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PHOTODEGRADABLE FILMS BASED ON POLYETHYLENE-CASSAVA STARCH BLEND USING BENZOPHENONE/ANTRA-QUINONE OR Fe(II) COMPOUND AS PHOTOSENSITIVE AGENTS

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SUMMARY

This paper is dealing with formulation of photodegradable films based on polyethylene-cassava starch blend using benzophenone/antraquinone or Fe(II) compound as photosensitive compound. Benzophenone, antraquinone and Fe(II) compound were synthesized in the laboratory and characterized by IR and NMR spectra. The films were obtained by extrusion-blowing method and showed good mechanical properties. They were exposed outdoor and indoor for photo-degradability testing. It showed that after four months outdoor their tensile at break decreased 85% and elongation at break about 90%. It is interesting to note that the films keeping 4 months inside the room showed little decrease in mechanical properties. The films are suitable to be used as mulch films and for other purposes.

Keyword*: Cassava starch, photodegradable film, photosensitizer.*

I - INTRODUCTION

Most polymers are, in their pure state, insensitive to sunlight (> 290 nm). However, the absorption spectra of commercial polymers are rather complicated and exhibit weak absorptions in the near-ultraviolet region. This is partly due to the existence of crystalline parts that scatter light in the UV-wave length region. Another factor that influences the light absorption is the thermal history of the polymers. Heat treatment (melting and extrusion) of polymers in the presence of air makes the susceptibility of polymers to sunlight increase through the formation of chromophores, such as carbonyl groups, hydroperoxides and unsaturated bonds. Metallic impurities such as iron and titanium incorporated into polymers during processing also act as chromophores.

Some chromophoric impurities are absorbed from the atmosphere during the storage of polymers. These impurities are such polynuclear aromatic compounds as anthracene, phenanthrene and naphthalene [1]. In order to produce photodegradable polymers, these chromophores are intentionally introduced into polymer structures either by copolymerization or by mixing with polymers.

Based on the fact that carbonyl groups act as chromophores, copolymer systems of olefin monomers, such as carbon monoxide and vinyl ketones, have been proposed.

Various substances have been tried as photosensitive additives for polymers. These materials are referred to as either photoinitiators or photosensitizers. The former are excited by photoenergy and decompose to give free radicals, which initiate the degradation of polymer molecules. The latter transfer the absorbed energy to the polymer molecules. Usually, it is rather difficult to distinguish between photoinitiators and photosensitizers because both initiation and sensitization may occur simultaneously with some additives.

Transition metal dithiocarbamates work as photoinitiators [2]. Ultraviolet energy absorbed by the metal complexes releases the metal ions, which then act as catalysts to break the polymer chains. Nickel, zinc and cobalt complexes act as sensitizers.

The effect of transition metal acetylacetonates, stearates, chlorides and ferrocene has been studied. The photodegradation is initiated by the radicals produced in the decomposition of these materials.

In this research work benzophenone, antraquinone as well as Fe(II) salt of fatty acid were synthesized and incorporated into polyethylene-cassava starch blend to make the films and to study their photodegradability.

II - EXPERIMENTAL

1. Materials

- Polyethylene and LDPE were obtained from Cosmothene (Singapore).

- Cassava starch was received from Ha Tay, Vietnam. The size of the starch granule was about 0.02 - 0.03 mm. Water content was about 12%.

- Polyethylene-g-maleic anhydride (MAPE) from Merck. MA content: 3%, melting point: 105°C.

- Glycerol from China.

2. Characterization methods

- Mechanical properties of the samples were measured on LLOYD Instruments (England) according to ASTM D638-99 [3].

- Scanning Electronic Microscope (SEM) pictures were obtained on JSM-6868 LV, JEOL (Japan).

- Thermogravimetric analysis (TGA) was performed on TGA-503 (Bärh, Germany).

- IR spectra were recorded on Nicolet-AVATA 360 FTIR.

^{1}H-NMR spectra were recorded on AVANC-500 Bruker (Germany), solvent was $CDCl_3$, at 500 MHz.

