

Chemiluminescence and reactivity of the composites based on blends of polypropylene and polyamide

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Abstract. The effect of the composition of blends based on isotactic polypropylene (PP) and aliphatic polyamide 6/66-4 (PA) on the rate of photo-oxidation of their mixtures in air at room temperature has been studied. The decay of photoinduced chemiluminescence was studied to determine the kinetics of peroxy radical termination in composites and the rate constants of this process depending on the composition of the mixtures. In the presence of PA, the rate of photo-oxidation of mixtures is much higher than the rates of photo-oxidation of separately taken components, PP and PA. Thus, the kinetics of photo-oxidation of mixtures differs from the simple sum of photo-oxidation kinetics of PP and PA, which should be expected in the absence of chemical and physical interaction of the components of the mixture. A decrease in the rate constants due to PA additives indicates a decrease in the mobility of molecules in the composites and explains the observed increase in photo-oxidation of mixtures.

1. Introduction

Blending has been recognized as the most versatile, economic method to produce materials able to satisfy complex requirements for application characteristics of products [1]. Blending may improve product performance by producing materials having a full set of the desired properties at lowest cost and improving specific properties such as toughening, heat-resistance, modulus, reactivity etc. [2, 3]. Chemiluminescence (CL) of polyolefins arises in the reaction of peroxy macroradical termination and is a convenient way to test the molecular mobility, which determines the rate and direction of polymer reactions. It is important that in this method the molecular mobility is tested in a place where the reaction centers are located [4]. Thus, free radicals act as molecular probes and inform about the changes of molecular movement of main chains of the polymers [5]. In addition to CL and electron spin resonance (ESR) methods, molecular mobility of blends can be tested by nuclear magnetic resonance (NMR). The molecular motion of poly(epichlorohydrin) (PECH) was studied by ¹³C NMR and showed different behavior in pure PECH and blend of PECH/PMMA. The line shape and temperature dependence of T₁ and T₂ in PECH indicate that the molecular motion of PECH is inhibited by surrounding PMMA chains and that the decrease in molecular motion depends on miscibility [6]. The radical decay in PMMA-PEO blends has been studied in the paper [7]. A slower decrease in the concentration of free radicals in a sample of a PMMA/PEO blend containing 50 vol% PEO compared to samples with 10, 30 and 70 vol% PEO is observed. The mixing for a blend PMMA-



PEO has been shown to affect molecular motions as a result of specific interactions between dissimilar PMMA and PEO chains [7, 8].

This work represents the study of chemiluminescence and reactivity of composites based on isotactic polypropylene (PP), which is the second most produced polymer, and polyamide 6/66 (PA). Creation of new polymeric materials with enhanced reactivity, which can improve the degradation by the action of photo-oxidation and other environmental factors, is a promising area of research projects aimed at reducing environmental pollution by polymer waste. The problem is solved effectively by creating polymer blends [3]. CL analysis is sensitive to detect the very first stage of oxidation of polymers, and does not require long periods of time to obtain the information [9].

2. Experimental

Isotactic PP (Kaplen 01030, TU 2211-015-00203521-99) was obtained from OAO Gaspromneft'-Moskovskiy NPZ. The melt flow index (MFI at 230°C and 2.16 kg load) was 3,0 g/10 min. PP's melting and crystallization temperatures were 163°C and 111°C, respectively as determined by differential scanning calorimetry (DSC). Aliphatic polyamide (PA 6/66-4, OST 2224-438-02099342-93) was obtained from OOO Anid. This PA is the polycondensation product of caprolactam and the salt of hexamethylenediamine and adipic acid with the viscosity number of the polyamide in metacresol equals to 134 cm³/g, moisture content no more 2,6 %, melting temperature 142°C, crystallization temperature 92°C as determined by DSC.

Compositions were prepared using a laboratory rotor mixer of Brabender type. Total sample weight was made 20 grams. Blending was carried out at a temperature of 190°C under an argon atmosphere. At the rotor rotation speed of 15 rpm, pelletized polyamide and pelletized polypropylene were added together into the mixing chamber, then rotation speed was increased to 30 rpm and blending continued for 5 minutes. After that, the blends were removed from the mixing chamber and cooled down at the room temperature. Composite materials of the following composition were objects of this study: PP with addition of 5, 10, 20, 30, 40 and 50 wt % of PA.

