Pulsed RF plasma-deposited polyacetylene : elaboration of new adhesive joint

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Abstract:

In a pulsed RF discharge, thin polyacetylene film was deposited by plasma enhanced chemical vapour deposition (PECVD). We studied a novel process for substrate–elastomer assembling by plasma technology in order to create adhesive joint as a vulcanization agent. Then, plasma parameters were optimized in order to prepare a thin layer bearing a high proportion of reactive groups towards the elastomer, here alkene groups. Finally, tensile test was conducted to evaluate the adhesion strength through the deposited plasma polymer.

Keywords: Acetylene plasma polymer, pulsed RF discharge, PECVD, polymer-elastomer assembly, adhesion test.

1.INTRODUCTION

Rubber and rubber products are widely used in the aviation, automotive and aerospace industry. Rubber products have the ability to resist to extreme temperatures and rubber material is particularly suitable to be component for various applications [1]. Thanks to its interesting properties against the vibrations generated during the operation time of the devices as motors, many industries try to develop the assemblies more efficiently. In fact, substrate-rubber assemblies are good shock absorbers thanks to their elastic and damping characteristics simultaneously. However, the adhesive bonding between substrate and rubber is prepared currently by one or more adhesive layers often run by repetitive manual coatings [2]. In addition, these adhesive layers are highly toxic products and are aqueous or organic liquid phases.

This study proposes a new approach to reach a unique bonding and homogeneous layer by PECVD method using the technique of pulsed RF plasma polymer deposition which is a more eco-friendly assembly process without solvent, as a substitution of the present wet chemistry and coating procedures. First, we studied the deposit of polyacetylene onto metal substrate as inox. All treated surfaces and obtained interfaces are characterized before the assembly. The chemical structure of plasmapolyacetylene deposited on the surface was characterized by usual techniques such as X-ray photoelectron spectroscopy (XPS) [3], Fourrier-transformed Infrared spectroscopy (FTIR) and contact angle measurements. The surface morphology is studied using atomic force microscopy (AFM). Once the surface has been characterized, we achieved the vulcanization of different elastomers as natural rubber (NR), nitrile rubber (NBR), silicone rubber (VMQ) and fluoro rubber (FKM) by rheological system. This second step reveals a viscoelastic behavior of the elastomer during the curing time depending on the temperature ramp and the crosslinking. Finally, the adhesion strength was measured directly after the vulcanization by tensile testing in order to evaluate the quality of the crosslinking and to determine the type of rupture.

2. EXPERIMENTAL SET-UP

2.1. Plasma chamber

The reactor used is a 310 mm x 255 mm rectangular aluminium chamber with its cathode linked to the generator and the anode grounded. The plasma is created by a radio-frequency 13.56 MHz generator through a capacitive coupling (Fig.1) with a matching box adjusting the generator impedance to limit the reflected power. The pumping stage was composed of a primary pump (CIT-ALCATEL Pascal NO 2010 SD) and a turbomolecular pump (ALCATEL ATP 80). The pressure was measured with a Pirani gauge (ACC 1009). Mass flowmeters (Aera FC 7700 CDC) controlled the amount of injected gas.



Fig. 1. Schematic diagram of the plasma reactor.

2.2. Rheological measurements

Dynamic rheological measurements were conducted during the vulcanization process using a TA Instruments strain controlled ARES-G2 rheometer with parallel plates of 8 mm in diameter and the gap was kept same as the thickness of uncured elastomer. The temperature was set to T = 30 °C before the vulcanization and controlled rates up to 60 °C/min via forced convection oven system (FCO). Then, certain axial force was applied when the density of crosslinking is stable in order to help the adhesion on the surface. A time-independent storage G' and loss modulus G'' was achieved, which typically took about 1000 s for each elastomer. The vulcanization of each elastomer has been done at atmospheric pressure in order to determine the origin of slippage of rubber on the surface.

3. RESULTS AND DISCUSSIONS

3.1. Influence of plasma parameters on chemical structure of the plasma polymerized acetylene.

To determine the optimum conditions for obtaining the vulcanization agent as presented in Fig. 2, four different plasma parameters were tested by design of experiments (DOE). DOE is widely used in industrial studies to evaluate the factors that control the value of a parameter or group of parameters. It allows for multiple input factors to be manipulated, determining their effect on a desired output which called "*response*". By manipulating multiple factors at the same time, important interactions can be identified contrary to an experiment varying one factor at a time. Tested plasma parameters are : i) post discharge period (t_{off} , 20-20 µs) in order to retain high proportion of alkene groups versus alkyle groups, ii) discharge power (*P*, 10-70 W), iii) gas flow (Q = 10 - 60 sccm) and iv) duration of deposition time (*t*, 1-60 min).



