

## Thermoplastic Composites from Natural Reed Fibers

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UNTREATED and benzylated reed fibers were used as reinforcing filler in thermoplastic composite. They were used to fill polypropylene, high density poly ethylene, low density poly ethylene, and polystyrene.

Benzylated reed was characterized by TGA to predict the appropriate temperature for pressing and the resulting composites were characterized mechanically and physically. Benzylated reed filled polypropylene, high density poly ethylene, low density poly ethylene, and polystyrene showed enhanced flexural modulus specially when filled polystyrene. Benzylation increases flexural modulus compared to untreated fibers. Among the thermoplastic polymers under investigation, polystyrene composite reinforced with benzylated reed showed the best MOR due to the similarity and compatibility between the phenyl-structure present in both benzylated reed fibers and polystyrene which makes them thermodynamically compatible with each other. This is also seen from SEM figures. Tensile strength of the benzylated reed composite improved to great extent. Also, the increase in tensile strength of the composites under investigation is confirmed by SEM images.

**Keywords:** Natural reed fibers, Thermoplastic composites, Benzylation of fibers, Environment friendly composites, Physical & chemical properties and Thermogravimetric analysis.

Lignocelluloses are favored new generation of reinforcing materials in thermoplastic composites. Among other things, lignocelluloses make the composite more environment friendly.

Reed fibers are important lignocellulosic raw material. Several research articles succeeded in introducing reed fibers for production of various types of paper and viscose pulps<sup>(1-5)</sup>.

The present work aims at preparing reed-based thermoplastic composite. Untreated and benzylated reed fibers were used individually to fill polypropylene (PP), polystyrene (PS), high density poly ethylene (HDPE), and low density poly ethylene (LDPE), two different filler contents namely 30% and 40% will be used. The obtained thermoplastic composites will be characterized through mechanical and physical properties as well as thermogravimetry and scanning electron microscopy.

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Lignocellulose fibers, due to the strong cellulose backbone structure, possess good strength properties compared to other reinforcing materials such as glass and minerals. However, the highly hydrophobic nature of certain thermoplastics, such as polyolefins, causes compatibility problems with the hydrophilic reinforcing materials such as lignocellulose. This is because compatibility is related to the interaction between the components. Therefore improvement of the interface and interphase interaction in polyolefin/lignocellulosic composites is essential. There are various methods for promoting interfacial adhesion in systems where lignocellulosic materials are used as fillers, such as esterification<sup>(6-9)</sup>, silane treatment<sup>(10)</sup>, graftcopolymerization<sup>(11)</sup> and use of compatibilisers<sup>(12, 13)</sup>. Coating of wood filler with thermoset resin has also been proved to enhance the mechanical properties of wood/polyolefins composites<sup>(14)</sup>. Also, these modifications may be extended to plasma treatment<sup>(15)</sup> and treatment with other chemicals<sup>(16)</sup>. Reaction with various monomers such as acetic anhydride, stearic acid<sup>(17)</sup>, maleic anhydride and silane and isocyanate is also used<sup>(18)</sup>.

These methods are usually based on the use of reagents which contain functional groups that are capable of reacting to form chemical bonds with hydroxyl groups of the lignocellulose material; while maintaining good compatibility with the matrix. Interfacial compatibilisation improves the stress transfer between the two components and leads to improvement of mechanical and physical properties of the produced product. On the other hand, the use of surface treatments has the disadvantages of increasing the cost of the final product. Thermoplasticization of plant fibers with adequate modifiers and modification rates has been proved to facilitate blending and improve compatibility of the wood material with plastics<sup>(19)</sup>.

In this work, chemical modification of reed fibers is carried out through etherification, namely benzylation. Benzylation of cellulose is typical Williamson synthesis which involves nucleophilic substitution of an alkoxide ion or a phenoxide ion for a halide ion.

