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The Effect of Wheat Straw Bleaching on the Some Mechanical Properties of Wheat Straw/LDPE Biocomposites

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Abstract
Using biocomposites contain wheat straw (WS) and synthetic polymers like polyethylene (PE) has gained tremendous popularity in recent years, but its application in the packaging industry is not substantial. Due to prevalence of color of raw WS which manifests itself in the WS/LDPE biocomposite, the present investigation is dedicated to fabrication of a bleached WS/LDPE composite. Thus, raw WS and the pulp of WS were treated with three levels of xylanase, five concentrations of hydrogen peroxide and five levels of sodium dithionite as bleaching agents. The bleached raw WS and its pulp were used to fabricate WS/LDPE composites and their colorimetric properties was measured using L*a*b* coordinates. The results indicated that "bleached raw WS with 4% H_2O_2" and "bleached WS pulp with 10 units of xylanase and by addition of 1%H_2O_2" demonstrate highest degree of lightness based on L* value. Then, 40% of above mentioned treatments were blended with LDPE to develop a biocomposite using a twin screw extruder. Further, lightness index and the mechanical properties of the final composites were measured. Results indicated that the composites containing unbleached raw WS had the lowest and the bleached WS pulp with 10 unites of xylanase and 1%H_2O_2 had the highest L* value amongst all treatments. Also the raw WS/LDPE and the bleached raw WS/LDPE composites had the highest and the lowest tensile strength respectively. It needs to be mentioned that the flexural strength of all treatments was higher than the control, whereas the impact resistance of them was lower than the control.

Keywords: Biocomposite, Bleaching, LDPE, Mechanical properties, Wheat straw

Introduction

Synthetic fibers have replaced most of the traditional metallic/ceramic materials for a number of applications because of their massive properties (Pappua et al., 2016). However, the use of plastic materials in the packaging industry has been rapidly increasing after end of World War II in 1945. Nowadays, application of synthetic polymers and plastics in the packaging industry is well recognized due to their ideal properties such as high flexibility, low density (0.9-1.5 g/cm3), relatively low price, high configurability in the packaging machineries, high resistance against acidic or alkaline materials, less energy requirement in production and forming than metal cans and glass bottles, the ability for adding additives to improve the properties, etc. Polyethylene (PE) is one of thermoplastic polymers that has the simplest basic structure amongst other polymers. In addition, as raw material it contributes highest

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share in the manufacture of plastic materials worldwide (DeArmitt, 2011; Khatibi, 2009; Tajeddin, 2009; Ward, 2004).

Despite many benefits of plastics, they have some problems and disadvantages as well. For example, persistence in the environment and slow degradability cause of great environmental concerns. A solution to reduce or improve their consumption is the search for renewable resources for preparing polymers or composites using plant residues or lignocellulosic materials. Biological macromolecules especially the cellulose, hemicellulose, lignin, etc. are potential engineering materials having considerable opportunity to be used as an environmental friendly reinforcing ingredient for developing of polymer based green materials. In general, composites are solids, synthetic or natural materials which are formed from two or more components (phases) and have the properties different from those of individual copmponents. The phases are different in point of chemical and physical characteristics and set together on a regular basis or dispersed form, and there is a common layer between them (Nishino, 2004; Mohanty et al., 2005; Raschip et al., 2006; Pappua et al., 2015). Biocomposites are a large category of composites that are obtained from natural fibers and synthetic polymers like PE and polypropylene (PP), (Mohanty et al., 2005; Selke, 2000; Tajeddin et al., 2010). In this context, lignocellulosic or agricultural materials (Agro-Polymers) are blended with industrial polymers. All these materials have at least two phases namely matrix and reinforcing/filler (Yu, 2006; Klyosov, 20007; Alemdar and Sain, 2008). Plant fiber reinforced thermoplastic composites have earned a lot of charm in the construction and automotive applications, but their commercial uses in the packaging industry is still limited (Tajeddin, 2014). Agricultural crop residues such as wheat straw (WS), bagasse, etc. are used as available natural resources for such applications (Mohammed et al., 2015; Clemons, 2002; Sain and Panthapulakkal, 2006).

