

INFLUENCE OF UV IRRADIATION AND TEMPERATURE ON THE STRUCTURAL CHANGES IN POLYAMIDE1010

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Abstract

Aliphatic polyamides are very important engineering polymers commonly used in textiles (Nylon 6, Nylon 66), in metal coatings (polyamide 11), flexible pipes for automotive or offshore applications (polyamide 11 and polyamide 12), and other applications. Our study is focused on polyamide1010 which is one of the most important polyamide engineering plastics exhibiting high strength, elasticity, and abrasion resistance. Some of the applications place high demands on the durability of polyamide1010 and, therefore, it is important to study the influences of the temperature and UV irradiation on the structural changes. The prepared samples of polyamide1010 were subjected to the two selected temperatures and UV-B irradiation. Two temperatures 180°C and 190°C were applied for 1 hour on the samples and UV-B irradiation was applied for 1 hour and 24 hours to evaluate structural changes in polyamide1010. The changes were studied by Raman microspectroscopy and Fourier Transform Infrared spectroscopy, the very sensitive techniques to the changes in molecular level.

Keywords:

Polyamide1010, Raman microspectroscopy, FTIR spectroscopy, UV irradiation, thermal treatment

1. INTRODUCTION

Aliphatic polyamides are very important engineering polymers commonly used in textiles (Nylon 6, Nylon 66), in metal coatings (polyamide 11), flexible pipes for automotive or offshore applications (polyamide 11 and polyamide 12), and other applications [1]. Some of these applications are highly connected to the durability of the polyamides, which are not intrinsically stable in the presence of the oxygen, therefore their stabilization is necessary [1]. Polyamide1010 is a relatively new kind of engineering plastics developed in China since 1970s. It has high strength, elasticity, and abrasion resistance [2] which leads to widely usage in the industry.

Polymer characterization is an essential step in working with polymers. The main characterization techniques involve the use of spectroscopic techniques (Fourier Transform Infrared Spectroscopy, Raman Spectroscopy). The structure and molecular confirmation of the macromolecules ultimately determine the mechanical, physical and chemical properties of polymers [3]. Thus precise characterization of molecular order is a primary prerequisite to understand macroscopic properties of polymeric materials [4,5].

The aim of this study is to evaluate the changes in polyamide1010 structure after thermal and UV-B treatment by spectroscopic techniques (Fourier Transform Infrared Spectroscopy and Raman Microspectroscopy).

2. EXPERIMENTAL

2.1 Sample preparation

Polymer polyamide1010 (PA) was prepared in BUCT (Beijing, China) laboratories. PA was dried at 70°C for 10 hours then melted in the extruder and after water cooling cut into small pieces. Final samples were obtained from this granular form using injection molding machine at the temperature zones among 220-245°C. PA samples were treated by UV-B irradiation for 1 (PA_UV1h) and 24 hours (PA_UV24h). Also thermal treatment was performed at 180°C (PA_180) and 190°C (PA_190) for 1 hour.

2.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectra were measured by Nicolet 6700 FT-IR spectrometer (Thermo Nicolet, USA) using reflection ATR technique with diamond crystal.

2.3 Raman microspectroscopy

Smart Raman Microscopy System XploRA™ (HORIBA Jobin Yvon, France) was used for measuring Raman spectra. Raman spectra were acquired with 532 nm excitation laser source, 100x objective and using 1200 gr./mm grating.

3. RESULTS AND DISCUSSION

The photos of the measured samples are shown in Figure 1 and it is clearly evident that UV-B irradiation has no influence to color change of the sample. However, the sample after thermal treatment at 180°C has different color (slightly orange) as well as the sample after thermal treatment at 190°C (dark orange/brown). Moreover, temperature 190°C caused melting of the sample and its shape is different.