## Experimental

### *Materials and methods*

Reed was collected and cut into small pieces and then dried to reduce moisture content to about 4–6%. The pieces were ground and screened through a mesh of 0.2 mm to remove larger particle size. Chemical composition of reed was analyzed to be 47.95% cellulose, 24.85% lignin, 22.3% pentosan, 2.9% ash, and 2.0% silica.

### *Plastics*

Four kinds of the most commonly used plastics were selected namely polypropylene (PP, M.P 190°C), high density polyethylene (HDPE, M.P 170°C), low density polyethylene (LDPE, M.P 160°C), and polystyrene (PS, M.P 185°C). They were delivered from Alcludia Company, Spain.

#### *Preparation of benzylated reed*

The screened reed was dried overnight under vacuum at 60°C before use. After being mixed with 40% NaOH solution for 0.5 hr, the mixture was transferred into three necked flask, benzyl chloride was added and the temperature was adjust to 110°C. The flask was connected with a condenser and stirrer; placed into oil bath for 6 hr with stirring. Products of benzylation after filtration were purified by washing with distilled water to remove salts and with ethanol to remove unreacted benzyl chloride as well as any byproduct and finally dried under vacuum at 60°C overnight.

#### *Preparation of thermoplastic composites*

The thermoplastic polymers were melted firstly in Electronic Plasticorder at temperatures of 190, 170, 170, and 185°C for PP, HDPE, LDPE, and PS, respectively. Untreated and benzylated reed were added in two different proportions (30 and 40%) to the melted polymer at the above mentioned temperatures. The time of the mixing process was about 8 min. The mixture was granulated and pressed at 3 N/mm<sup>2</sup> (pressure) and 10 min (time of pressing). The pressing was carried out at the same melting temperatures.

### **Results and Discussion**

In order to prepare benzylated cellulose, various conditions in the treatment of reed fibers were applied. Among these conditions are the high concentration of NaOH (40%) accompanied by time (6hr) and temperature (110°C) of reaction. Such variation will result in differences in the degree of polymerization, degree of order, the proportion of smaller molecules, and substitution of the benzyl groups with their heterogeneous distribution throughout the cellulose chain; such differences will be reflected on the thermal behavior of the final product.

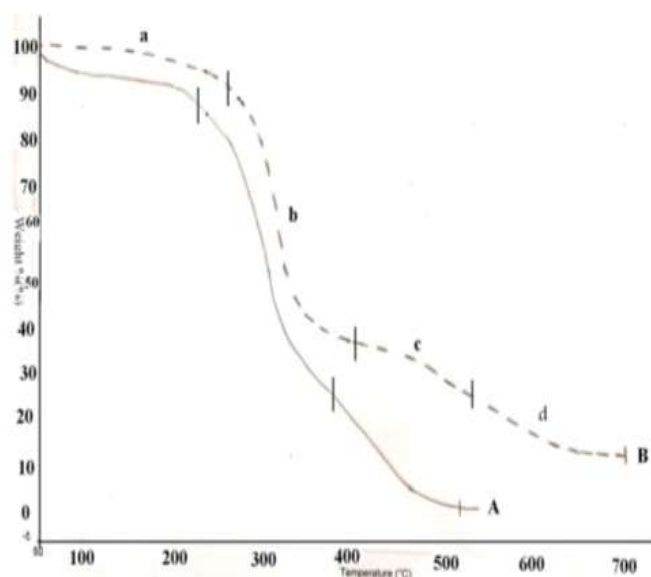
Benylation of lignocelluloses has led to a mass gain of 81 %. Characterization of the benzylated reed was carried out through TGA,

#### *Thermogravimetric analysis of benzylated reed (TGA)*

The TGA curves of untreated and benzylated lignocelluloses (A, B) are illustrated respectively in Fig. 1. The degradation of the untreated sample proceeds, via three stages denoted as a, b and c. while the degradation of benzylated sample appears to proceed through four stages a, b, c and d.