WS is one of the agricultural materials that are commonly found in many countries. It is mainly for animal feed and animal bedding. WS is also effective in preventing the soil from water and wind erosion. In addition, WS increases the soil organic matter and improves its structure when added to the soil. However, in most cases, it is not utilized. The chemical composition of WS is mainly consists of about 72.9% holocellulose (a set of cellulose and hemicelluloses), and 20.5% lignin (Bajpai, 2012).

Lignin, a branched non-carbohydrate polymer is one of abundant organic materials and renewable resources on the planet that is one of the main ingredients of WS (Sun and Tomkinson, 2000). It is hydrophobic, and creates a certain degree of roughness to the cell wall due to its structure. Lignin combination with the hemicelluloses makes a lignocellulosic composite structure that has a certain flexibility and strength. A lignin compound prevents the penetration of microorganisms' enzymes into the cellulose. It improves mechanical properties of composites due to its phenolic structure, when combined with plastics (Khatibi, 2009).

The WS/PE composites were fabricated and were studied the characteristics of the composites for packaging applications (Tajeddin, 2013). Although the obtained composites had a color and smell almost same as that of natural raw WS, which may be an advantage in some applications, it be considered as a disadvantage once used as packaging material, because it may affect the marketability. Hence, in this study the different bleaching methods including some chemical methods, using enzyme, and preparation of WS pulp were investigated for excluding the natural color of WS. The bleached WS were then blended with LDPE to prepare the WS/PE biocomposites. Mechanical properties of these biocomposites

are discussed in this paper as well. It should be noted that the results of colorimetric properties of WS/LDPE composites has already published (Tajeddin and Ansari, 2016).

Materials and methods

Materials

Wheat straw (WS)- Pishtaz variety as natural filler was obtained from the Seed and Plant Improvement Institute (SPII), Karaj, Iran. The WS was then cut into small pieces, approximately 3-5cm length and was ground using a mill (Retsch GmbH-SK1 Mill, Germany). The ground samples were then sieved using a shaker (Scl-ST11, Iran) and were passed through a 40 mesh (0.40 mm) sieve. LDPE, grade LF0200, having density of 0.92 g/cm3 and melt index of 2g/10min in granule form was supplied from Imam Khomeini petrochemical industry, Iran. Maleic anhydride grafted polyethylene (MAPE) in granule form with viscosity 500cP (140^0C) from Sigma-Aldrich that were prepared through Payam Ahora chemical and industrial company, Tehran, Iran. The xylanase of Thermomyces lanuginosus, powder, ≥2500 units/g was purchased from Sigma-Aldrich. The optimum temperature and pH for activity of this enzyme was 65^0C and 6.5, respectively. It was used in levels of 5, 10, and 20 units per gram of the raw material (lignocellulosic pulp). Chemicals such as hydrogen peroxide (H_2O_2) and sodium dithionite ($Na_2S_2O_4$) were used in levels of 1, 2, 3, and 4 percent of the raw WS and WS pulp. In addition, 1 normal NaOH and Na_2SO_3 solutions were applied.

Methods

Bleaching

Raw WS powder and WS pulp was bleached using chemical and natural methods as following (Zhao et al., 2005; Enayati et al., 2006):

A) Bleaching of WS with hydrogen peroxide (H_2O_2). The H_2O_2 solution at 1%, 2%, 3%, 4%, 5% (by weight of WS) was prepared. One gram of WS was then mixed with 50 ml of each H_2O_2 solution levels. Their pH was fixed at 11.5 using 1 normal NaOH solution. The 11.5 pH mixed solutions were then placed in the hot water bath at a temperature of 80oC for two hours. After that, they were filtered by filter paper and wash with distilled water. The bleached WS was dried at oven and was then milled by a laboratory mill (model SK1-Retsch, Germany) to separate the sticking fibers. Finally, the colorimetric test of these bleached WS was performed using a colorimeter instrument based on L*a*b* coordinates (Konica Minolta, model CR-400, Japan).

B) Bleaching of WS with sodium dithionite ($Na_2S_2O_4$). One gram of WS was mixed with 50 ml of each $Na_2S_2O_4$ solution levels (1, 2, 3, 4, 5%). The mixed solution pH was about 3-4 that was fixed at 5 using 1 normal NaOH solution. The 5 pH mixed solutions were then placed in the hot water bath at a temperature of 60^0C for two hours. After that, they were filtered, dried, and milled. The color of the samples was then measured using a colorimeter instrument (Konica Minolta, CR-400 model, Japan).

