

CHARACTERIZATION AND EFFECT OF UV IRRADIATION ON POLYAMIDE1010 AND POLYAMIDE1010/KAOLINITE

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Abstract

Polyamides are significant engineering polymers with various applications, e.g., flexible plastic pipes for the liquid and the gas transport. Nowadays, high and persistent activity in research area of clay-based polymer fillers is apparent. Clay incorporation could bring the significant improvement of the mechanical properties of polymers. This contribution is focused on (1) the study of the polymer polyamide1010 and polyamide1010 filled with kaolinite and (2) characterization of UV induced changes in morphology and structure of the prepared samples. For this study two types of samples were prepared: pure polyamide1010 and polyamide1010 containing 20 wt.% of calcined kaolinite at 600 °C. Both samples were treated by UV-B irradiation for 24 hours. Morphology and changes in surface roughness were observed in three-dimensional images obtained from both samples by atomic force microscopy. Structural changes in the polymers after incorporation of the clay into the polymer matrix and after UV irradiation were characterized by Raman and Fourier Transform Infrared spectroscopy, which are very sensitive to structural changes. In addition, X-ray diffraction analysis was performed on all samples.

Keywords: Polyamide1010, composite, UV-B irradiation, spectroscopy, atomic force microscopy

1. INTRODUCTION

Polyamides are polymers which contain repeating amide, -CO-NH-, linkages. They can occur both naturally and artificially. Examples of naturally occurring polyamides are proteins, such as wool and silk. Artificially made polyamides can be prepared by polymerization or synthesis. Polyamide1010 (PA) is a semicrystalline polymer and it is one of the most important engineering plastics produced and widely used in industry in China [1-3]. PA is characterized by excellent mechanical properties such as high strength, elasticity, wear resistance in comparison with other polyamides [1, 4]. Due to the good properties PA is used for various applications, e.g., flexible plastic pipes for the liquid and the gas transport.

Nowadays, high and persistent activity in research area of clay-based polymer fillers is apparent. Clay incorporation could bring the significant improvement of the mechanical properties of polymers. In our study the kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) was used as an additive. Kaolinite consists of successive layers of octahedral alumina and tetrahedral silica, which alternate to form plate-like hexagonal particles [5]. Kaolinite is widely used as paper filler or coating pigment and is not often used in polymer industry. Only few studies dealt with its use in polymers for improving of the mechanical or fire retardant purposes [6-8].

Experimental techniques such as Raman and Fourier Transform Infrared spectroscopy, X-ray diffraction analysis and atomic force microscopy were used in this study for the characterization of the prepared samples. Raman and FTIR spectroscopy provides information about molecular vibrations, which are specific

to symmetry of molecules and chemical bonds. Such kind of information is a valuable for determining of the structural changes in polymer structure. X-ray diffraction is also suitable technique to obtain information about structure of the polymers and its changes.

In this study the atomic force microscopy (AFM) was used for observation of changes in the surface topography of the samples. AFM provides 3D images in nanoscale. Its outstanding advantage is its ability to acquire an image of almost any type of surfaces, for example powder samples, polymers, ceramics, composites, glass, and thin layers.

Aim of the study was to evaluate changes in PA structure induced by 24 hours irradiation of UV-B and to compare PA behavior with composite polyamide1010/kaolinite (PAKA) treated at the same conditions.

2. EXPERIMENTAL

2.1. Preparation of samples

Polymers and polymer composites were prepared in BUCT (Beijing University of Chemical Technology) laboratories. Polyamide1010 (PA) was dried at 70 °C for 10 hours. In the next step the dried polymer was mixed with calcined (1 h at 600 °C) kaolinite (SAK47 – LB Minerals s.r.o.). The PAKA composite contained 20 wt.% of calcined kaolinite. The paraffin and silane coupling agent were added to the mixture and the mixture was melted in extruder and after water cooling cut into small pieces. Then, the pellets were injected into the composite samples by injection molding machine at the temperature zones among 220-245 °C. Final samples were obtained by injection moulding technique. PA and PAKA samples were treated by UV-B irradiation for 24 hours (PA_UV and PAKA_UV).