In order to account for the effect of substitution on the thermal stability of the benzylated reed the starting temperature and the corresponding weight loss of the main degradation stages (b, c and d) are clear from Fig 1. The onset temperatures of the weight loss stage b were 205 and 225°C for untreated and benzylated lignocellulose, respectively. On the other hand, the onset degradation temperatures of stage c were 390, and 405°C for untreated and benzylated sample, respectively. The onset degradation temperatures of stage d were 500°C for benzylated sample. It is clear that the substitution of benzyl groups, results in

a sample of higher thermal stability. This may be due to the incorporation of benzyl groups in the reed raw material which increases its resistance toward thermal degradation <sup>(20)</sup>. Furthermore, ash formation stage for untreated reed is achieved at 500°C with weight residue 7%, while ash formation of benzylated reed is at 700°C with weight residue 17.3%. The fourth stage of degradation of benzylated reed may be ascribed to splitting of the molecules into smaller ones accompanied by their recombination at higher temperature.



**Fig. 1.** TGA curves of untreated A (—), and benzylated reed fibers B (-----).

### *Mechanical properties*

#### *Flexural strength and modulus*

Figure 2 (A, B) shows the flexural strength and moduli for untreated and benzylated reed fibers filled PP, PS, HDPE and LDPE with 30 and 40% fiber content, respectively. When combining untreated reed fibers with all the polymers, the flexural strength is reduced if compared with that of pure polymers, due to the differences in polarity between the lignocellulosic materials (polar) and thermoplastic matrix (non polar). In reed, cellulose and hemicelluloses are hydrophilic while most of the thermoplastics (polyolefins) are hydrophobic. This leads to the presence of voids or porosity, and to weak fiber-matrix interfaces and poor overall mechanical properties. Significant improvement in the flexural strength of the benzylated reed thermoplastic composites is obtained; where benzylation improved the compatibility between cellulose and thermoplastic matrices, and improved fiber-matrix adhesion. Also, this compatibility is clear in the SEM figures. Benzylated reed filled polystyrene showed the best flexural strength due to the similarity between the phenyl-structure present in both benzylated reed fibers and polystyrene, which makes

them thermodynamically compatible <sup>(21)</sup>. However, the flexural strength of the benzylated reed thermoplastic composite is greater than that of the pure polymer. Improvement in the flexural strength was expected due to increasing the fiber content from 30 to 40 %, *i. e.* increasing the adhesion and compatibility between the fibers and matrices. Unfortunately a slight deterioration in the flexural strength of 40 % reed content of the benzylated reed thermoplastic composite was observed.