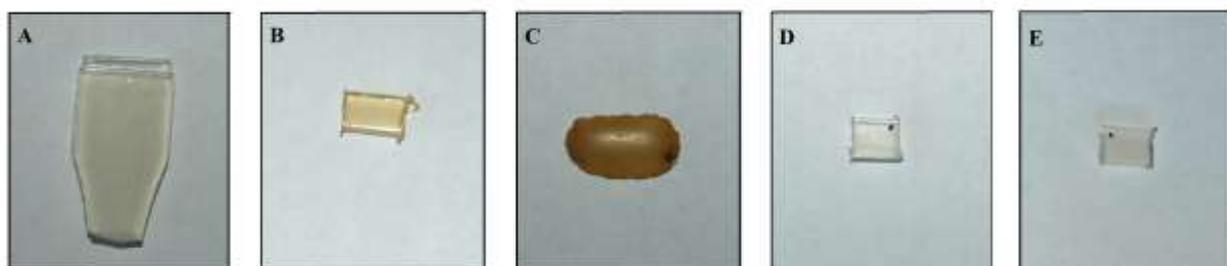


Figure 1: Photos of all measured samples – PA (A), PA_180 (B), PA_190 (C), PA_UV1h (D) and PA_UV24h (E).

3.1 Influence of temperature

The structure of the PA sample was confirmed by FTIR (see Figure 2) and Raman microspectroscopy (see Figure 3). Characteristic bands for polymer with amide group are present at 3330 (N-H stretching vibration), 1633 (Amide I. stretching vibration), 1536 (Amide II. stretching vibration), 1466 (N-H deformation vibration) and 1274 cm^{-1} (Amide III. stretching vibration) [6]. Very intensive bands in higher wavenumbers 3078, 2917 and 2849 cm^{-1} correspond to C-H asymmetric stretching vibration, CH_2 asymmetric stretching vibration and CH_2 symmetric stretching vibration, respectively. CH_2 deformation vibrations (asymmetric and scissoring) represent themselves also by bands at 1536 and 1466 cm^{-1} . Other small bands present in the lower wavenumbers 1450 - 400 cm^{-1} belong to bending, stretching and deformation vibrations of C-C bonds [6]. Intensities of the spectra after thermal treatment are lower than intensities in the spectrum of PA and vibrations at 1049 cm^{-1} and 1176 cm^{-1} (skeletal vibration) are missing. Band at 3078 cm^{-1} (C-H asymmetric stretching vibration) has lower intensity after thermal treatment [7].

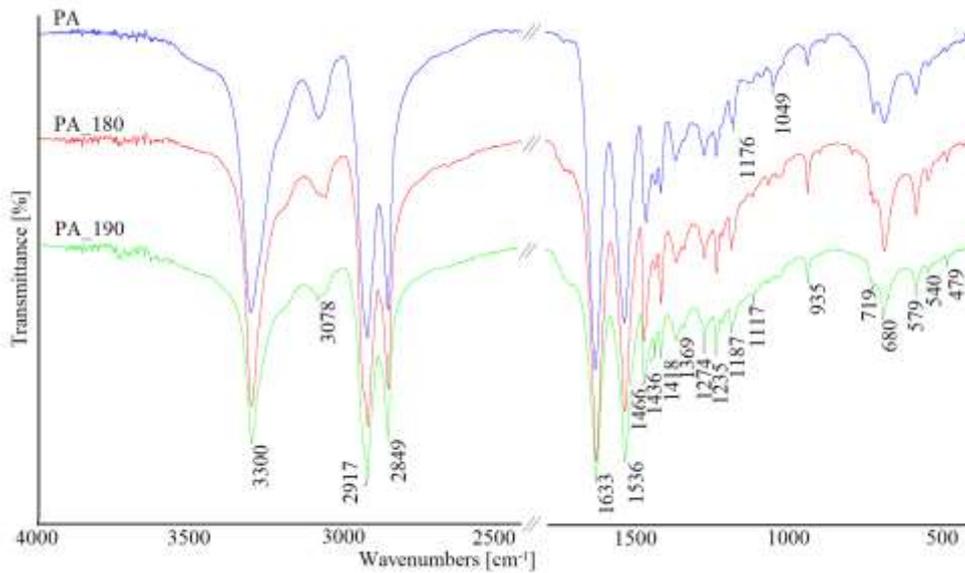


Figure 2: Measured Raman spectra of PA and after thermal treatment

On the contrary, the Raman spectra show significant differences after thermal treatment – no spectra but only fluorescence backgrounds were detected.