C) Bleaching of WS pulp with xylanase and by addition of H_2O_2. At first, WS pulp was prepared from WS powder through sulfite process at cylindrical mini digester (model STALSVETS, Sweden). For pre-bleaching of WS pulp by xylanase, enzyme at 5, 10 and 20 units per gram pulp were added to 200 ml flasks contain of 10 g pulp and distilled water. After setting of pH at 6.5, the solutions were placed in the hot water bath at a temperature of 65^0C for three hours with stirring. They were then filtered using filter paper and funnel Buchner

and dried in the oven at a temperature of 65^0C for 5 hours. Six gram of pre-bleached WS pulp with 1%, 2%, 3%, 4% (by weight of WS pulp) levels of H_2O_2 solutions were then mixed with distilled water in 300 ml flasks. Their pH was fixed at 11.5 using 1 normal NaOH solution. The

11.5 pH mixed solutions were placed in the hot water bath at a temperature of 80^0C for two hours. After that, they were filtered by filter paper and wash with distilled water. The bleached WS pulp was dried at oven with a temperature of 60^0C for six hours. The color of the pulp samples was measured using a Konica Minolta (CR-400 model, Japan).

Preparation of Biocomposites

According to the results of preceding studies in which using 40% raw WS showed better mechanical properties for the PE/WS biocomposites among different formulations (Tajeddin, 2013; Lewin et al., 2000), 40% of filler material (WS) were used in this study. On the other hand, the colorimetric results of bleaching treatments in terms of brightness (L*) indicated that the treatments "raw WS bleached with 4% H_2O_2 namely BWS" and "WS pulp bleached with 10 unites of xylanase and by addition of 1% H_2O_2 namely BWS pulp" are the best treatments Tajeddin and Ansari, 2016).

Therefore, the above mentioned treatments were used to fabricate the WS/LDPE biocomposites. For this purpose, the bleached raw WS powder and the bleached WS pulp and LDPE (in ratios of 40 to 60), and MAPE as a compatibilizer (in ratios of 10 percent of LDPE) were placed in the twin screw extruder (model Dr. Collin-GmbH, d-8017, Germany). Different formulations of WS/LDPE biocomposites are shown in Table 1.

Table 1. Formulations of treatments

Treatments	Formulation
T_1	60% LDPE + 40% WS + MAPE (10% (w/w) of LDPE)
T_2	60% LDPE + 40% BWS + MAPE (10% (w/w) of LDPE)
T_3	60% LDPE + 40% BWS pulp + MAPE (10% (w/w) of LDPE)
T (Control)	100% LDPE

WS: raw WS powder; BWS: bleached raw WS powder; BWS pulp reagents bleached WS pulp

Fig 1. WS/LDPE biocomposite granules contain raw WS (a), BWS (b), and BWS pulp (c)

Mixing of samples was carried out at 145^0C temperature with rotor speed of 60 rpm in this machine. The extruded compounds were then placed in the grinder (model Weiser WE-LS

200/200, Austrian) to be converted into the granular form (Figure 1). 2.2.3. Mechanical Properties

The prepared specimens converted into dumbbell-shaped with 3.2 mm thickness and 10.40 mm length using the injection machine (Imen machine company, Iran) at 165-195^{0}C to study the mechanical properties. Therefore, the tensile strength (TS) was determined by five replications of samples for each composition by an Instron Universal Testing Machine (model Hounsfield-H5KS, UK) with a load capacity of 1 KN according to the ASTM D638 (ASTM, 2005a). The cross-head speed was set at 50 mm/minute. The specimens were placed vertically in the grips of the testing machine. Data was processed with computerized Instron software.

To determine the impact strength of samples, five replications of notched and un-notched rectangular-shaped samples were conducted on a Pendulum Impact Tester (model H3018, Germany) according to the ASTM D256 (ASTM, 2005b). Hammer energy was two Jules and hammer angle in the impact time was 160 degree.

Flexural tests were carried out according to the ASTM D790 (ASTM, 2005c). Three point bending tests of rectangular-shaped specimens were performed at room temperature using an Instron Universal Testing Machine (model 6025, UK).