2.2. Raman spectroscopy

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.

2.3. Fourier transform infrared spectroscopy

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

2.4. X-ray powder diffraction

The XRPD patterns were recorded under CoK α irradiation ($\lambda = 1.789 \text{ \AA}$) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a fast position sensitive detector VANTEC 1. Measurements were carried out in the reflection mode, powder samples were pressed in a rotational holder. Phase composition was evaluated using database PDF 2 Release 2004 (International Centre for Diffraction Data).

2.5. Atomic force microscopy

Morphology and changes in surface roughness of the all prepared samples were studied using atomic force microscope SolverNext (NT-MDT) operated in semicontact (tapping) mode. The noncontact probes NSG30 were used for imaging and the images were evaluated using Gwyddion software.

3. RESULTS AND DISCUSSION

The structure of the PA sample was confirmed by FTIR and Raman spectroscopy. Typical IR spectrum of polyamide is shown in Figure 1. Characteristic bands for polymer with amide group are present at 3306 (N-H stretching vibration), 1634 (Amide I. stretching vibration), 1534 (Amide II. stretching vibration), 1466 (N-H deformation vibration) and 1274 cm⁻¹ (Amide III. stretching vibration) [9]. Very intensive bands in higher wavenumbers 3078, 2917 and 2850 cm⁻¹ corresponds to C-H asymmetric stretching vibration, CH₂ asymmetric stretching vibration and CH₂ symmetric stretching vibration, respectively. CH₂ deformation

vibrations (asymmetric and scissoring) represent also bands at 1534 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. From Figure 1 it is clearly evident that no significant changes were observed in spectra after UV-B irradiation (PA-UV) [10].

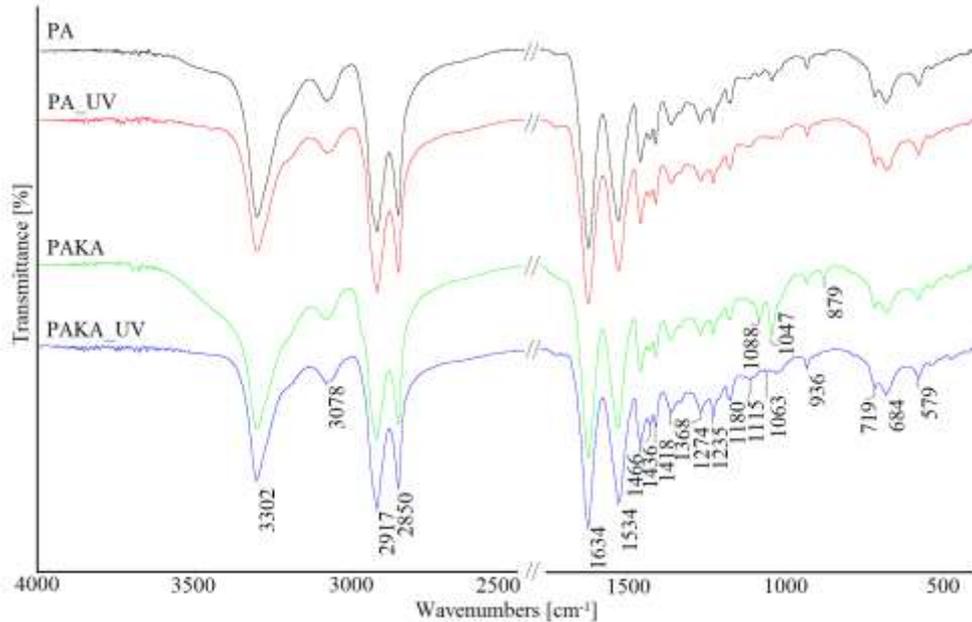


Fig. 1: Measured FTIR spectra

FTIR spectrum of PAKA (Figure 1) shows three new bands which are not visible in PA spectrum (1088, 1047 and 879 cm^{-1}). These bands are related to the presence of calcined kaolinite in the polyamide1010 and correspond to Si-O and Al-OH vibrations [10]. Other bands characteristic for kaolinite could not be detected in spectrum because after calcination at 600 $^{\circ}\text{C}$ the transformation of kaolinite to metakaolinite is observed. After UV-B irradiation these bands disappear from the PAKA_UV spectrum and spectrum corresponds to the original PA spectrum.

