

Polymerization of Acrylic Acid by a 4kJ plasma focus device

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Abstract

The most conventional way for polymerization of acrylic acid on different substrates is using RF devices and introducing of other devices is under way. In this work we have a new study on formation of polymer Acrylic Acid using APF plasma focus device. The formation of plasma polymer acrylic acid is discussed using results obtained from attenuated total reflectance infrared spectroscopy (ATR). The results show that after 15 shots, nitrogen pulses performed polymerization on the specimens and the main peaks of ATR spectra assured poly acrylic acid formation on SBR substrate.

Keywords: Plasma polymerization, APF Plasma focus device, Acrylic acid, ATR-FTIR

1. Introduction

Plasma polymerization is one of the well-known techniques for depositing thin layers on different substrates without affecting their bulk properties [1-4]. Generally, plasma polymerization is accomplished by introducing different types of monomer precursors (vapour or aerosol) into a plasma reactor chamber leading to the deposition of so-called plasma polymers. The -COOH group in figure.1 plays the main role in ppAAs and the main goal in this area of research is to gain a surface with high density carboxylated surfaces which can be used for immobilization of bio-molecules, high retention of carboxylic acid groups, improving hydrophilicity and wrinkle recovery angle of some textile surfaces [1, 3]. We used SBR (Styrene-Butadiene-Rubber) (figure.2) as substrate and nitrogen as medium gas. Plasma can be used as a means of providing hydrophobicity to rubber [4,5]. SBR is one of the most important synthetic rubbers. It accounts for about 40% of the total synthetic elastomer production [6], so it can be a good candidate for investigation in this study.

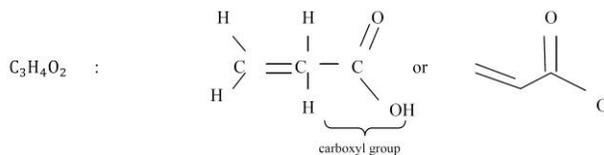


Figure 1. Chemical structure of acrylic acid

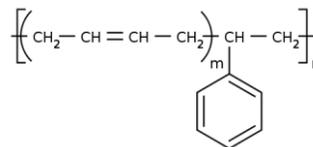


Figure 2. Chemical structure of SBR

Although some other devices like DBD (Dielectric Barrier Discharge) was introduced for polymerization of acrylic acid [4], but our device characteristic is more similar to RF reactors/generators in case of pressure (both continuous and pulsed [7]) ranging from 3-50 Pa (23-375 mTorr) [1-3, 8-10] which are commonly used in recent studies.

In pulsed discharges of the plasma focus device, the accelerated current sheath forms a dense (10^{25} - 10^{26} m^{-3}) short lived (~ 100 ns), and high temperature (1-2keV) plasma pinch column [11]. Due to $m=0$ instability the plasma pinch is broken and the resulting induced electric field accelerates electrons and ion beams ($V \geq 10^7$ cm/s). The details of the plasma focus device have been published earlier [12-16]. Nitrogen plasmas and their characteristics, suggest that they provide significant plasma densities and populations of reactive species for effective plasma treatments on a variety of materials [17]. As it shown in figure.3, the ions in the plasma help breaking C=C bonds to C-C preparing the acrylic acid to form poly acrylic acid.

In the present work, we investigated formation of ppAA by APF device. After 15 shots, nitrogen pulses performed polymerization on the specimens and the main peaks of ATR spectra assured poly acrylic acid formation on SBR substrate.

2. Experiments

The APF is a 4 kJ plasma focus of Mather type. The condenser bank consists of a single low inductance capacitor of 36 μF capacitance, 30nH inductance, and maximum potential of about 16kV. The measured total external inductance of the device is 115nH [18]. A parallel plate spark gap with a swinging cascade configuration was used as a high voltage switch. The experimental set up is shown in figure.4. The gas (nitrogen) was fed to the discharge tube by using a needle valve and pressure is read with a pirani gauge.

After adjusting the working pressure, transfer of energy from the capacitor to coaxial electrodes is made by a rail gap switch.