Film samples were obtained from crushed blends using a laboratory hydraulic press equipped with an electronic module of plate heating at a temperature of 190°C and a pressure of 60 atm on a cellophane substrate. Crushed samples of the blends were evenly distributed on the substrate. Pressing time was equal to 2 minutes. After that, the obtained samples were quickly cooled down in air at temperature of approximately 24°C. The obtained samples were films of 110 ± 20 μm thickness.

The films of PP, PA and PP-PA blends were irradiated by light of UV lamp OKUF-5M with a wavelength of 254 nm in air at room temperature. After a short-term irradiation of the films the light was switched off, the films were put in CL camera and the CL intensity was measured [10]. The kinetics of CL decay in the dark was measured one minute after irradiation.

3. Results and discussion

The low temperature photo-oxidation of polymers is a complex process consisting of several main stages: photoinitiation, termination, propagation (see Scheme 1). According to common scheme of low temperature polymer oxidation CL arises in reaction of peroxy radical termination. Free radicals are produced by UV light in the first stage of oxidation. In the second stage they transform into peroxy radicals via their reaction with oxygen, then free radicals take part in reaction of oxidation chain propagation. At low radical concentrations as in the case of measurements by sensitive CL method the rate of second order termination is negligibly low compared to linear chain termination. In the case of the first order termination CL intensity J_{CL} is proportional to the rate of radical termination and quantum yield ϕ of CL equation (1). So the rate of photo-oxidation W is proportional to CL intensity according to equation (2).

$$J_{CL} = \phi k [ROO\cdot] \quad (1)$$

$$W = k_p [RH][ROO\cdot] \sim J_{CL} \quad (2)$$

In equations (1, 2) k is the rate constant of linear radical termination, $[ROO\cdot]$ is a free peroxy radical concentration, k_p is the rate constant of oxidation chain propagation. As can be seen from equation 2, CL intensity in the moment of light off is proportional to photo-oxidation rate.

Scheme 1. Reactions of polymer photo-oxidation



Figure 1 shows the example of dependence of CL on the duration of UV irradiation for PA. As can be seen the intensity of CL rapidly reaches a stationary level, corresponding to the stationary concentration of radicals during photo-oxidation.

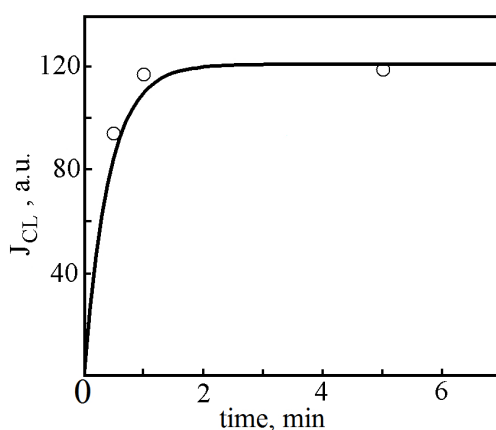


Figure 1. The dependence of CL intensity on the duration of UV irradiation for pure PA.

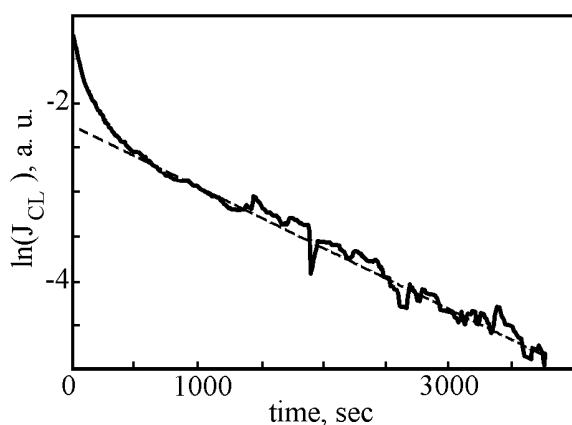


Figure 2. CL decay of pure PP in the air at room temperature after 1 min UV-irradiation.

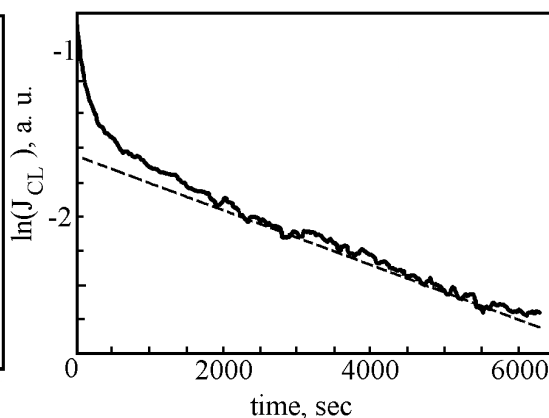


Figure 3. CL decay of pure PA in the air at room temperature after 1 min UV-irradiation.