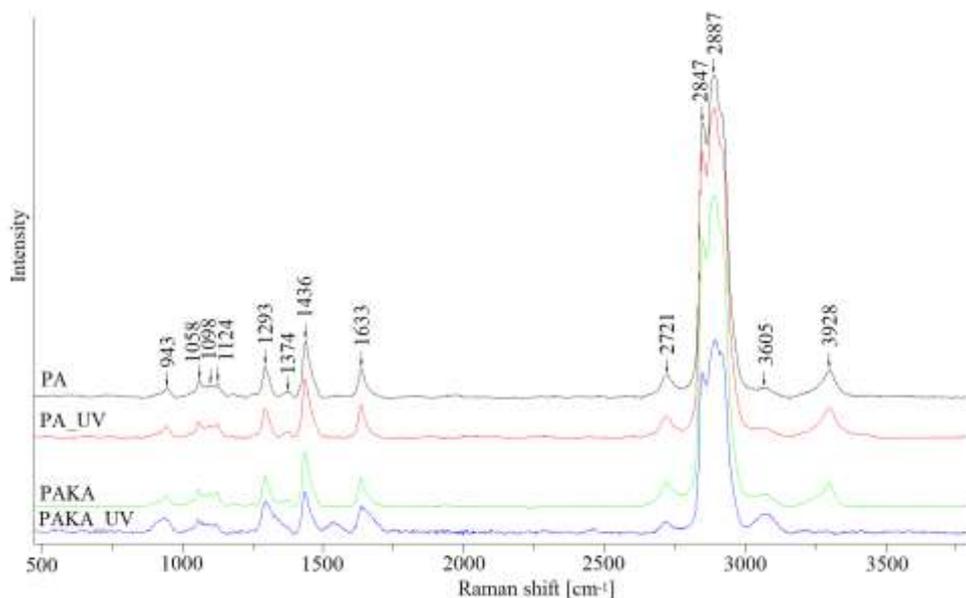


Fig. 2: Measured Raman spectra

In the Figure 2 Raman spectra for all the measured samples are presented. PA spectrum contains 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 bands 2721 and 3065 cm^{-1} are probably overtones. Other bands present in the PA spectrum 1400-900 cm^{-1} belong to bending, stretching and deformation vibrations of C-C bonds [11]. Again Raman spectra show no significant difference in spectra after UV-B irradiation as well as no any significant difference was observed in spectrum PAKA. Kaolinite or metakaolinite is not visible in the spectrum of PAKA, because of fluorescence of the clay [12]. After the UV-B irradiation the spectrum of PAKA_UV has lower intensities of the CH_2 asymmetric and symmetric bands, bands at lower wavenumbers are broader and noisier, and band corresponding to N-H stretching vibration vanished. Other bands and positions remain the same.

The surface morphology of all studied samples could be seen in Figures 3 and 4. There are many asperities on the surface of the sample PA as visible from Figure 3a in comparison to the surface of the sample PA_UV showed in Figure 3b. The surface of PA_UV sample is moreover smooth. As we can see in Figure 4, the surface of PAKA sample is different compared to pure PA. The surface of sample PAKA (see Figure 4a) shows significantly wavy character and forms strips which could be caused by the presence of the kaolinite in the polymer. The surface of the sample the PAKA_UV (see Figure 4b) shows closely similar morphology as in PAKA but the stripes show less sharp character.

