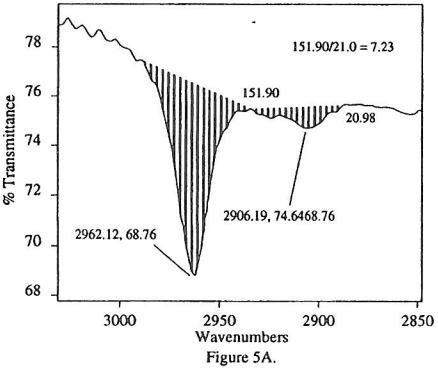


Figure 5A.

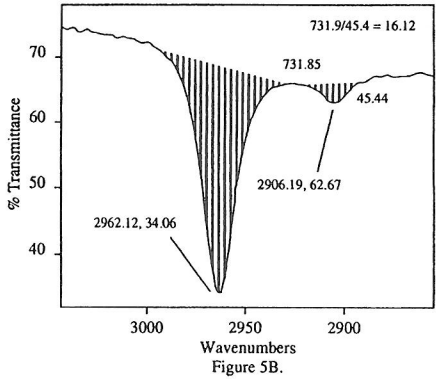


Figure 5B.

layers). Only about 100 A thickness of the surface layers are detected by ESCA anaysis, while IR data reflect the bulk structure of the samples.

Table 1. Surface atomic compositions (ESCA) of plasma synthesized polysiloxane-based polymeric thin films compared to standard PDMS

Sample	Relative Atomic Composition %		
	Si	O	C
Plasma PDM on Al (Shiny Face)	19.10	66.26	14.63
Plasma PDMS on Al (Matt Face)	12.01	64.13	23.75
Standard PDMS	25	25	50

DTA-TG data are in good agreement with FT-IR and ESCA findings. Comparative DTA-TG estimation carried out under nitrogen atmosphere on standard PDMS (Figure 7, A) and the plasma generated polymeric layers (Figure 7, B) clearly indicate that oxygen plasma induced crosslinking processes have taken place. A significantly higher thermal stability can be noticed for plasma synthesized layers in comparison to standard PDMS. The plasma polymer samples, regardles of the nature of the substrates, exhibit a decomposition initiation temperature of about 340°C, while unmodified PDMS starts to decompose at 290°C. A relatively intense endothermic effect is associated with the thermal decomposition of plasma polymers (Fiure 7, B, DTA); a phenomenon obviously related to the decomposition of the crosslinked structures. It is noteworthy that treatments caried out at low substrate temperatures (liquid nitrogen temperature), and higher powers (200W) produce even higher thermal stability plasma polymers (Figure 8).

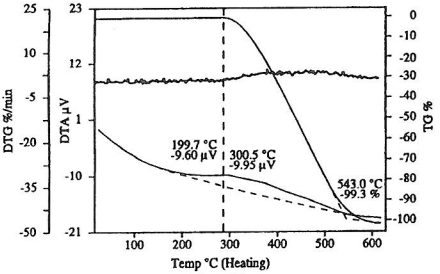


Figure 7A.

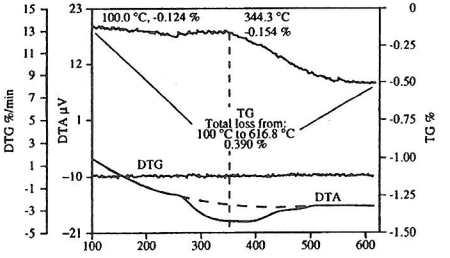


Figure 7B

High resolution MS (HR-MS) thermal decomposition of plasma-PDMS (400°C) emphasize predominantly CH_2 and CH_3 group losses, indicating demethylations of the non-crosslinked portions of the macromolecules. Figure 9 shows a typical portion of HR-MS diagram.

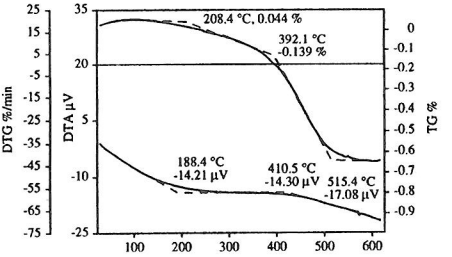


Figure 8

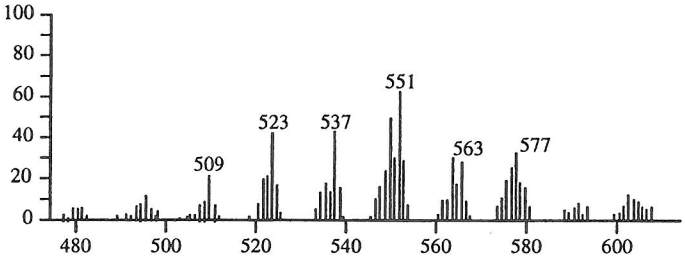


Figure 9.

CONCLUSIONS

- An RF-oxygen plasma is suitable for converting liquid phase PDMS into a solid state network.
- CH_X-O-CH_X crosslinks are responsible for the three-dimensional structure.
- The plasma produced polymeric layers are transparent, smooth and thermally stable.
- The technique does not require the use of solvents.
- The uniformity of the deposited linear polysiloxanes can be controlled by the temperature (surface tension) of the substrates;
- Large surface areas can be uniformly coated by this technique in comparison to conventional plasma approaches, where reactor geometry dependent plasma parameter gradients limit this possibility.
- Polymeric thin films will be formed only on precoated substrates, avoiding depositions on other surfaces which limit the plasma.
- By using non-polymer forming gases, contamination problems are significantly diminished.
- One step thin-layer polymer composite depositions are also possible from mixtures of polymers with various particulate materials (e.g. silicon dioxide, graphite, powdered metals, etc.).

ACKNOWLEDGEMENTS

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