
คุณสมบัติทางกายภาพของเทอร์โมพลาสติกสตาarch จากแป้งข้าวเหนียวเสริมแรงด้วยเส้นใยเซลลูโลส
จากกระดาษหนังสือพิมพ์รีไซเคิล

Physical Properties of Thermoplastic Glutinous Rice Starch Reinforced with
Recycled Newspaper Cellulose Fibers

ศุภาวุธ ภาชนะ^{1,2*}, อำนวย วัฒนกรศิริ³ และสุปราณี แก้วภิรมย์¹

¹ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยบูรพา

²ศูนย์ความเป็นเลิศด้านอนามัยสิ่งแวดล้อม พิษวิทยาและการบริหารจัดการสารเคมี

³ภาควิชาเกษตรและสิ่งแวดล้อม คณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยราชภัฏสุรินทร์

Katavut Pachana^{1,2*}, Amnuay Wattanakornsiri³, and Supranee Kaewpirom¹

¹Department of Chemistry, Faculty of Science, Burapha University.

²Center of Excellence on Environmental Health, Toxicology and Management of Chemicals.

³Department of Agriculture and Environment, Faculty of Science and Technology, Surindra Rajabhat University.

บทคัดย่อ

ไบโอคอมโพสิตเป็นวัสดุที่เป็นมิตรต่อสิ่งแวดล้อม เนื่องด้วยผลิตจากทรัพยากรหมุนเวียนและสามารถย่อยสลายได้โดยธรรมชาติ งานวิจัยนี้ผู้วิจัยสกัดเส้นใยเซลลูโลสจากกระดาษหนังสือพิมพ์รีไซเคิล เพื่อใช้เสริมแรงในเทอร์โมพลาสติกสตาarch เพื่อที่จะปรับปรุงคุณสมบัติทางกลและการต้านทานความร้อนของเทอร์โมพลาสติกสตาarch ไบโอคอมโพสิตถูกเตรียมจากแป้งข้าวเหนียวโดยใช้กลีเซอรอลเป็นพลาสติกไซเซอร์ในปริมาณ 30% โดยน้ำหนักของกลีเซอรอลต่อแป้ง เรียกว่าเมตริกซ์ ซึ่งจะถูกเสริมแรงด้วยเส้นใยเซลลูโลสปริมาณ 0 ถึง 8% โดยน้ำหนักของเส้นใยเซลลูโลสต่อเมตริกซ์ คุณสมบัติเชิงกลของไบโอคอมโพสิตถูกศึกษาโดยการทดสอบแรงดึงทางกล และคุณสมบัติทางกายภาพถูกศึกษาโดยเครื่องวิเคราะห์ทางความร้อนโดยดิฟเฟอเรนเชียลสแกนนิ่งแคลอริเมทรีและเทอร์โมแกราวิเมทริก และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด ผลการศึกษาแสดงให้เห็นว่าปริมาณเส้นใยเซลลูโลสเพิ่มขึ้นจะเพิ่มค่าความต้านทานแรงดึงสูงสุด (6.69 ± 0.29 MPa) และค่ามอดูลัสยืดหยุ่นสูงสุด (137.40 ± 3.84 MPa) ถึง 305% และ 546% ตามลำดับเมื่อเปรียบเทียบกับเทอร์โมพลาสติกสตาarch ที่ไม่มีการเสริมแรง ความเสถียรภาพทางความร้อนและอุณหภูมิการย่อยสลายทางความร้อนของไบโอคอมโพสิตเพิ่มขึ้นจากการเสริมแรงด้วยเส้นใยเซลลูโลส นอกจากนี้ภาพจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดแสดงถึงการติดยึดกันอย่างดีระหว่างเมตริกซ์และเส้นใยเซลลูโลส

คำสำคัญ: ไบโอคอมโพสิต คุณสมบัติทางกายภาพ กระดาษรีไซเคิล เทอร์โมพลาสติกสตาarch กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด

*Corresponding author. E-mail: biotite59@hotmail.com

Biocomposites have resulted in a renewed interest in environmentally friendly materials for biodegradable renewable resource. In this work, cellulose fibers extracted from recycled newspaper were used as reinforcement for thermoplastic starch (TPS) in order to improve its mechanical and thermal resistance properties. The biocomposites were prepared from glutinous rice starch plasticized by 30% wt/wt glycerol. The starch as matrix was reinforced by the extracted cellulose fibers with fibers content ranging from 0 to 8% wt/wt of fibers to matrix. Mechanical properties of biocomposites were measured by mechanical tensile tests, and their physical properties were studied by differential scanning calorimetry, thermogravimetric analysis and scanning electron microscopy. The results showed that higher fibers content increased the ultimate tensile strength and elastic modulus up to 305% and 546%, respectively, when compared to the non-reinforced TPS. The thermal stability and degradation temperatures of biocomposites were improved by reinforcing with the cellulose fibers. In addition, scanning electron microscopy illustrated a good adhesion between matrix and fibers.

Keywords : biocomposites, physical properties, recycled paper, thermoplastic starch, scanning electron microscopy

Introduction

There is growing interest to develop new biodegradable materials based on agricultural materials (Curvelo *et al.*, 2001; Ma *et al.*, 2005). One of the most studied and promising raw materials for producing biodegradable plastics is starch that is a naturally carbohydrate polymer, which is cheap and plentiful (Angellier *et al.*, 2006; Teixeira *et al.*, 2009). Starch is extracted from many botanical sources including corn, tapioca, rice, potato, wheat and so on, and exists in a granular structure (Prachayawarakorn *et al.*, 2010). Starch can be transformed into thermoplastic starch (TPS) through disruption of its granular structure with plasticizers under the action of high temperature and shear force (Forsell *et al.*, 1997; Hulleman *et al.*, 1998). Plasticizer molecules penetrate the starch granules and destruct the inner hydrogen bonds while increasing molecular space (Ma *et al.*, 2005; Prachayawarakorn *et al.*, 2010). Traditional plasticizers for preparing TPS are polyols such as glycerol and sorbitol, but the main plasticizer is glycerol (Ma *et al.*, 2005; Angellier *et al.*, 2006; Teixeira *et al.*, 2009) because of giving the best results in decreasing the friction between starch molecules (Janssen & Moscicki, 2006)

TPS has been prepared from various sources of starch, including corn starch (Curvelo *et al.*, 2001; Ma *et al.*, 2005), tapioca starch (Teixeira *et al.*, 2009), rice starch (Prachayawarakorn *et al.*, 2010), potato starch (Thuwall *et al.*, 2006), and wheat starch (Rodriguez-Gonzalez *et al.*, 2004). However, to our knowledge TPS prepared from glutinous rice starch has not been so far employed. Glutinous rice is a type of short-grained Asian rice that is especially sticky when cooked and contains high and low amount of amylopectin and amylose, respectively.

Generally, applications of TPS are still restricted because of poor mechanical properties, compared to most conventional plastics currently used (Averous & Boquillon, 2004; Teixeira *et al.*, 2009). One approach to increase mechanical properties is the reinforcement of

TPS with cellulose fibers. Previous researches have been carried out on cellulose fibers from different types of botanical source in association with TPS e.g. flax and ramie fibers (Wollerdorfer & Bader, 1998), potato pulp fibers (Dufresne & Vignon, 1998; Dufresne *et al.*, 2000), bleached leafwood fibers (Averous *et al.*, 2001), bleached eucalyptus pulp fibers (Curvelo *et al.*, 2001), wood pulp fibers (Carvalho *et al.*, 2002), and cassava bagasse fibers (Teixeira *et al.*, 2009). These researches have shown that tensile strength and elastic modulus increased since these naturally botanical fibers were mixed with TPS due to a good compatibility between both polysaccharides, i.e. starch and cellulose fibers (Wollerdorfer & Bader, 1998; Curvelo *et al.*, 2001; Averous & Boquillon, 2004).