CL decay of pure PP and pure PA after irradiation are shown in figures 2 and 3 respectively. After relaxation, the radical decay of the first order is established with the rate constant, the value of which is equal to the slope of the trend line (dashed line in figures 2 and 3). It was studied how the composition of PP-PA mixtures affects the rate of composite photo-oxidation and the rate constant of peroxy macroradicals linear termination. The data on CL decay in two samples of PP-PA composites are presented in figures 4 and 5.

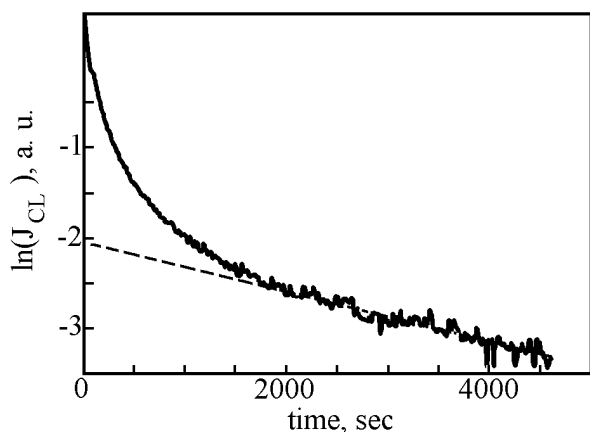


Figure 4. CL decay of blend with 90 wt.% PP and 10 wt.% PA after UV-irradiation in the air at room temperature.

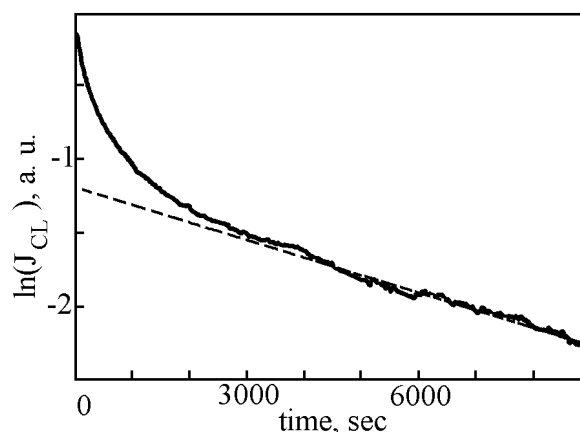


Figure 5. CL decay of blend with 70 wt.% PP and 30 wt.% PA after UV-irradiation in the air at room temperature.

The results of measurements of both initial CL intensities of composites and rate constant of radical decay are presented in figures 6 and 7 respectively.

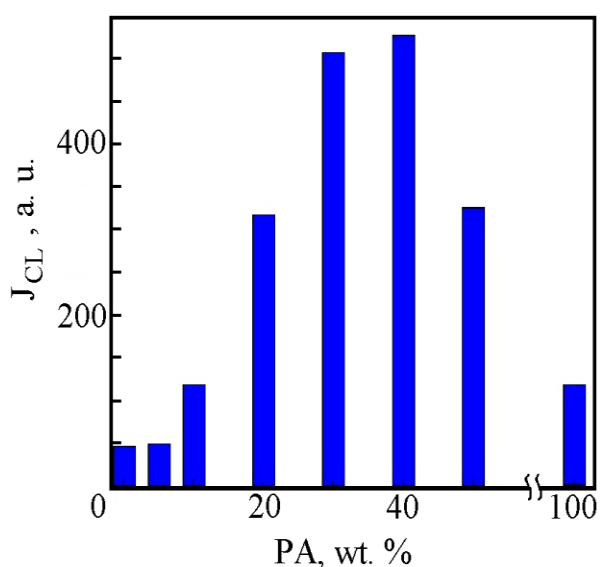


Figure 6. The dependence of initial CL intensity of PP-PA blends on PA content.