Fig. 2. Chemical structure of polyacetylene.

In order to retain the highest concentration on alkene functions, the ratios between the concentration of C=C bond and C-H bond was calculated according to FTIR spectra. FTIR analysis shows mostly the presence of C=C stretching at 1629 cm⁻¹, C-H stretching at 1446, 1375 cm⁻¹ suggesting the presence of CH₂ and CH₃. There are no bands at 2200 and 2100 cm⁻¹ corresponding to C=C stretching of used acetylene. Acetylene molecule is fragmented into C=C, C-C and C-H group. Some stretching bands of carbonyl and hydroxyl functions are noticed respectively at 1731 and 3446 cm⁻¹. It relates to post-oxidation of plasma polymer with air after the deposition rather than to plasma phase contamination [4-7].

X-ray photoelectron spectroscopy (XPS) was used to confirm the FTIR results. According to the XPS wide spectra, the plasma-polymer is essentially composed of carbon and oxygen which is in good agreement with FTIR results. Indeed, the presence of oxygen is explained by the fact that the plasma-polymer surface remains active and reacts with atmospheric oxygen after the films are removed from the reactor chamber.

The DOE revealed that working at mild plasma conditions, the initial structure of the monomer is retained, thus high concentration of alkene groups. On the other hand, the chemical structure changes due to the high fragmentation at severe plasma conditions.

3.2. Surface properties of the different materials

In order to achieve such an efficient assembly, the interface energy between the plasma-deposit and the elastomer must be as weak as possible. Therefore, the different surface energies were determined and compared to those of liquid adhesive usually preconized. For such a measurement, deionized water and diiodomethane were used. Fig. 3. shows different surface energies between plasma polyacetylene, liquid adhesive layer and uncured elastomers.



Fig. 3. Surface energy of plasma-polymer film, liquid adhesive layer and uncured elastomers.

After plasma polymerization of acetylene, the total surface energy of the deposited layer corresponds to 48.3 mJ/m², while the liquid adhesive one is 56.2 mJ/m² The respective total surface energy of the four uncured elastomers is 31.1 for NR, 40.9 for NBR, 42.6 for FKM and 16.4 mJ/m² for VMQ which were comparable to the literature [9-10]. Therefore, the plasma-polyacetylene has a lower surface energy than the liquid adhesive joint and closer to those of elastomers.

3.3. Assembly preparation and characterization.

In this study, elastic modulus of NR was studied in function of curing time with temperature ramp. The vulcanization step is on three steps (fig. 4) whatever the type of rubber (the time given is for NR):



Fig. 4. Elastic modulus (G' and G'') in function of curing time.

- 1) Increase of viscosity with temperature thus storage modulus (G') decreases.
- 2) High density of cross linking (hardening of elastomer).
- 3) End of the vulcanization (stable temperature), plateau obtained.

After the vulcanization, a tensile testing was carried out systematically to evaluate the adhesion and the assembly mechanical failure, i.e. if it is adhesive or cohesive. Table 1 illustrates the value of axial force needed to tear out completely in function of strain. Hence a plasma-deposit is prepared, the adhesion of the NR is twice of the value with the pristine inox substrate. This result proves that the plasma-polymer is able to crosslink as a real "*Plasmabond*" through the elastomer matrix and the value given for polyacetylene 4.7 N is close to the liquid adhesive layers 5.2 N. The interesting point is that the failure on the polyacetylene is homogeneous ($\sigma = 17.3 \pm 2.1$) while for the liquid adhesive layer, the rupture is non homogeneous ($\sigma = 18.6 \pm 13.3$) shown in the error bar of strain value (σ).

	F(N)	σ (%)
Pristine substrate	2.3 ± 0.6	7.0 ± 0.2
Deposited acetylene film	4.7 ± 0.3	17.3 ± 2.1
Liquid adhesive layers	5.2 ± 0.007	18.6 ± 13.3

Table 1. Tensile testing results between pristine substrate, plasma-deposited polyacetylene film and liquid adhesive layer.

4.CONCLUSIONS

In this study, an illustration of cold plasma polymerization of acetylene is given according to an environmentally friendly approach. The synthesized polyacetylene by PECVD shows the possibility to create plasma-bond thanks to alkene functions through the elastomer matrix during curing time. It is concluded from tensile testing measurements of different assemblies with various type of treatment. The strategy developed in this paper is a promising approach to prepare substrateelastomer assemblies in a eco-friendly way with high homogeneity.

AKNOWLEDGEMENT

The authors thank the *Agence National de la Recherche* for their financial support.

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