Since the goal of this study is the formation of ppAA regardless of thickness of layers, instead of introducing acrylic acid to the chamber we carefully coat our substrate with thin layer of acrylic acid (99%, Merck KGaA). Commercial SBR substrates are cut and prepared to stand in the holder. Specimen (size $20 \times 15 \times 10 \text{ mm}^3$) were introduced into the plasma focus chamber and mounted axially above the anode at a distance of 8 cm. Neither bias voltage nor auxiliary heating is applied to the specimen. Schematic diagram of plasma focus electrodes configuration is illustrated in figure.4.

Throughout the experiment, the filling gas pressure is kept at 2 Torr to obtain strong focusing action. The focusing efficiency is monitored using Rogowski coil, Farady cup and scintillation detector. After 15 shots ppAA was produced on the substrate.

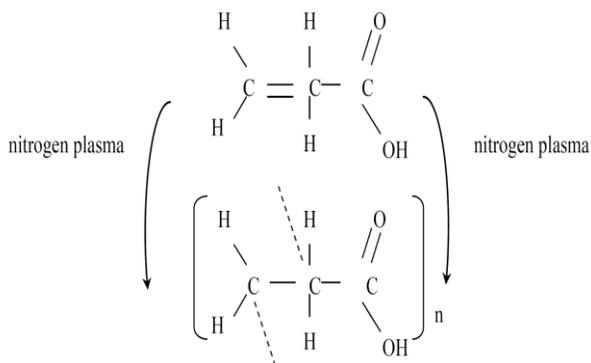


Figure 3. Acrylic acid polymerization

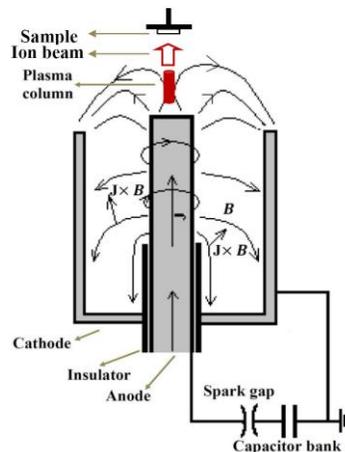


Figure 4. Sketch of APF plasma focus device

The chemical composition of plasma-polymerized coating is obtained using Fourier transform infrared spectroscopy (FTIR) on a Bruker Equinox 55 equipped with ATR accessory with 0.4 cm resolution and 32 scans for each spectrum in the range between $600-4000 \text{ cm}^{-1}$.

3. Results and discussion

ATR-FTIR Results

To confirm the polymerization of acrylic acid and before this analysis one should know assignments of FTIR-ATR of each chemical band for both before and after of polymerization of main specimen [19] and also probable reaction which may occur. Since except C=C band all other bands are the same in both acrylic and poly acrylic acid the full spectrum in references would be useful [20, 21] to distinguish between them. Assignments for main absorption bands and potential

C-N band are shown in table 2. More accurate analysis can be done by knowing the peaks of each specimen using references and comparing the full spectra which are also may be available in some FTIR-ATR devices libraries. In this case we introduced some main peaks (without mentioning their band) of SBR, acrylic and poly acrylic acid in table 3.

Type of vibration	Wave number (cm ⁻¹)
OH broad band	2800-3500
CH stretch band	2800-3000
C=O	1695-1725
OH deformation	910-950
C=C	1617-1634
CH ₂ bending	1430
C-O vibration	1167-1250
C-N stretch band	1055-1175

Table 2. Assignments of FTIR-ATR absorption bands (excluding SBR)

Compound	Wave number (cm ⁻¹)
Poly acrylic acid	<i>2940,1715,1420,1400,1250,1190</i>
Acrylic acid	2992,1704,1637,1617 1435, 1299, <i>1060,985</i>
SBR	2900,2800,1650,1480,1440, <i>960,900,700</i>

Table 3. Compounds main peaks wave number (actual data may vary. italic numbers observed) [20, 21]