3. Synthesis of photosensitizers and films formulation

- Salt Fe(II) was synthesized according to the procedure of the Lab.

- Benzophenone and antraquinone were synthesized according to the procedure in [4].

- Thermoplastic cassava starch (TPS) was obtained according to procedure in [5].

- Formulation of predegradative pellets: LDPE, TPS (15 wt% to LDPE), MAPE (3 wt% to LDPE). Fe(II) salt or benzophenone, or antraquinone (1 wt% to LDPE) were mixed together and extruded on a twin-crew extruder at 165°C, with the crew speed 45 r/min, then were cut into pellets.

- Formulation of photodegradation films: LDPE and predegradative pellets in definite ratios were mixed and blown into films on an extrusion-blowing machine at 180°C, crew speed: 35 r/min. The films had the thickness of 0.02 - 0.03 mm.

III - RESULTS AND DISCUSSION

1. Synthesis of benzophenone, antraquinone and Fe(II) compound

Benzophenone and antraquinone were synthesized according to the modified procedures described in [4]. The reaction yield reached 75 - 80% for both compounds. Their structures were confirmed by IR and ^{1}H-NMR spectra.

It showed that the synthesis of those compounds was quite simple and both compounds had lower cost compared to the commercial one.

2. Mechanical property deterioration of the films exposed to the outdoor weather conditions

The film samples prepared contained 3%, 2%, 1.5% and 1% Fe(II) compounds (sample A, B, C and D, respectively). They were exposed to the outdoor conditions from January to May, 2006. After 1, 2, 3 and 4 months they were taken for mechanical property testing. The tensile strength and elongation at break were shown in figures 1 and 2.

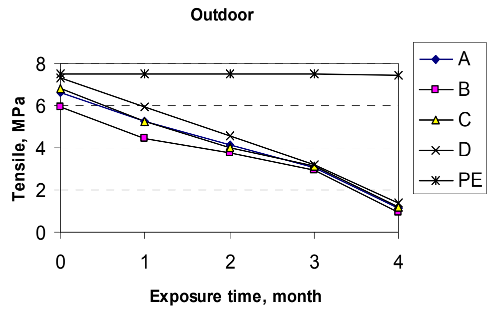

Figure 1: Tensile strength upon outdoor exposure time

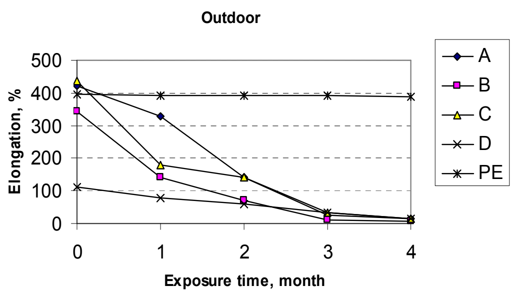

Figure 2: Elongation at break upon outdoor exposure time

It showed clearly that the tensile and elongation at break of the samples containing Fe (II) compound decreased rapidly after 4-month outdoor exposure (about 85%), meanwhile the PE sample remained almost unchanged. Especially the elongation at break of the testing samples decreased almost 50% after only one month and about 90% after 4-month exposure. It was also worthy to note that the mechanical properties generally depended on Fe(II) compound contents, but after 3 months outdoor exposure they decreased to the definite value (of tensile and elongation). So, the 1 or 2 wt% of Fe (II) compound seemed to be adequate for further application. It showed that after 4 months the films became brittle and was easily broken into small pieces. This made the films useful to be used as mulch films, for example, for peanut cultivation land the crop of which takes 4 - 5 months long.

In the other experiment the film samples were kept in the room, their mechanical properties were also measured. The results were shown in figures 3 and 4.