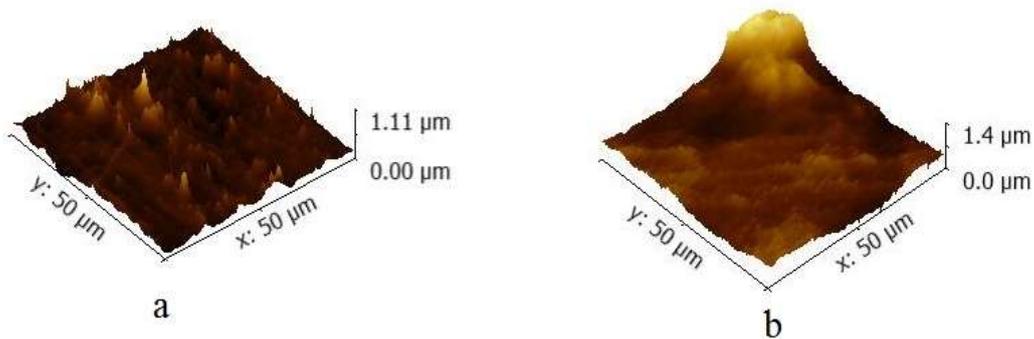


Fig. 3: AFM images of the surface of the PA sample before (a) and after (b) UV-B irradiation.

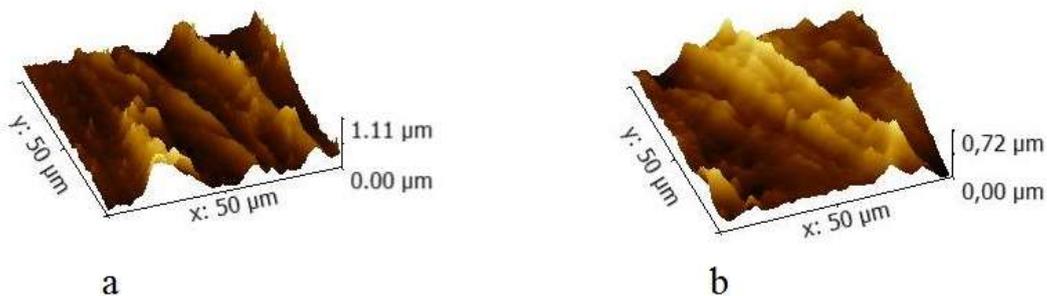


Fig. 4: AFM images of the surface of the PAKA sample before (a) and after (b) UV-B irradiation.

XRD measurements (see Figure 5) show presence of the α -PA1010 (100 and 010, triclinic system) [13]. Presence of reflections characteristic for silicates in XRD patterns of PAKA samples proved the presence of the kaolinite in structure of prepared polymer composites. The observation of 001 basal diffraction line of kaolinite proved that 1 h long thermal treatment of kaolinite at 600 $^{\circ}\text{C}$ did not cause complete dehydroxylation of kaolinite. Regarding to the diffraction peaks belonging to α -PA1010 it can be stated that there are not any significant structural changes induced by UV-B irradiation.

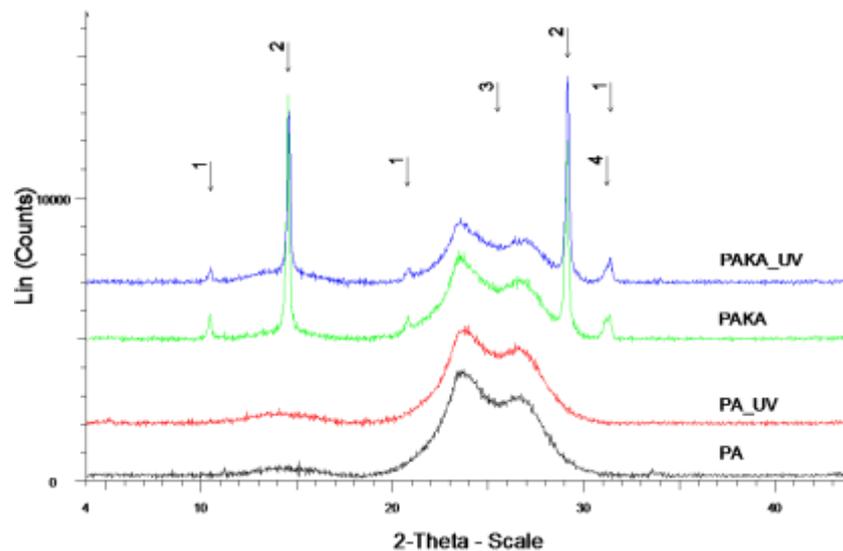


Fig. 5: Measured XRD patterns with detected phase composition: 1 – muscovite, 2 – kaolinite, 3 – α -PA1010 and 4 – quartz.

