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Review

Investigation on electrical properties of thermally aged PMMA by combined use of FTIR and impedance spectroscopies

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Abstract

Effects of thermal aging on electric properties of polymethyl methacrylate (PMMA) polymer are reported in this paper. PMMA samples are submitted to successive heat-cooling cycles ($T_{max} = 45\,^{\circ}C$ and $T_{min} = 20\,^{\circ}C$) in the ambient air. Different complementary techniques are thus employed to investigate structural modifications, conduction processes and dielectric relaxations. These are the Fourier Transform Infra Red (FTIR) spectroscopy, impedance spectroscopy and current–voltage technique. Results are discussed in terms of FTIR bands intensities, relaxation frequencies and electrical conductivity. We demonstrated that thermal aging favors oxidation phenomenon. This causes an increase of free radicals leading to space charge amount increasing. PMMA polymer presents therefore a less insulating character.

Keywords: PMMA; Thermal aging; Complex impedance; Relaxation frequency; Electrical conductivity

Contents

1. Introduction

PMMA, which chemical structure is represented in Fig. 1, is one of the best polymeric materials broadly used for insulation devices manufacture. Its electric properties are highly influenced by many environmental parameters such as temper-

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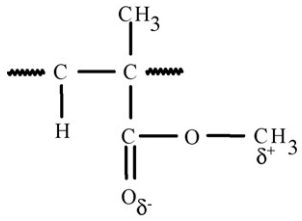

Fig. 1. PMMA monomer.

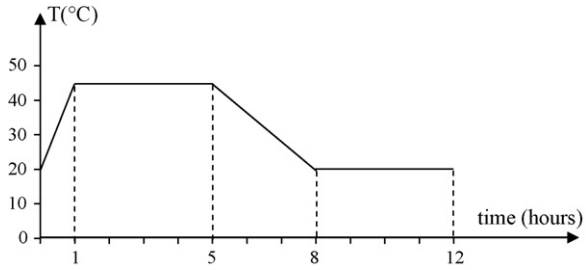

Fig. 2. An applied heat-cooling cycle. $\Delta T = 25\,^{\circ}C$.

ature, UV radiations, oxidation, ... therefore, investigations on the effects of these parameters have been made by numerous research teams. Muderra [1] has shown an increase of PMMA electrical conductivity after heating at temperatures superior to the glass transition temperature T_g. In our case, we have chosen to submit PMMA samples to successive heat cooling cycles where the applied temperature is inferior to T_g which equals 110 °C.

This paper focuses on the evolution of structural and electrical properties of PMMA subjected to thermal aging. In the first part, FTIR spectroscopy is investigated to explore effects of heat treatments on PMMA samples. In the second part, impedance spectroscopy, which is one of the most convincing techniques devoted to conduction processes and dielectric relaxations studies, is used to determine an equivalent electric circuit and to study variations of the relaxation frequencies versus the number of applied cycles. In the last part, current voltage measurements have been carried to follow the effects of thermal aging on the electrical conductivity of PMMA samples.

2. Characterization methods

2.1. Infrared spectroscopy

Fourier-transform infrared (FTIR) spectroscopy is used to gather informations about a compound's structure and to assess its purity. In favorable cases, IR analysis can be quantitative and permits to identify the compound.

In our case, spectra are acquired with a NICOLET 510 FTIR spectrometer in the 400–4000 cm^{-1} region with a resolution of 2 cm^{-1}.

2.2. Impedance spectroscopy

Impedance spectroscopy consists in analysis of both capacitive and resistive properties of materials. It is based on frequency-dependent impedance measurement, as response to a small periodic excitation signal. The measured impedance permits to extract an equivalent electrical circuit for the electrode-sample-electrode system, which is suitable for useful interpretation of the sample's electric properties. The measurements are performed with a Hewlett Packard 4192A impedance analyser in the frequency range 5 Hz to 13 MHz on weak thick samples.

2.3. Current–voltage measurements

Measurements are performed using "DEL" DC high Voltage generator and a Keithley 6514 electrometer.

Before measurements, each sample is coated with circular silver electrodes, of 3 cm diameter on both sides.

3. Results and discussion

3.1. Samples preparation

Samples used in this study are from commercially available PMMA (MADREPELA, Italy). All have a parallelepipedic shape and are cut from the same 2 mm thick plaque. Samples used for current–voltage measurements have 50 mm × 50 mm dimensions. Dimensions of 10 mm × 10 mm are used for infrared and dielectric characterization. For the last ones, gold electrodes of 3 mm diameter are deposited on both sides of each sample.

In all cases, PMMA samples are submitted to an accelerated thermal aging by application of successive cycles of heat-cooling ($\Delta T = 25\,^{\circ}C$). 4, 8, 14, 24, 48 and 72 cycles are applied to samples, each cycle lasting 12 h as illustrated in Fig. 2.

3.2. Infrared results

FTIR studies are done in order to explore structural effects of thermal aging on PMMA polymer. Only the region from 1800 to 800 cm^{-1} is investigated for identifying the presence of specific functional groups in PMMA aged samples.

Fig. 3, shows the infrared spectrum of the virgin sample; the C=O stretching vibration of ester group appears around 1725 cm^{-1}, the two doublet bands at (1140, 1190 cm^{-1}) and

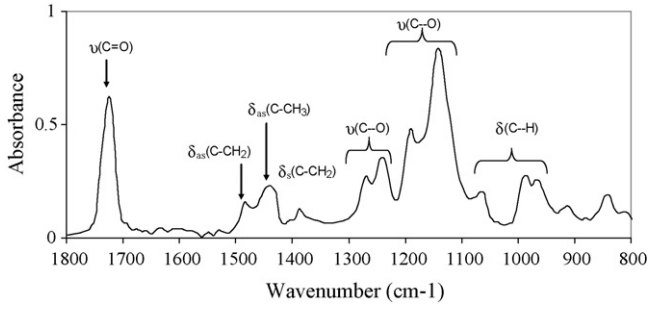

Fig. 3. Infrared spectrum of a virgin PMMA sample.