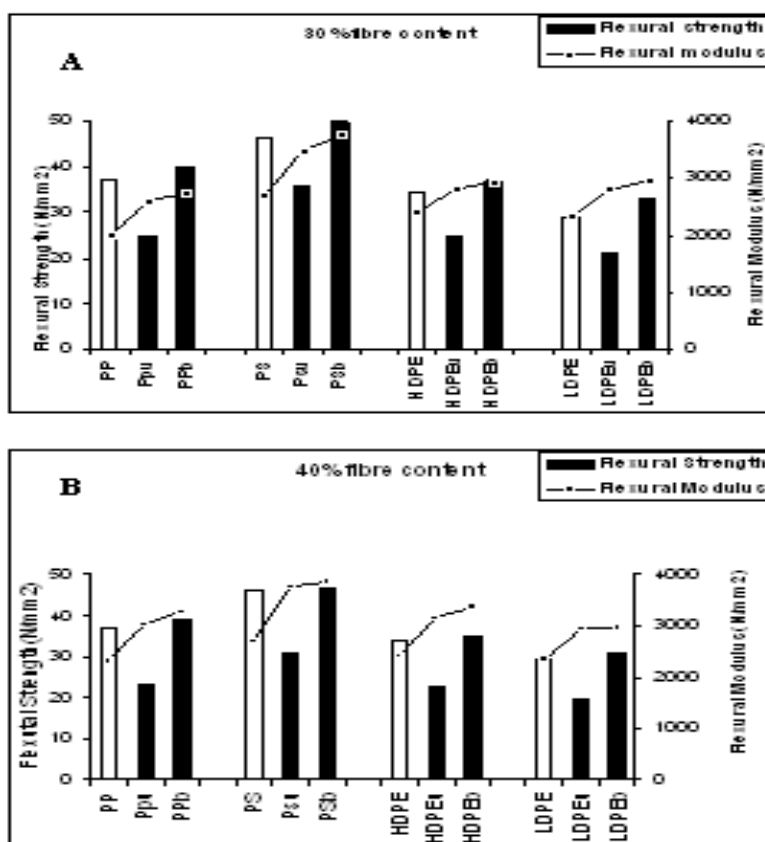


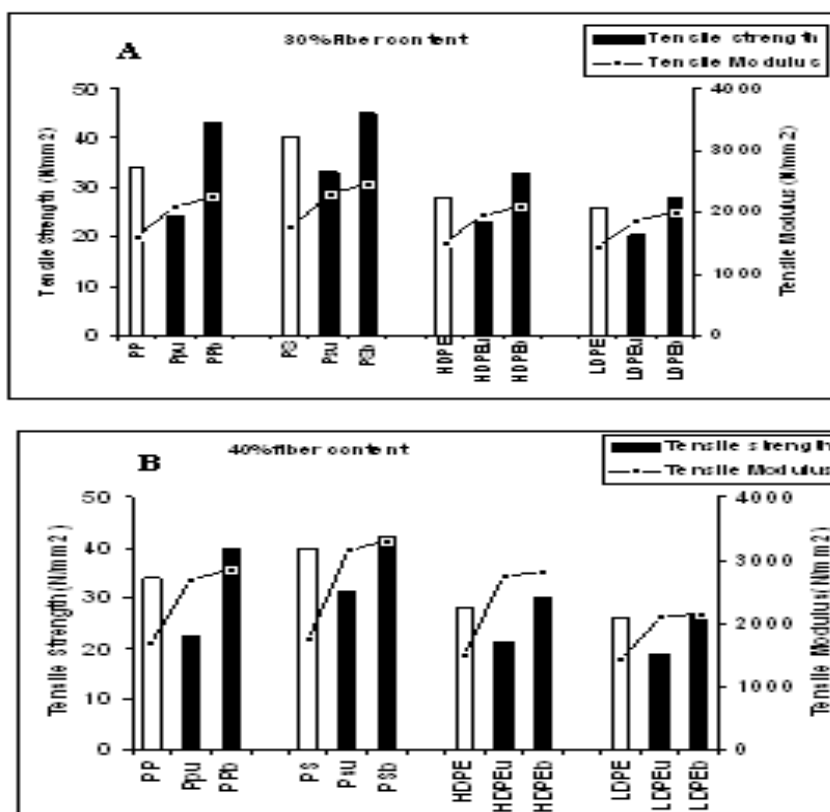
Fig. 2. Flexural strength and modulus of untreated and benzylated reed fibers filled PP, PS, HDPE and LDPE with 30 % (A) and 40% (B) fiber content.

This slight deterioration may be due to the decrease in the thermoplastic polymer ratio which is responsible, to great extent, for the improved mechanical properties and predominance of the nature of the benzylated fibers over the adhesion and the compatibility between benzylated reed and the thermoplastic polymers. A significant increase in the flexural modulus due to filling untreated and benzylated reed in all the polymers for both cases (30, 40% fiber content). This increase may be ascribed to the random orientation of the short untreated

and benzylated fibers used. This increase is due to mainly the presence of the fibers whether untreated or benzylated.