The use of commercial paper pulp fibers has been recently applied to reinforce TPS (Averous & Boquillon, 2004); nevertheless, cellulose fibers extracted from used paper have never been so far employed. In this present work, we prepared TPS from glutinous rice starch by using glycerol as plasticizer and modified the TPS matrix by reinforcing with cellulose fibers extracted from newspaper fibers by a deinking-washing process. Mechanical properties of TPS/fibers composites were measured using mechanical tensile test; besides, their physical properties i.e. thermal stability and degradation, and morphologies were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and scanning electron microscopy (SEM), respectively.

Materials and methods

Materials

Regular glutinous rice starch (Bangkok Interfood, Thailand) with 98% amylopectin content and glycerol (Sigma-Aldrich) with 99.5% purity were used to prepare the TPS matrix. Starch, being dried at 60 °C for 24 h in an oven, and glycerol (30% wt/wt of glycerol to starch) were manually pre-mixed in a polyethylene bag for 15 min until a powder was obtained. Our preliminary experiments illustrated that the optimal glycerol content should be

was observed. Both the fibers and composites were sputtered with a thin layer of gold to prevent electrical charging during the observation, and then observed at the operating acceleration voltages of 2.5 kV and 15 kV, respectively.

Results and discussion

The extracted fibers were like ribbons with rough surface from optical microscopy (OM) micrograph (Fig. 1) and SEM micrograph (Fig. 2). Average fiber length was 1.8 mm and aspect ratio of length/diameter was 65, as evaluated with the aid of ImageJ software on 20 fibers samples SEM micrograph (Fig. 2).

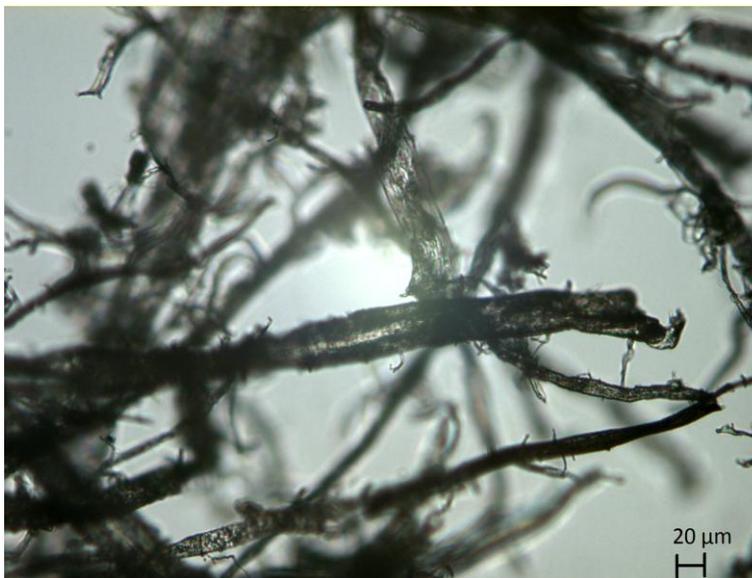


Fig. 1 OM micrograph at 500X magnification of cellulose fibers from used newspaper (scale bar: 20 μm)

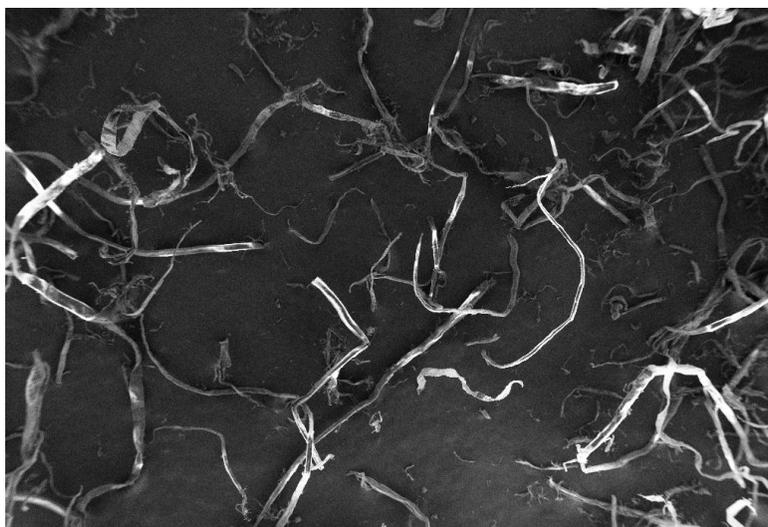


Fig. 2 SEM micrograph of cellulose fibers from used newspaper (scale bar: 100 μm)

The non-reinforced TPS and composites prepared in this work were homogenous, since an agglomeration of cellulose fibers was not visually observed. In this paper, the terms GRS-NF0, and GRS-NF2, 4, 6 and 8 are used to indicate the non-reinforced TPS, and TPS composites containing 2, 4, 6 and 8% by weight of cellulose fibers, respectively.