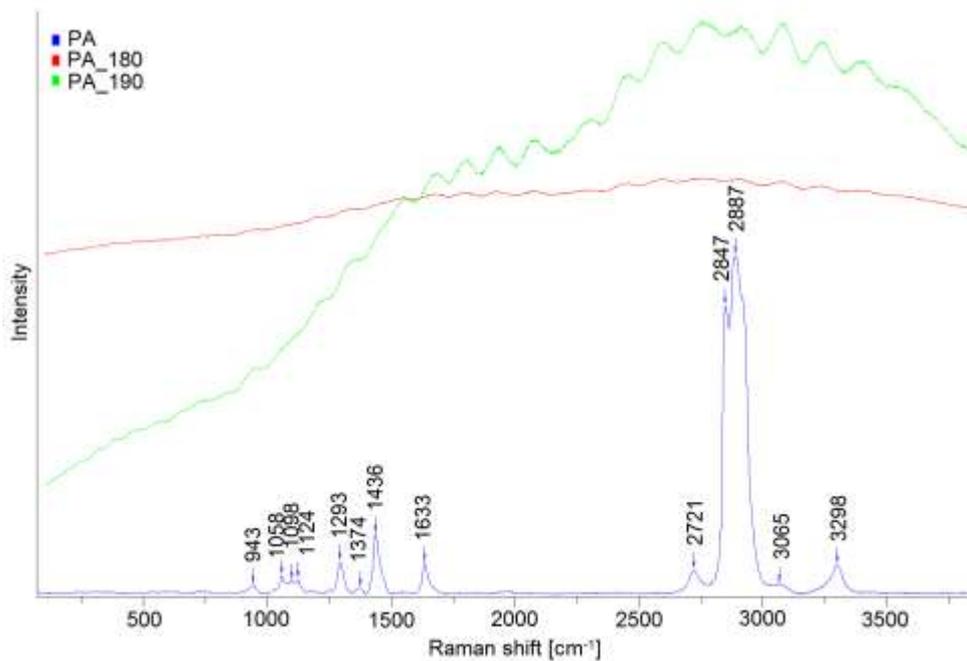


Figure 3: Measured Raman spectra of PA and after thermal treatment.

Spectrum of the pure PA sample (see Figure 3) shows characteristic bands of polyamide, where bands at 3298 (N-H stretching), 1633 (Amide I.), and 1293 cm^{-1} (Amide III.) correspond to the presence of amide group in the polymer. Most intensive bands at 2887 and 2847 cm^{-1} belong to the CH_2 stretching asymmetric and symmetric vibrations. Two indistinct bands 2721 and 3065 cm^{-1} are probably overtones. Other bands

present in the range of 1400-900 cm^{-1} belong to bending, stretching and deformation vibrations of C-C bonds [7].

3.2 Influence of UV-B irradiation

FTIR and Raman spectra of samples after UV-B irradiation are presented in the Figures 4 and 5. All FTIR spectra are almost identical; only one band at 1049 cm^{-1} (skeletal vibration) vanished in the spectra of UV-B treated sample. It is the same band which was missing in the PA_180 and PA_190 spectra. As well as in the Raman spectra no changes in the structure were observed. All measured spectra have same bands at same positions.