#### *Tensile strength and modulus*

Tensile strength and tensile modulus of pure polymer composite, untreated and benzylated reed thermoplastic composite filled PP, PS, HDPE and LDPE with 30 and 40% fiber content are shown in Fig. 3 (A and B) respectively. The same trend for the tensile strength and modulus measurements is observed as those of the flexural strength and modulus. Untreated reed thermoplastic composite filled PP, PS, HDPE and LDPE possess lower tensile strength compared to the pure polymer composite.



**Fig. 3.** Tensile strength and modulus of untreated and benzylated reed fibers filled PP, PS, HDPE and LDPE with 30 % (A) and 40% (B) fiber content.

The decrease is ascribed to the incompatibility between the hydrophobic thermoplastic polymers and the hydrophilic reed fibers. This chemical incompatibility results in low interfacial adhesion between the thermoplastic layer and the fiber. The high crystallinity and high molecular mass of cellulose are likely to contribute to the weak chemical interaction between the two phases<sup>(22)</sup>. Tensile strength is extremely dependent property on interfacial adhesion between

*Egypt. J. Chem.* **58**, No. 3 (2015)

the phases. If the adhesion is not perfect a gap will come up and the material will break in the interfacial region. The lack of adhesion makes this region weaker<sup>(23, 24)</sup>. Tensile strength of the benzylated reed thermoplastic composite is improved to great extent. This improvement of tensile strength is based on the previously mentioned reasons resulting from benzylation of reed fibers. The tensile modulus increases significantly with the filler concentration increasing (Fig. 3). It is assumed that reed fibers are stiffer than pure polymers resulting in a higher tensile modulus of the composite. Benzylation has no sizable effect on the tensile modulus when compared to untreated fiber.

#### Water absorption

Water absorption (WA) of lignocellulosic fiber composite is an important characteristic that determined the end use applications of these materials. Figure 4 shows the water absorption of untreated and benzylated reed filled PP, PS, HDPE and LDPE at 2hr and 24hr (A, and B) respectively. It is obvious from the figure that WA of benzylated fiber is reduced significantly compared to untreated reed fiber in all composites that is because benzylation of reed fiber reduces the hydroxyl groups in the cell wall of reed fiber molecules, thus reducing the water absorption of reed fiber reinforced composites, but still higher than the pure polymer composites.

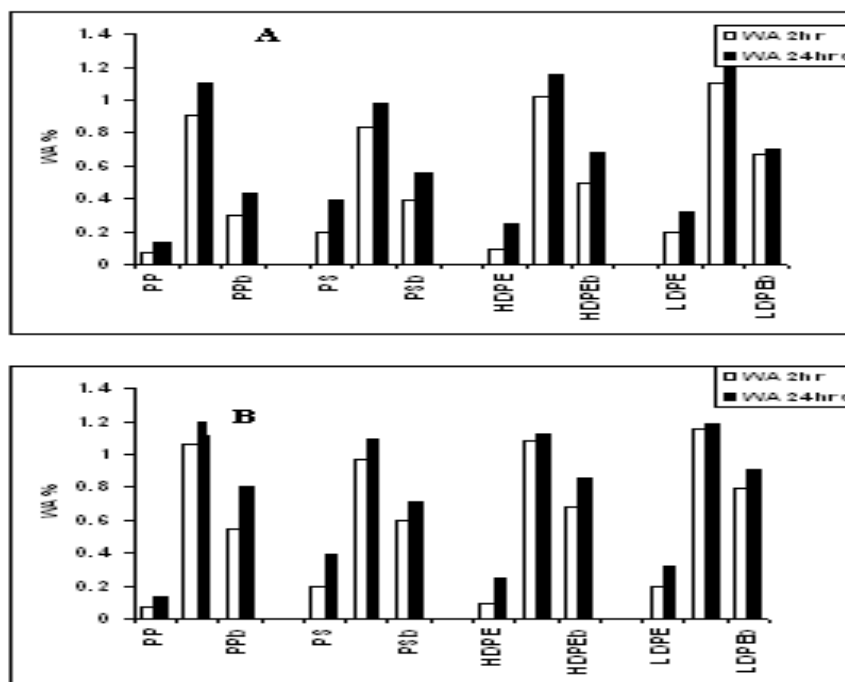


Fig. 4. Water absorption of untreated and benzylated reed fibers filled PP, PS, HDPE and LDPE with 30 % (A) and 40% (B) fiber content.