Mechanical properties

The progress of the mechanical properties, i.e. UTS and E , as a function of cellulose fibers content is presented in Fig. 3 for the non-reinforced TPS and composites. Both

of UTS and E of the composites rose with the increase of the fibers weight content. The addition of 8% wt/wt of fibers to matrix improved the UTS and E up to 305% and 546%, respectively, when compared to the non-reinforced TPS. The mechanical properties enhancement confirms the interfacial adhesion and the strong interaction between matrix and cellulose fibers (Martins *et al.*, 2009). This behavior probably results favored by the chemical similarities between starch and cellulose fibers (Averous & Boquillon, 2004; Ma *et al.*, 2005).

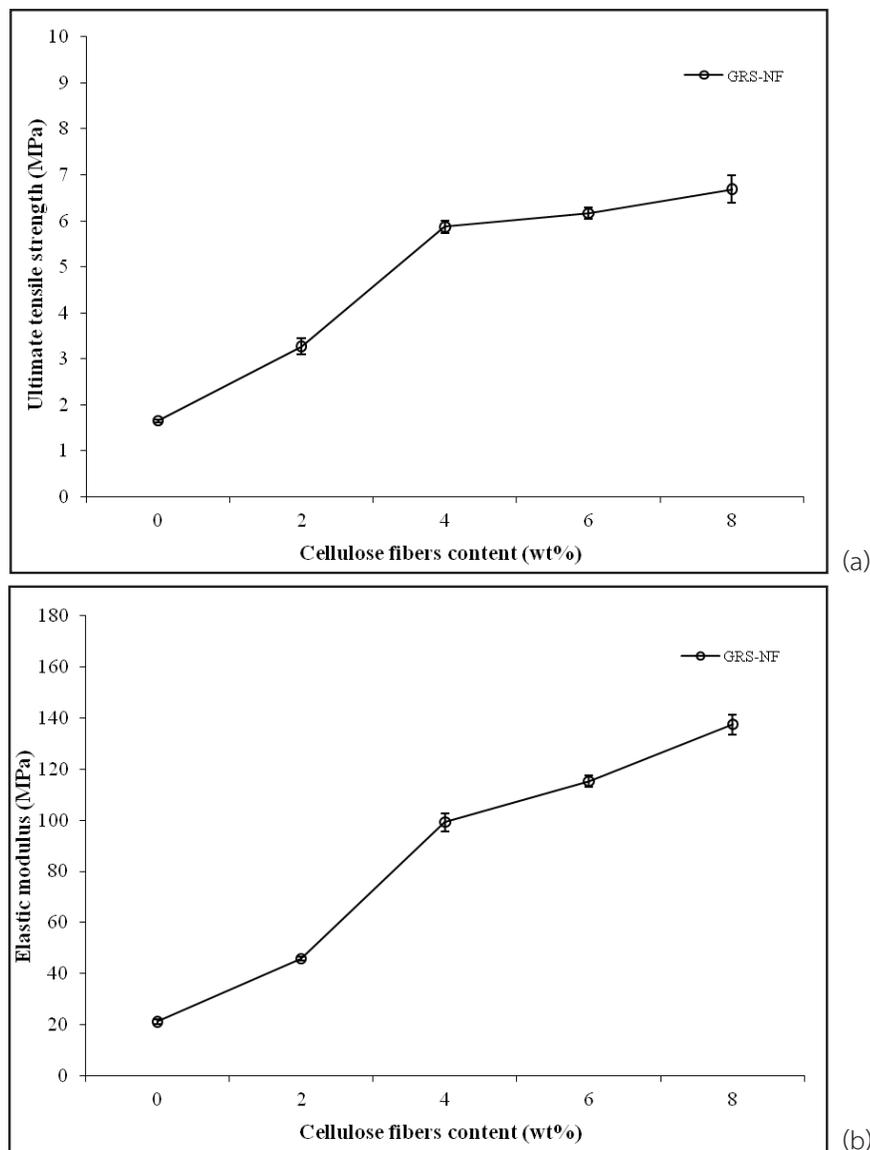


Fig. 3 Effect of cellulose fibers content on the mechanical properties, (a) ultimate tensile strength and (b) elastic modulus, of non-reinforced TPS and composites

Thermal properties

The DSC results indicated thermal transition traces of the non-reinforced TPS and composites as shown Fig. 4. Two glass transitions were detected in TPS as shown in Table 1 according to the literature data concerning starch-glycerol systems (Curvelo *et al.*, 2001; Averous & Boquillon, 2004). The two glass transitions were related to phase separation phenomena that could occur in starch-glycerol system with glycerol/starch ratio higher than 0.2 (Lourdin *et al.*, 1997).

The lower transition (T_{t1}) was clearly attributed to a starch-poor phase, referring to the glycerol glass transition, which is about -75 °C, while the higher glass transition