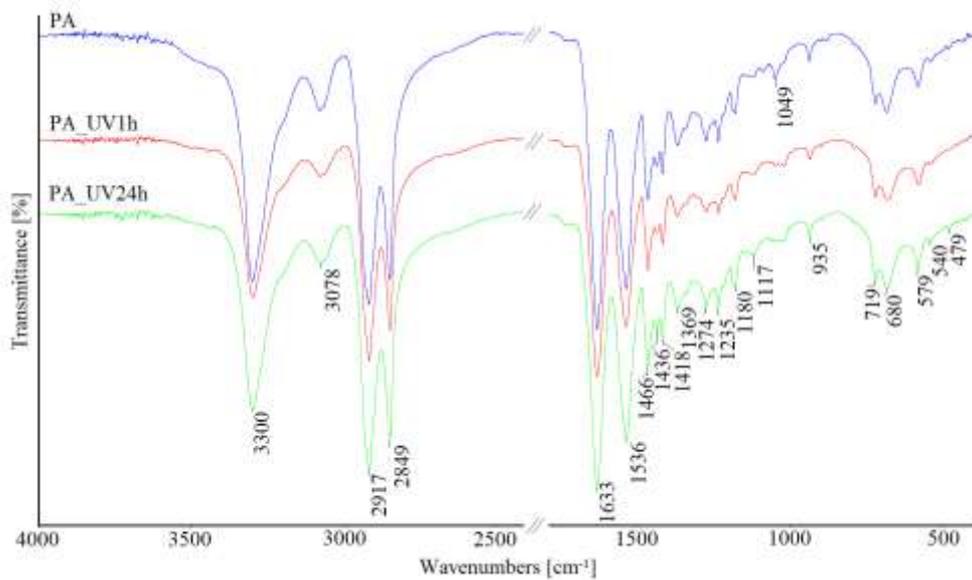


Figure 4: Measured FTIR spectra of PA and samples after UV-B irradiation.

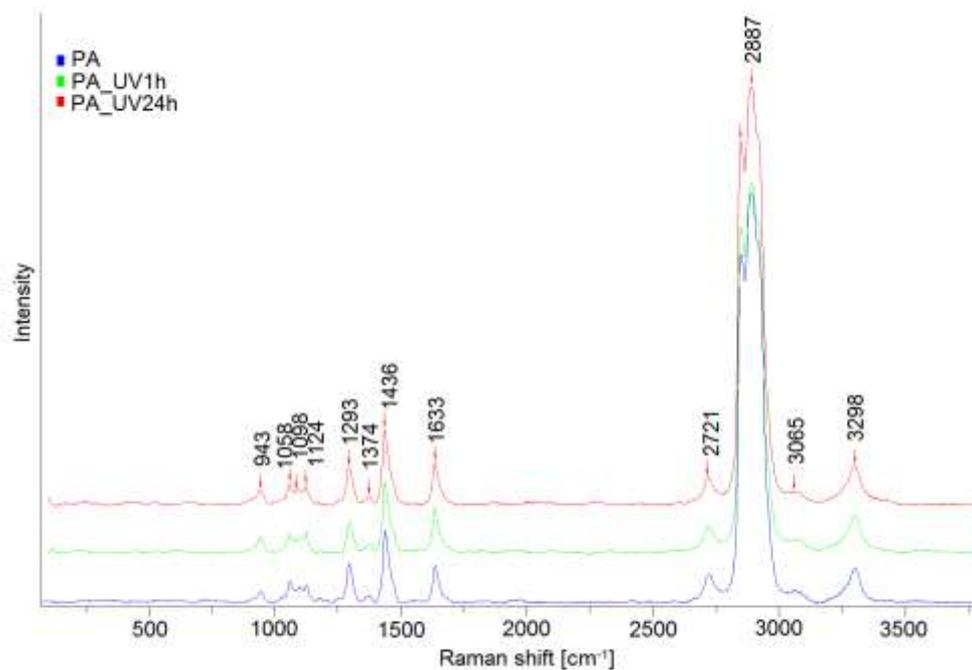


Figure 5: Measured Raman spectra of PA and samples after UV-B irradiation.

4. CONCLUSIONS

Prepared polyamide1010 was thermal (180 and 190°C) and UV-B treated (for 1 and 24 hours) and studied by spectroscopic methods (FTIR and Raman spectroscopy). FTIR spectroscopy revealed small changes in the skeletal vibrations after thermal and UV-B exposure. Measured Raman spectra shows no changes in samples after UV-B irradiation, but no spectra were detected after thermal treatment, only fluorescence background was observed. Also after thermal treatment the color change was observed and, moreover, the PA_190 sample was melted. Polyamides have wide ranges of usage and stabilization of their structure by adding admixtures (e.g. nanocomposites) could improve their properties and this is the direction of our following research.

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