*SEM photographs of fracture surface of thermoplastic polymer composite*

Figure 5 A, C, E, and G showed fracture surface of 30% untreated fibers filled PP, PS, HDPE, and LDPE, respectively. The images show poor interaction between the fibers and the matrices with debonding phenomena of the fiber. In this case the fiber surface is free of plastic particles, and a relatively strong fiber pull-out is observed. Both findings indicate that there is a poor adhesion between the two phases. Figure 5 B, D, F, and H of fracture surface of 30% benzylated reed filled PP, PS HDPE, and LDPE, respectively, showed that the surface is embedded with the plastic particles. This indicates that a stronger adhesion exists between fibers and the matrices; this stronger adhesion leads to improvement in the mechanical properties of the composite made from benzylated fiber with the thermoplastic polymer.

*TGA of untreated and benzylated reed-ps thermoplastic composites*

Thermogravimetric curves of untreated and benzylated reed-PS composites containing 30% fiber are shown in Fig. 6. The temperature range used for the analysis is 50–650°C. It is found that in the case of benzylated reed-PS composites, the extent of degradation, *i.e.* percent weight loss at a given temperature is less than that of untreated reed-PS composite.

The degradation temperature is shifted to a slightly higher region in the case of benzylated reed-PS composites than that of untreated composite. This is due to the improved fiber/matrix adhesion during benzylation. This adhesion is confirmed by SEM images as referred above.

**Conclusion**

Lignocelluloses are favored new generation fillers since they make the composite –among other things- more environment friendly. In the present work, untreated and benzylated reed fibers were used as reinforcing filler in thermoplastic composite. The proportion of untreated and benzylated reed were 30% and 40%. Benzylation increases flexural modulus compared to untreated fibers. Among the thermoplastic polymers, polystyrene composite reinforced with benzylated reed showed the best MOR due to the similarity between the phenyl-structure present in both benzylated reed fibers and polystyrene, which makes them thermodynamically compatible with each other. This is also seen from SEM figure. Tensile strength of the benzylated reed composite improved to great extent.



