

Accelerated Photo-Oxidation of Polyamide 11 Nanocomposites under Various Clays Nanofillers

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Abstract

The effect of various clays nanofillers on the photo-oxidation of polyamide 11 (PA11) has been investigated by accelerated ultraviolet (UV) test up to 780 h. Organo-modified montmorillonite, halloysite nanotubes, and sepiolite were selected and incorporated separately to PA11 at 5 wt.%. The samples were prepared by melt compounding. Fourier transform infrared (FTIR) data showed a linear increase of carbonyl index (CI) in the first 360 h of exposure indicating a rapid oxidation of all samples without any induction period. Further, the nanocomposite samples exhibit faster oxidation kinetics than PA11, being however less pronounced for PA11/sepiolite. This is consistent with both the yellowing index (YI) evolution determined by UV-Vis spectroscopy and also the onset oxidation temperature (OOT) determined by differential scanning calorimetry (DSC).

Keywords: clays; nanocomposites; PA11; photo-oxidation

1 Introduction

The study of polymer aging under accelerated UV conditions is difficult due to the complexity of the photo-oxidation process and the various factors that affect its course.^[1] The photo-oxidation process depends mostly on the polymer structure, the processing history, the presence of additives, and the environmental conditions.^[2] In this respect, Lemaire et al.^[3] reported that during photo-degradation, polymeric materials behave like heterogeneous reactors and the application of conventional kinetics developed for homogeneous media is therefore limited. The main effect of interactions between the UV light and polyamides under air is the formation of free radicals, whose further evolution can cause scission resulting in the molecular weight decrease or crosslinking, yellowing, loss of mechanical properties, and embrittlement.^[4] In the family of polyamides, polyamide 11 (PA11) has attracted considerable interest as it is one of important commercial polymers, derived from a renewable resource (castor oil).^[5] PA11 is an engineering thermoplastic, which offers excellent piezoelectricity, a low wear and abrasion, and a high chemical resistance.^[6] However, PA11 has poor impact, tensile strength, and thermal properties.^[7] To improve the mechanical properties of PA11, one of the most common strategy is to compound PA11 with clay nanofillers.^[8] The latter can be classified depending either on

their aspect ratio or on the organic modification for improving their compatibility with the polymer matrix. These aspects have a direct effect on the polymer–filler interactions, and consequently, the materials properties. To the best of our knowledge, there is a few literature data available on the degradation of PA11/clays nanocomposites, although the photo-oxidation is considered as one of the primary sources of damage of polymer materials in ambient conditions.^[9] In this work, the objective was to investigate the process of photo-oxidation under accelerated UV test of PA11/clays nanocomposite films through changes in the chemical structure and physical properties. Three clays of different aspect ratios and surface chemistry were incorporated separately to PA11 at 5 wt.% including organo-modified montmorillonite (Cloisite 30B), unmodified sepiolite (SEP), and unmodified halloysite (HNT) to produce thin films by melt compounding. The effects of clays on the photo-oxidation kinetics of both neat PA11 and PA11/clays nanocomposites were evaluated by carbonyl, yellowing indexes (YIs) and onset oxidation temperature (OOT).

2 Results and Discussion

2.1 FT-IR Analysis

The absorption band at 1690 cm^{-1} was used to evaluate the formation rate of imide groups at different photooxidation times.^[2] **Figure 1** compares the photo-oxidation rates through the evolution of $\Delta\text{Abs}_{1690\text{cm}^{-1}}$ as a function of exposure time for neat PA11 and PA11 nanocomposites of different clays. It is observed from the plots, the absence of induction period for carbonyl groups as reported in literature.^[10] Accordingly, Richaud et al.^[11] argued that in aliphatic amide oxidation, α -amino methylenes are more reactive species than the other methylene ones, so that they undergo firstly oxygen attack. This leads to formation of α -amino hydroperoxides, which are strongly destabilized by the inductive effect of neighboring nitrogen atom. The decomposition of α -amino hydroperoxides by unimolecular mode is responsible for the absence of induction period even at low temperatures. Furthermore, it is clearly observed in **Figure 1** that at the initial stages of exposure until almost 360 h, all irradiated samples exhibit a rapid increase in the kinetics curves of $\Delta\text{Abs}_{1690\text{cm}^{-1}}$ with slope related to auto-oxidation rate. However beyond 360 h, the photo-oxidation rate substantially decreases. For Ivanov et al.,^[12] the decline of the imide rate formation at longer exposure time is attributed to the screening action of oxidation products and also by the change in the kinetic characteristics due to the consumption of α -methylene groups and the formation of new functional groups. **Figure 1** also shows that the photo-oxidation rate of PA11 is affected by the nature of clays, although the curves display the same trend, that is, a hyperbolic shape. The kinetics plots show a rapid increase in photo-oxidation rate of PA11 nanocomposites samples compared with PA11, however much slower for PA11/SEP. One of the main factors responsible for the rapid photo-oxidation rate of PA11 nanocomposites compared with the neat polymer is the presence of many transition metal ions in the clay structure such as Fe (II), Mg (II), and Al (III) at different contents, which can easily increase the radical concentration of the polymer matrix during the photo-oxidative degradation by hydroperoxide decomposition.