CONCLUSIONS

Prepared polyamide1010 and composite with calcined kaolinite were treated by UV-B irradiation and characterization by FTIR spectroscopy, Raman microspectroscopy, AFM and XRD. No significant structural changes were observed by XRD, FTIR, and Raman spectroscopy after UV-B irradiation. FTIR and XRD revealed the presence of the kaolinite in the samples PAKA. Atomic force microscopy revealed the difference in the surface topography of the samples after the UV-B treatment whereas the surface of UV-B treated samples can be considered as smoother.

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REFERENCES

- [1] LI B., ZHANG L.: ESR approach to free radicals trapped in irradiated polyamide-1010. *Radiation Physics and Chemistry*. 1997, Vol. 49, No. 5, pp. 575-579.
- [2] ZHANG L., ZHANG H., CHEN D.: WAXD and SAXS study on gamma-radiation damage to polyamide-1010 crystal structure. *Radiation Physics and Chemistry*. Vol. 47, No. 4, pp. 523-526.
- [3] ZHANG H.F., ZHANG L.H., YANG B.Q., MO Z.S.: The influence of γ -radiation on polyamide 101 aggregate structures. *Polymer Degradation and Stability*. 1995, Vol. 50, pp. 71-74.
- [4] LI Y., MA Y., XIE B., CAO S., WU Z.: Dry friction and wear behavior of flame-sprayed polyamide 1010/n-SiO₂ composite coatings. *Wear*. 2007 Vol. 262, pp. 1232-1238.
- [5] KRÁSNÝ I., LAPČÍK L. LAPČÍKOVÁ B., GREENWOOD W.R., ŠAFÁŘOVÁ K., ROSON A.N.: The effect of low temperature air plasma treatment on physic-chemical properties of kaolinite/polyethylene composite. *Composite: Part B*. 2014, Vol. 59, pp. 293-299.
- [6] BATISTELLA M., OTAZAGHINE B., SONNIER R., CARO-BRETELLE A.S., PTER C., LOPEZ-CUESTA J.M.: Fire retardancy of ethylene vinyl acetate/ultrafine kaolinite composites. *Polymer Degradation and Stability*. 2014, Vol. 100, pp. 54-62.

- [7] WANG L., XIE X., SU S., FENG J., WILKIE C.A.: A comparison of the fire retardancy of poly(methyl methacrylate) using montmorillonite, layered double hydroxide and kaolinite. *Polymer Degradation and Stability*. 2010, Vol. 95, pp. 572-578.
- [8] VAHABI H., BATISTELLA M.A., OTAZAGHINE B., LONGUET C., FERRY L., SONNIER R., LOPEZ-CUESTA J.M.: Influence of a treated kaolinite on the thermal degradation and flame retardancy of poly(methyl methacrylate). *Applied Clay Science*. 2012, Vol. 70, 58-66.
- [9] MAHDI H.A.: An FTIR Study of Characterization of Neat and UV Stabilized Nylon 6,6 Polymer Films. *Ibn Al-Haitham Journal For Pure And Applied Science*, 2011, Vol. 24, pp. 86-90.
- [10] VAN DER MAREL H.W., BEUTELSPACHER H.: *Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures*, Elsevier Science Ltd., Amsterdam, 1976.
- [11] CHO L.-L.: Identification of textile fiber by Raman microspectroscopy, *Forensic Science Journal*, 2007, Vol.6, pp. 55-62.
- [12] FROST L. R., RINTOUL L.: Lattice vibrations of montmorillonite: an FT Raman and X-ray diffraction study, *Applied Clay Science*, 1996, Vol. 11, pp. 171-183.
- [13] ZENG H., GAO C., WANG Y., WATTS P.C.P., KONG H., CUI X., YAN D.: In situ polymerization approach to multiwalled carbon nanotubes-reinforced nylon 1010 composites: Mechanical properties and crystallization behavior. *Polymer*. 2006, Vol. 47, no. 1, pp. 113-122.