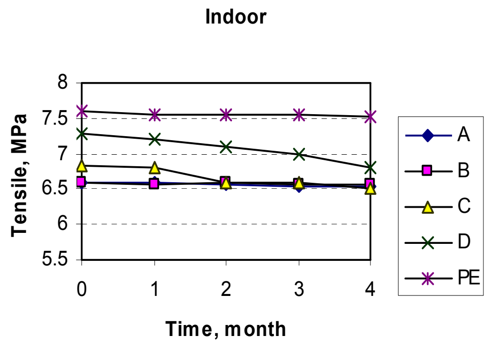

Figure 3: Tensile strength upon indoor exposure time

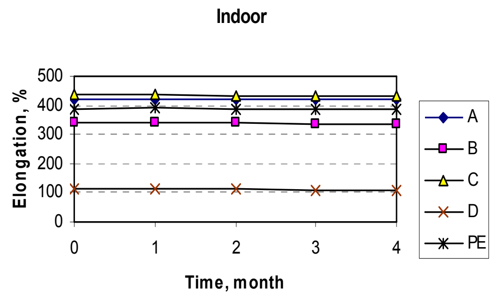

Figure 4: Elongation at break upon indoor exposure time

We can see that under this condition the mechanical properties of the film samples were almost unchanged after 4months. This proves that the natural light had an important role for photodegradation.

The film samples containing 1, 2 and 3 wt% benzophenone (benzo-1, benzo-2 and benzo-3 respectively) were also exposed to the outdoor condition (sample benzo-4 contained mixture of benzophenone and antraquinone (1:1)). After 1, 2 and 3 months they were taken for mechanical property testing. The results were shown in figures 5 and 6.

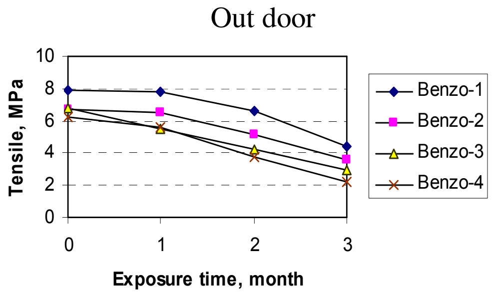

Figure 5: Tensile strength upon outdoor exposure time

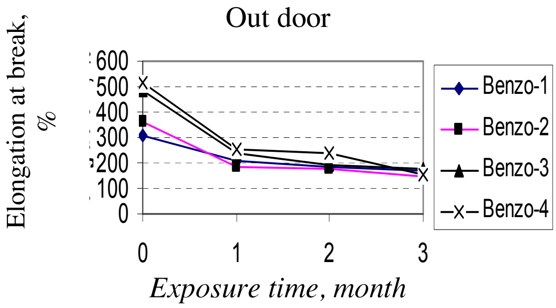

Figure 6: Elongation at break upon outdoor exposure time

We can see that the mechanical property decreased quite rapidly after 3 months. The elongation at break decreased almost 50% after one month exposure. It could be that in photodegradation, beside the carbonyl groups absorbed UV energy initiating free radicals to break down the linkages in PE, there would be also contribution of cassava starch, at least in terms of physical aspect. This issue will be discussed later in more detail.

3. Study on thermo-resistance of photodegradative PE-Cassava starch films

In order to confirm the photodegradability of the PE-cassava starch films, the film samples were subjected to determine their thermodegradation upon the exposure time. The weight loss of the film samples upon the exposure time was shown in figure 7. In the figure 7 there are 3 thermodegradation curves. The film samples PE-TB contains 3 wt% of Fe(II) compound. The curve PE-TB-0T is of initial sample (not exposed). The curve PE-TB4T - sample exposed for 4 months. It can be seen from the figure 7 that PE had the highest thermoresistance. The thermoresistance of PE-TB-4T was much less than that of PE-TB-0T. It could be that after the UV light was absorbed under the action of Fe(II) compound, the chemical structure of the film PE-TB started to be deteriorated leading to less thermo-resistance. By the way, that the starch removed from the PE matrix during the film exposed under the light could make the PE structure weaker and contribute to less thermoresistance of the PE-Starch films.