(T_{t2}), occurred in the range of -50 to -70 °C, was due to a starch-rich phase, attributing to the TPS glass transition (Forsell *et al.*, 1997; Ma *et al.*, 2008). The obtained data for the transition temperatures are illustrated in Table 1. With increasing fibers contents, both transition temperature values shifted to higher temperatures, as a result of the interfacial interactions between polar components of fibers and matrix with the hydrogen bond (Averous *et al.*, 2001; Averous & Boquillon, 2004). Besides, the difference of the glass transition for the non-reinforced TPS and composites is due to the interaction between fibers and plasticizer once the matrix in the composites was less plasticized than the pure matrix (Curvelo *et al.*, 2001).

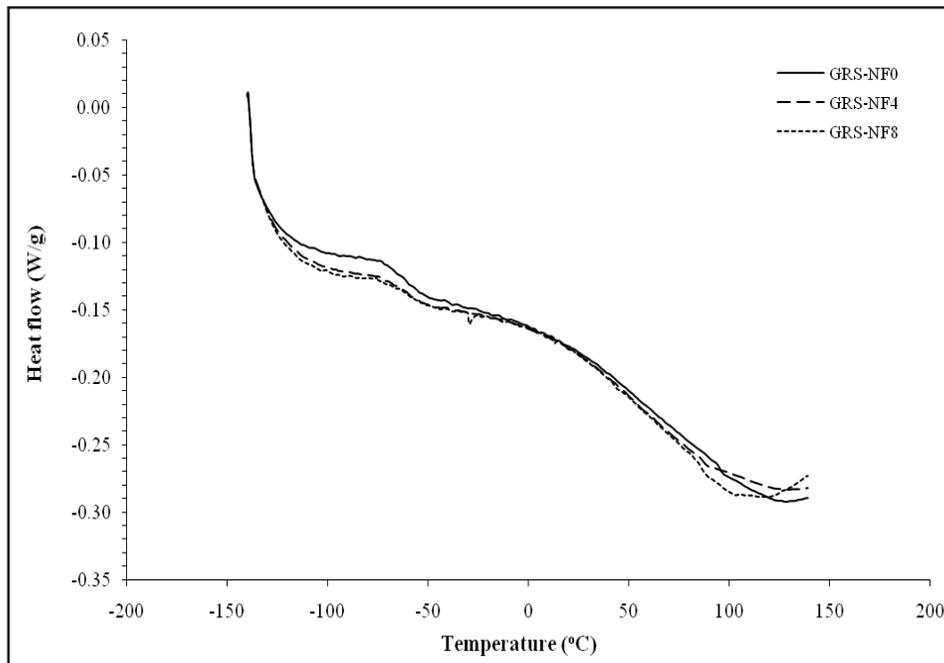


Fig. 4 DSC scans for non-reinforced TPS and composites

The TGA results are shown in Fig. 5 and Table 1 for thermal degradation of non-reinforced TPS and composites. The behavior of TGA mass loss curves was similar in the non-reinforced TPS and composites and the weight loss decreased with raising of fibers contents. The loss variations were because the composites had lower

water content, when compared to the non-reinforced TPS, at equilibrium (Averous *et al.*, 2001). In addition, crystalline cellulose fibers decreased their polar character; therefore, the addition of fibers into the matrix decreased the global water content of the composites (Averous & Boquillon, 2004; Martins *et al.*, 2009).