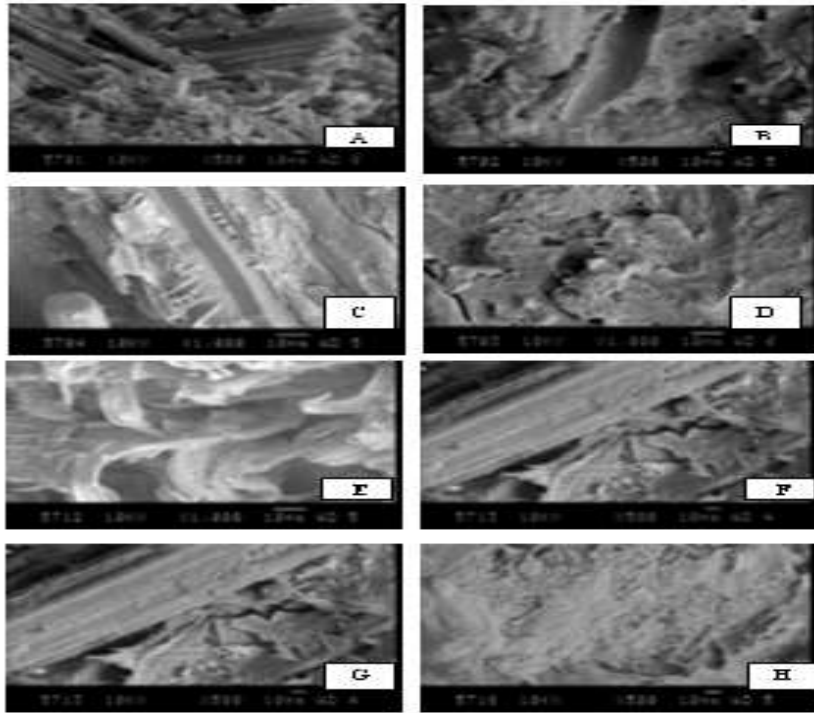


Fig. 5. SEM photographs of fracture surface of untreated reed filled PP (A), PS (C), HDPE (E), and LDPE (G), and benzylated reed filled PP (B), PS (D), HDPE (F), and LDPE (H).

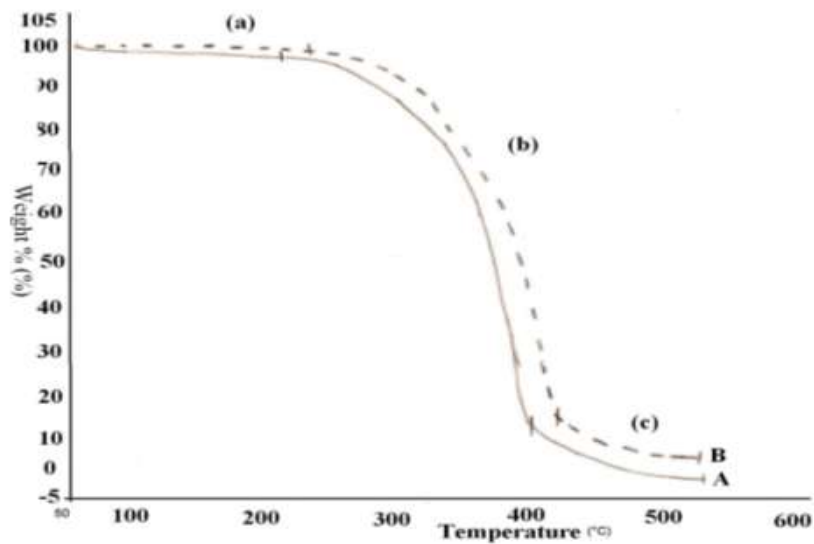


Fig. 6. TGA curves of untreated and benzylated reed-PS composite A (—), B (-----) respectively.

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(Received 14/12/2014 ;  
accepted 2 / 2 / 2015 )

### متراكبات اللدائن الحرارية من الياف نبات الغاب الطبيعية

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مصر .

في هذا البحث تم استخدام الياف نبات الغاب الغير معالج وكذلك المعالج بالبنزلة كمادة مألثة لللدائن الحرارية وكما تم استخدامه فى ملء البولي بروبيلين، بولي إيثيلين عالي ومنخفض الكثافة، وكذلك البولي ستيرين. وقد تم عمل توصيف لالياف الغاب المعالج بالبنزلة باستخدام التحليل الحرارى لاستنباط درجة الحرارة اللازمة لكبس المتراكبات. كما تم توصيف المتراكبات المحضرة بواسطة قياس الخواص الميكانيكية مثل قوة الشد والخواص الفيزيائية مثل قياس تشرب الماء ووجد ان عملية المعالجة بالبنزلة تزيد من الخواص الميكانيكية بالمقارنة بالالياف الغير معالجة. ومن بين البوليمرات المستخدمة وجد ان المتراكبات الناتجة بملء الالياف المعالجة للبولي ستيرين تعطى اعلى خواص ميكانيكية وذلك للتشابه بين تركيب الفئيل الموجود فى كل منهما والذي يجعلهما متوافقين بشكل ديناميكي حراري مع بعضها البعض وهذا واضح فى الأشكال الناتجة من الميكروسكوب الاليكترونى. وقد تم تحسين الخواص الميكانيكية الى حد كبير.