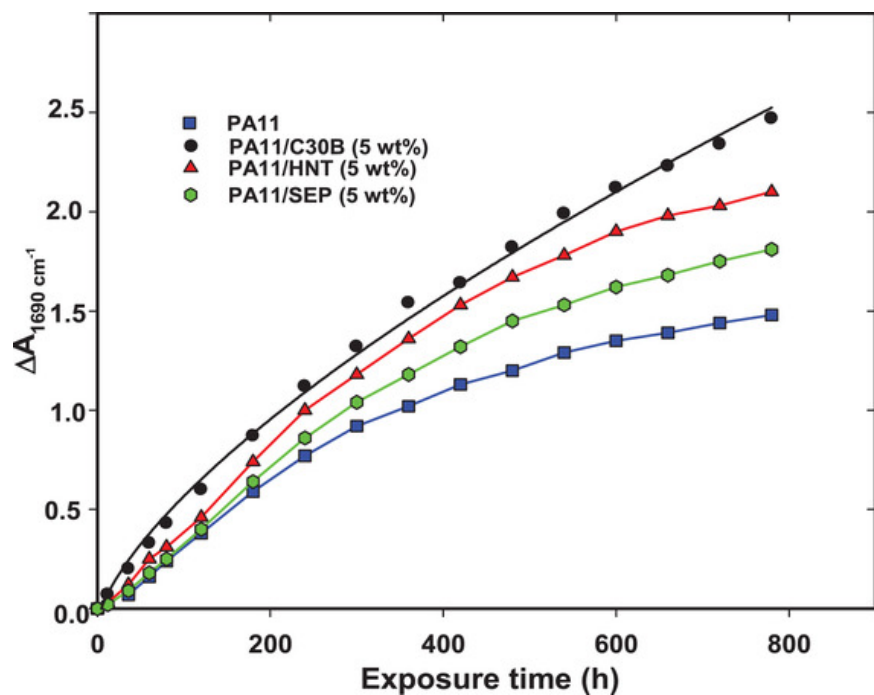


Figure 1. Carbonyl index evolution as a function of exposure time for neat polyamide 11 (PA11) and PA11 nanocomposites.

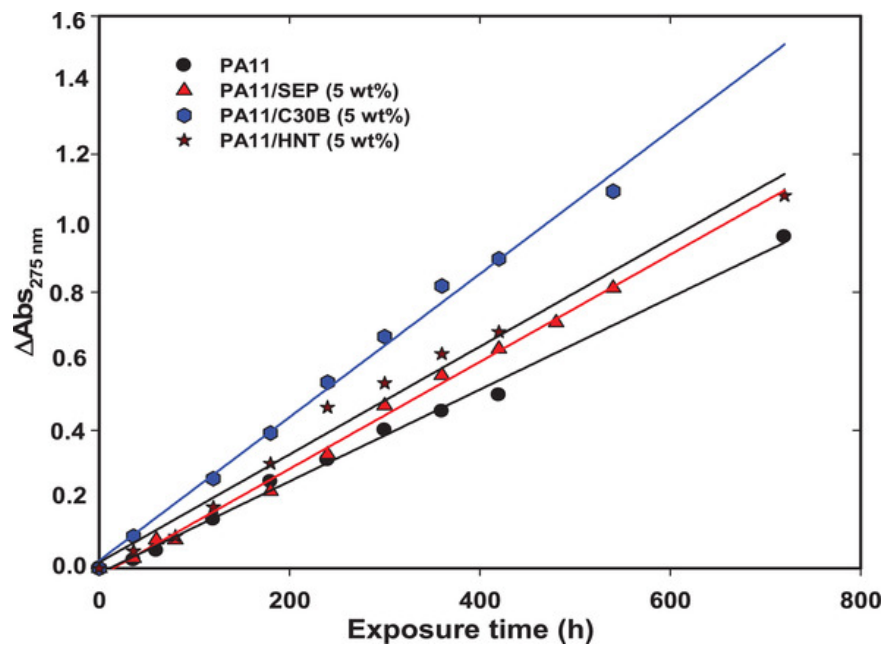


Figure 2. Yellowing index evolution as a function of exposure time for neat polyamide 11 (PA11) and PA11 nanocomposites.