To investigate the uniformity of polymerization we shall discuss ATR spectrum of ppAA layers on SBR substrate at the centre and the edge of a typical substrate in figures 6 and 7 respectively. In figures 6 and 7 some main peaks that illustrate formation of poly acrylic acid are as follows. CH stretch band between 3000-2800cm⁻¹ which is more intensive at the edge of the substrate, CH₂ bending band approximately in 1453cm⁻¹ at the centre and 1442cm⁻¹ at the edge of the substrate, C-O band in about 1173cm⁻¹ at the centre and 1181cm⁻¹ at the edge, C=O band in about 1719cm⁻¹ at the centre and 1725 cm⁻¹ at the edge, and small OH deformation peak in around 912 cm⁻¹ for both of them. These peaks are the main peaks to assure formation of poly acrylic acid.

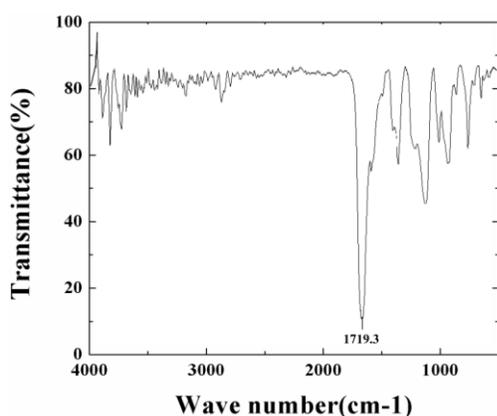


Figure 6. ATR spectra of ppAA layers at the centre of SBR substrate

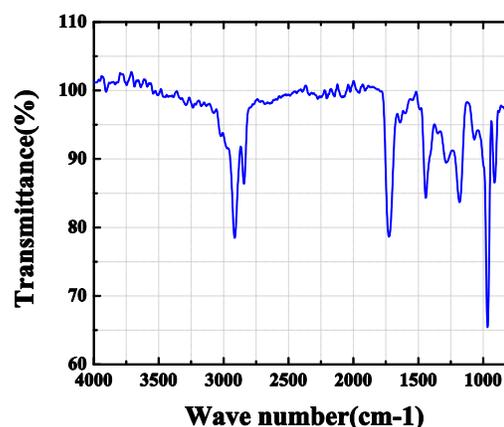


Figure 7. ATR spectra of ppAA layers at the edge of SBR substrate

To assure the formation of polymer in the centre, the centre spectra is checked with device ATR library in figure.8 which is well matched.

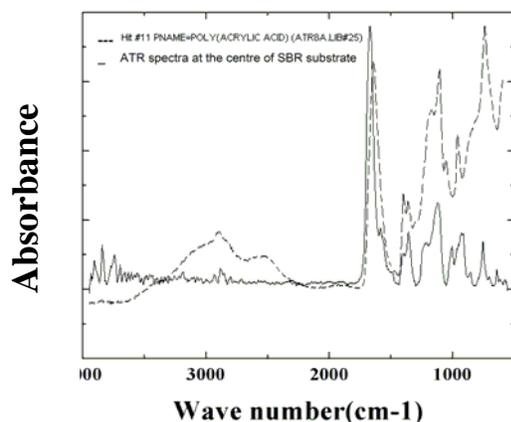


Figure 8. Comparison of experimental spectrum of specimen at the centre with one obtained from ATR device library

4. Conclusions

This paper provides new information about formation of plasma polymer acrylic acid by APF device. Setting the device for most optimum ion characteristics lead us to plasma polymer acrylic acid after few shots on discharge energy of about 1.8kJ. Optimum number of shots to achieve stable polymers without side effects is one of the concerns. Styrene-Butadiene-Rubber used as substrate and nitrogen puffed into the chamber as medium gas. After 15 shots, nitrogen pulses performed polymerization on the specimens and the main peaks of ATR spectra assured poly acrylic acid formation on SBR substrate. Increasing the plasma treatments to more than 30 shots give an enhanced adhesion and sputtered Cu layers on SBR substrate observed.

References

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