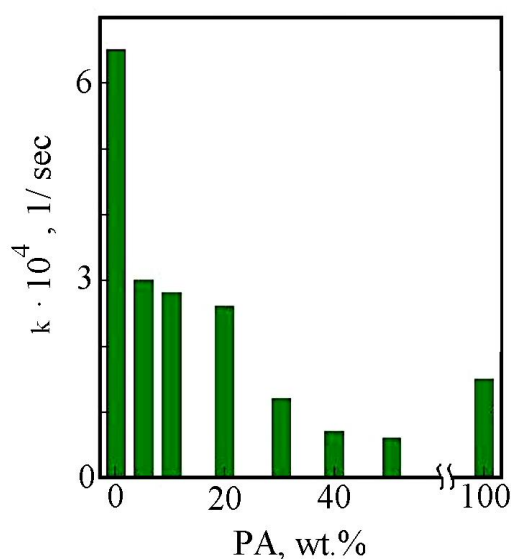


Figure 7. The dependence of rate constant for radical decay of PP-PA blends on PA content.

As can be seen from figure 6, the PA additives significantly increase the rate of photo-oxidation of composites. In the presence of PA, the rate of photo-oxidation of mixtures is much higher than the rates of photo-oxidation of separately taken components, PP and PA. Thus, the kinetics of photo-oxidation of mixtures differs from the simple sum of photo-oxidation kinetics of PP and PA, which should be expected in the absence of chemical and physical interaction of the components of the mixture. The highest photo-oxidation rate is observed at 40-50% PA in the PP-PA mixture.

The dependence of rate constant for radical decay in PP-PA blends on PA content is presented in figure 7. The rate constant of radical decay decreases with increasing PA content and reaches its lowest value at 40-50% PA. From the comparison of figures 6 and 7 one can see some relation between photo-oxidation rate and rate constant of radical decay for different values of PA content.

Thus, the photo-oxidation rate increases with decrease in the rate constant of radical decay. The rate constant of radical decay is a measure of molecular mobility. So decrease of rate constant indicates a decrease in the molecular mobility of composites. Thus, increased both photo-oxidation rate and radical concentration is due to lowered molecular mobility in blends. Immiscible polymers in mixtures are known to affect the structure of each other due to specific interactions between polymer chains. For instance changes in polymer structure are observed in blends of PP and polyethylene [11]. Other examples of lowering the molecular mobility in polymer mixtures are given in [6, 8].

4. Conclusion

In this paper, the rate constants for the peroxy radical decay in PP-PA mixtures were measured from the kinetics of photoinduced CL decay. These rate constants were compared with the data on the initial intensity of CL which is proportional to the concentration of peroxy radicals and consequently to the rate of photo-oxidation of the PP-PA blends. The photo-oxidation rate is shown to increase with decrease in the rate constant of radical decay. The free radical decay of irradiated polymers is controlled by segmental movements of macromolecular chains. The rate constant of free radical decay provides information about the molecular dynamics of the examined polymer system. It is assumed that increase in both the rate of photo-oxidation and the concentration of radicals during photo-oxidation (which are proportional to the initial CL intensity) is due to decrease in the mobility of polymer chains of PP-PA mixtures.

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References

- [1] Utracki L 2014 *Polymer Blends Handbook* ed L Utracki and C Wilkie (New-York: Springer Reference) p VIII
- [2] Chandrasekharakurup S, Shanks R A and S Thomas 2014 *Nanostructured Polymer Blends* ed S Thomas and R Shanks et al (Oxford: Elsevier) p 1
- [3] Krištofič M and Ujhelyiová A 2012 Compatibilisation of PP/PA Blends *Fibres & Textiles in Eastern Europe* **20** 93
- [4] Nedorezova P, Chapurina A, Klyamkina A, Aladyshev A, Popov A, Shibryaeva L, Monakhova T, Margolin A 2011 *Polymer Science, Series B* **53** 448
- [5] Szocs F, Klimova M, Chodak I and Chorvath I 1996 *European Polymer Journal* **32** 401
- [6] Yamanaka A, Kaji A and Murano M 1998 *Polymer Journal* **30** 210
- [7] Miklesova K and Szocs F 1992 *European Polymer Journal* **28** 553
- [8] Sonnier R and Taguet A 2012 *Functional Polymer Blends: Synthesis, Properties, and Performance* ed V Mittal (New-York: CRC Press) p 261
- [9] Corrales T, Catalina F, Peinado C, Allen N, Fontan E 2002 *Journal of Photochemistry and Photobiology A: Chemistry* **147** 213
- [10] Margolin A, Shlyapintokh V 1999 *Polym. Degrad. Stab.* **66** 279
- [11] Mastalygina E, Shatalova O, Kolesnikova N, Popova A and Krivandin A 2016 *Inorganic Materials: Applied Research* **7** 58