2.2 Evaluation of Yellowing

The absorbance at $\lambda_{\max} = 275$ nm corresponds to a shoulder that comes out at the initial stages of UV irradiation of the PA11 and PA11-based nanocomposites samples and grows during photo-oxidation process. This shoulder can be taken arbitrarily as a relevant YI.^[2] In this topic, **Figure 2** shows the kinetics curves of YI for the neat PA11 and the nanocomposite samples up to 780 h. It is observed a fast growth of YI at the beginning of exposure up to almost 360 h, before decreasing slightly. Furthermore, the kinetics curves display any induction period. It is further noted that all nanocomposites show relatively higher YI kinetics than the neat PA11. However, YI kinetics of PA11/SEP nanocomposite appear to be very close to PA11. This result is consistent with the data obtained by FT-IR analysis.

2.3 DSC Analysis

The determination of OOT is widely used method in the thermal analysis of polymers to evaluate their stability under oxidative conditions. **Figure 3** shows the variation of OOT with exposure time for the neat PA11 and PA11 nanocomposites. Before exposure, all the PA11 nanocomposites have lower OOT values than that of PA11, which decrease linearly with exposure time in the course of photo-oxidation without any induction period. From Figure 3, PA11/C30B nanocomposite exhibits the lowest OOT value of 303°C representing a decrease of 8°C compared to that of the neat polymer, which is almost 311°C. It is further noted that the OOT values of PA11/SEP nanocomposite are close to those of PA11. This is consistent with FT-IR and UV-Vis data.

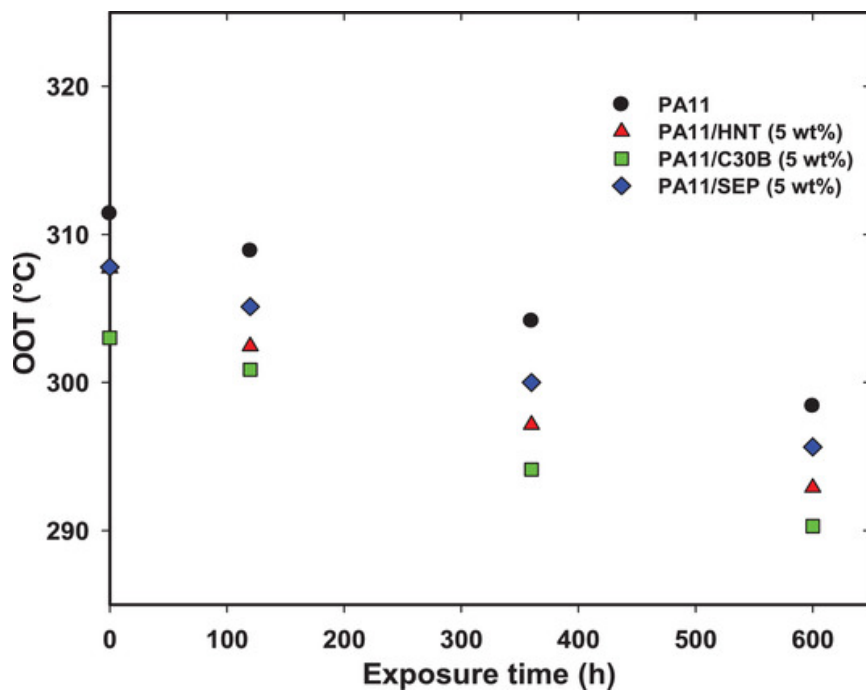


Figure 3. OOT evolution as a function of exposure time for neat PA11 and PA11 nanocomposites. OOT, onset oxidation temperature; PA11, polyamide 11.