Statistical Analysis

Data were analyzed by one-way analysis of variance (ANOVA) based on a completely randomized factorial design through SAS 9.2 software and graphs were drawn by Excel software. Differences with a probability value of $p<0.01$ were considered significant.

Results and discussion

Gorjani (2004) prepared the WS/recycled PE biocomposites, at a weight ratio of 15, 30 and 40% WS. The results showed that increasing of WS to 30 percent improves the tensile and flexural properties (Gorjani and Omidvar, 2006). However, as be shown in Figure 2, the tensile strength of all biocomposites is less than pure LDPE at 95% confidence level, in this study.

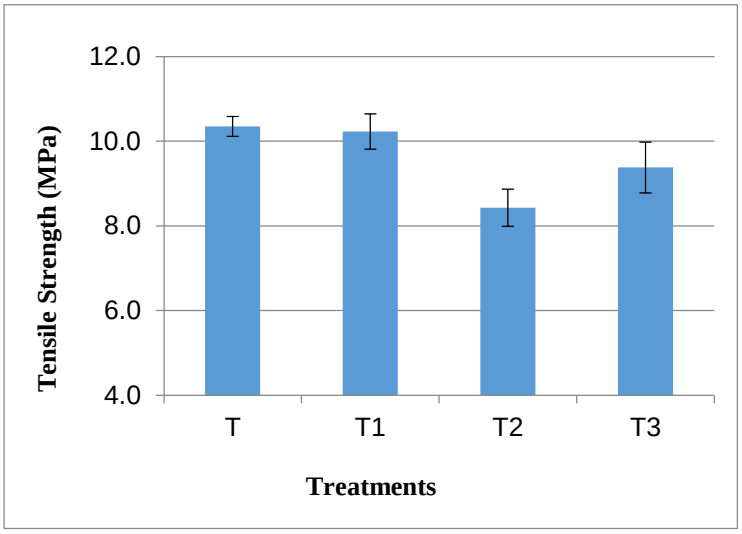

Fig 2. Tensile strength of treatments

Raw WS/LDPE biocomposite (T1) has the high tensile strength and it is very close to the TS of the pure LDPE (T). The minimum tensile strength belongs to the BWS/LDPE samples

(T2). It may be due to changes in the WS properties during the bleaching process with H_2O_2 in which some of the hemicellulose and lignin are removed. The TS of (T3) is higher than that of (T2). It can be due to removing more lignin and hemicelluloses, in which, the remaining cellulose contain active hydroxyl (OH) groups can be more reacted with MAPE. In view of decrease in the value of TS of the BWS/LDPE and the BWS pulp/LDPE biocomposites and in case if the color of the fabricated biocomposites is not considered as an important criterion, then the use of raw WS is recommended.

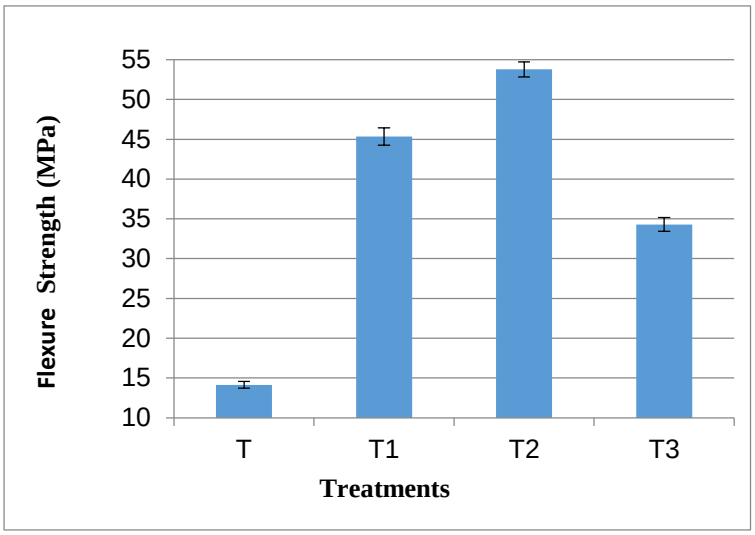

Fig 3. Flexure strength of treatments

Flexure strength of all treatments is more than control. The dispersed phase or WS is significantly multiplicative factor for flexure strength of biocomposites (Figure 3).