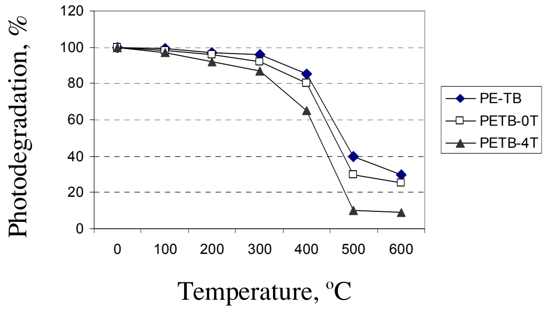

Figure 7: Thermo-resistance of the photodegradation film

4. Study on photodegradation by the SEM method

Photodegradability has been also studied by the SEM method. The pictures are presented in figure 8.

PE-TB-0T is the initial sample (not exposed) containing 3 wt% of Fe (II) compound. It showed that in this case the starch was compatible well with PE. Somewhere it can still be seen the starch granule although the interface adhesion between PE and starch was quite good, there was almost no gaps in the interface boundary. After 2-month exposure the sample PE-TB-2T showed the holes that could be because the starch granules were removed from the PE-TB matrix leaving PE with loose structure. This explains why the mechanical properties of the sample PE-TB-2T decreased. The sample PE-TB-4T (exposed for 4 months) showed very brittle, was easy to be broken. The cross-section changed remarkably. There were many small holes proved the fact that a lot of small starch granules was removed from the PE matrix due to C-C linkages was damaged. This again explained why after 4-month exposure the films showed very bad mechanical properties.

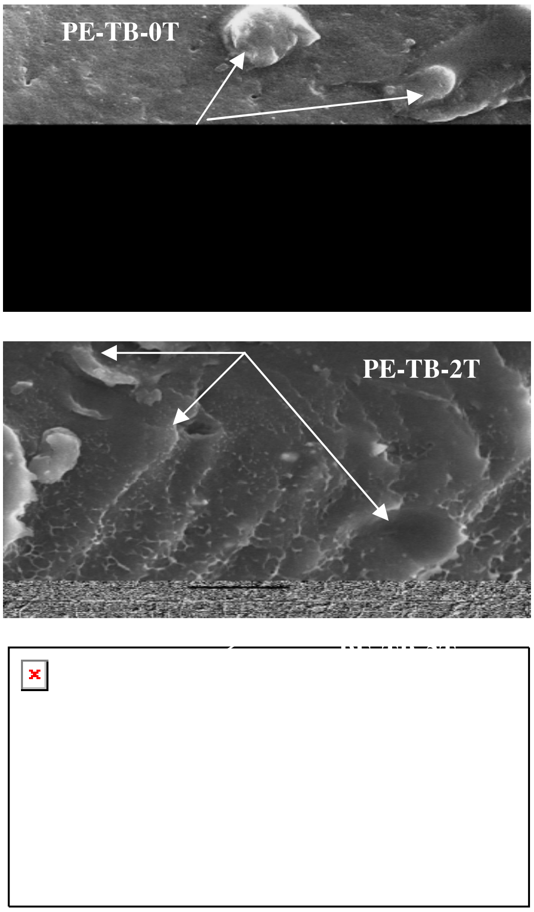

Figure 8: SEM pictures of the PE-TB films

IV - CONCLUSIONS

- The photosensitizers: benzophenone, antraquinone and Fe (II) compound were synthesised, their structures were confirmed by IR and ^{1}H-NMR spectra.

- The photodegradation films based on LDPE, thermoplastic cassava starch and photosesitizer mentioned above was formulated and exposed to the outdoor and indoor natural conditions to test their photodegradability.

- It showed that after 3(4)-month outdoor exposure the mechanical properties of the testing film samples decreased remarkably, especially the films containing the Fe(II) compound become brittle, easy to be broken into small pieces, meanwhile in the indoor condition the films remained almost unchanged.

- The deterioration in properties of the PE-starch blend films due to photodegradation was also proved by DTA and SEM methods.

- The films are suitable to be used as mulch films and for other purposes.

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