3 Conclusion

Nanocomposite films based on PA11 were successfully prepared by melt processing with different clays involving Cloisite 30B, sepiolite, and halloysite loaded at 5 wt.%. The objective was to evaluate the effect of clay type on the photo-oxidation process of PA11 nanocomposite under accelerated UV test. FTIR data showed that the photo-oxidation rate of PA11/clays nanocomposites was higher than that of the neat polymer in the order: PA11/C30B > PA11/HNT > PA11/SEP > neat PA11. Further, the YI determined by UV–Vis spectroscopy followed similar trend as the carbonyl index. Additionally, OOT measurements have confirmed the data obtained by FTIR and UV–Vis analyzes.

4 Experimental Section

Materials Used

PA11 was provided in powder form by Arkema (France) under the grade Rilsan ES Naturelle. The polymer was compounded with different clays, that is, Cloisite 30B, unmodified sepiolite, and Algerian halloysite; all are different in nature and shapes. Cloisite 30B was supplied by Southern Clay Products Inc. (USA) and named C30B. Sepiolite (SEP) was supplied by Tolsa (Spain) under the commercial name Pangel S9. Algerian halloysite (HNT) was supplied by SOALKA Company (Algerian Company of Kaolin).

Sample Preparation

Various clays were melt-compounded with PA11 at filler content of 5 wt.%. The compounding process was carried out using a Nanjing Only Extrusion Machinery Co., Ltd (Model TE-30/600-11-40) corotating twin-screw laboratory extruder (diameter = 30.0 mm, $L/D = 40:1$) operating at a feed rate of 2 kg/h at 230°C and 27 rpm. The extruded materials passed through a cooling water bath system, pelletized, and finally dried in a convection oven at 40°C for 4 days. Film samples were prepared by using a cast single screw extruder of Model Collin CR 72T, Esberg, Germany. The average film thickness was $60 \pm 5 \mu\text{m}$ depending on the sample formulation.

Accelerated UV Test

A UV weathering tester made by the Q-Panel Company (Cleveland, Ohio) and equipped with 6 UVA-340 lamps was used to accelerate the photo-aging of the film samples. These lamps were the best available simulation of sunlight in the short-wavelength region between 295 and 365 nm. Film bands of $\times 107$ dimensions from neat PA11 and various PA11/clays nanocomposites were exposed to UV light at 63°C. Specimens were taken out at regular intervals for testing up to 780 h.

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Conflict of Interest

The authors declare no conflict of interest.

References

1. M. Kaci, T. Sadoun, K. Moussaceb, N. Akroune, *J. Appl. Polym. Sci.* 2001, 82, 3284.
2. M. Kaci, N. Dehouche, W. W. Focke, E. M. van der Merwe, *Polym. Eng. Sci.* 2019, 59, 2449.
3. J. Lemaire, J. L. Gardette, A. Rivaton, A. Roger, *Polym. Degrad. Stab.* 1986, 15, 1.
4. T. Mazan, R. Berggren, J. K. Jørgensen, A. Echtermeyer, *J. Appl. Polym. Sci.* 2015, 132, 41971.
5. C. Laqraa, M. Ferreira, A. Rashed Labanieh, D. Soulat, *Coatings* 2021, 11, 770.
6. A. Hao, I. Wong, H. Wu, B. Lisco, B. Ong, A. Sallean, S. Butler, M. Londa, J. H. Koo, *J. Mater. Sci.* 2015, 50, 157.
7. G. Stoclet, M. Sclavons, J. Devaux, *J. Appl. Polym. Sci.* 2013, 127, 4809.
8. A. da Costa Rodrigues, I. N. Bastos, M. A. A. Kappel, C. R. Nascimento, L. S. Ferreira, A. L. N. da Silva, *Fibers Polym.* 2021, 1. <https://doi.org/10.1007/s12221-021-0391-5>
9. E. Olewnik-Kruszkowska, *J. Therm. Anal. Calorim.* 2015, 119, 219.
10. O. Okamba-Diogo, E. Richaud, J. Verdu, F. Fernagut, J. Guilment, B. Fayolle, *Polym. Degrad. Stab.* 2015, 120, 76.
11. E. Richaud, O. Okamba-Diogo, B. Fayolle, J. Verdu, J. Guilment, F. Fernagut, *Polym. Degrad. Stab.* 2013, 98, 1929.
12. V. B. Ivanov, I. I. Barashkova, V. V. Selikhov, V. N. Vysotsky, Yu. Yu. Yakovlev, R. A. Sadekova, N. N. Barashkov, *Polym. Degrad. Stab.* 1992, 35, 267.