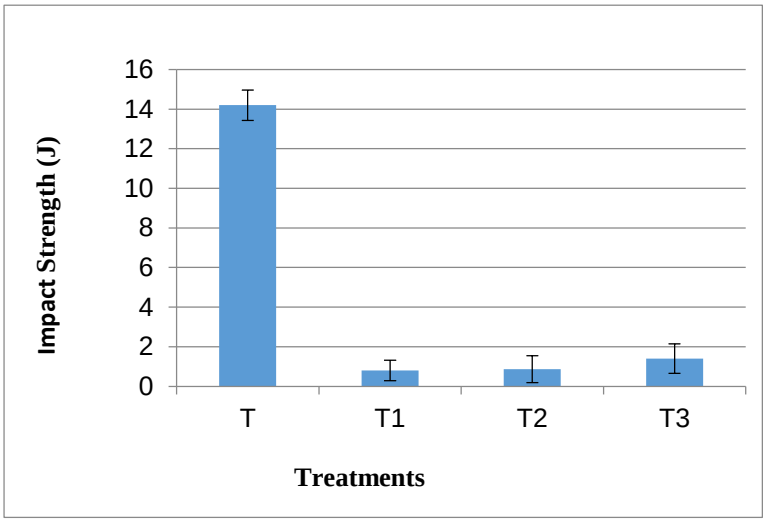

Fig 4. Impact strength of treatments

Fiber reinforcements contains particles that have a high ratio of length to diameter (L/D), and it makes the most of stresses to be transferred to the fiber phase of polymers and thus the composite resistance increases against the bending flexure (Khatibi, 2009).

The impact strength of any material presents its energy loss level. Factors affecting on the impact strength are the amount of dispersed component, type of component, its structure and mechanism of energy absorption (Tajeddin, 2013). The impact strength of all treatments is less than control and they have brittle behavior in comparison to the control (Table 4). The biocomposite of BWS pulp and PE (T3) has the highest impact strength and the lowest impact strength belongs to the raw WS/PE biocomposites (T1). It may be because of changes in the WS properties during the bleaching process with H_2O_2 in which some of the hemicellulose and lignin are removed.

Conclusions

The use of biocomposites consisting of seasonal or annual plants such as wheat straw (WS) and synthetic polymers like polyethylene (PE) has gained tremendous popularity in recent years, but due to lack of in depth research its application in the packaging industry is not substantial. However, due to prevalence of color of raw WS which manifests itself in the WS/LDPE biocomposite, it has not gained acceptance accordingly in the market place. Thus, in order to enhance the marketability of any new WS/PE composites, associated challenges should be overcome. Therefore, present investigation was dedicated to fabrication of a WS/PE composite which benefits from market acceptance. In this study, firstly raw WS and the pulp of WS were treated with xylanase enzyme, hydrogen peroxide and sodium dithionite as bleaching agents. The agents consisted of three levels of xylanase (5, 10 and 20 units per gram of WS pulp), five concentrations of hydrogen peroxide (1, 2, 3, 4, and 5%), and five levels (1, 2, 3, 4, and 5%) of sodium dithionite. Brightness indicator (L) as the most important index from **L*a*b* coordinates** of colorimetric test was then evaluated for the various bleaches and unbleached raw WS and WS pulp treatments. The best result in terms of brightness was determined namely bleached raw WS with 4% H_2O_2 and bleaching of WS pulp with 10 unit xylanase and by addition of 1% H_2O_2. Next step was to blend the above mentioned treatments with PE in order to fabricate the WS/PE composites and finally the mechanical properties of fabricated biocomposites were analysed by applying one-way analysis of variance (ANOVA) based on a completely randomized factorial design. Results showed that the overall tensile strength of biocomposites is less than pure PE. Among treatments, raw WS/PE and BWS/PE composites had the highest and the lowest tensile strength, respectively. It needs to be mentioned that Flexural strength of all samples was higher than control. All treatments had lower impact strength as compared to the control. WS pulp/PE and raw WS/PE biocomposites had the highest and the lowest impact strength respectively. In view of decrease in the value of tensile strength of the bleached WS/PE and the bleached WS pulp biocomposites and in case if the color of the fabricated biocomposites is not considered as an important criterion, then the use of raw WS is recommended.

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