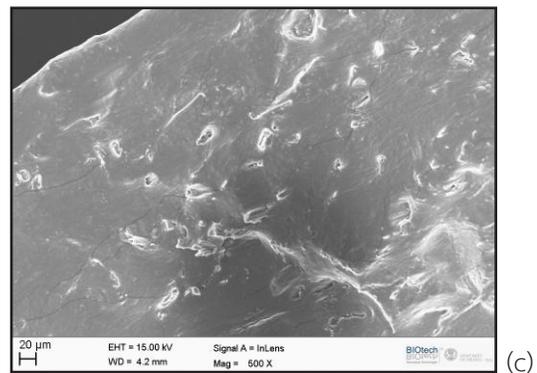
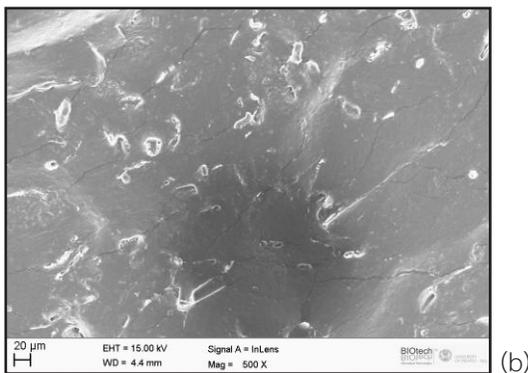
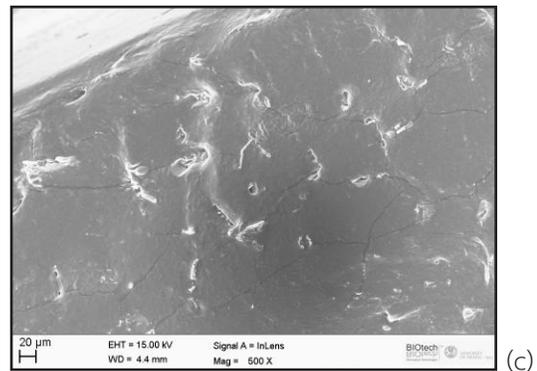
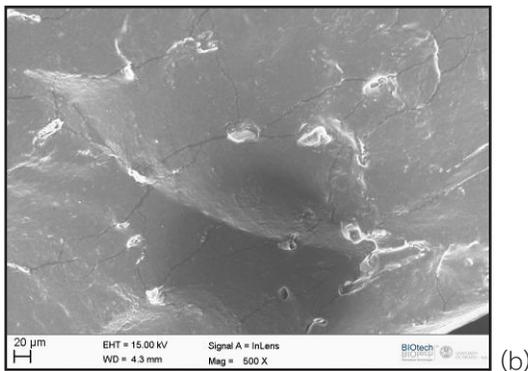
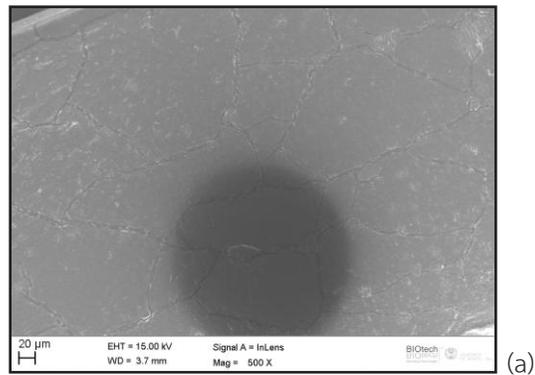


Fig. 6 SEM micrographs of fragile fractured surface of (a) non-reinforced TPS and composites filled with different fibers contents, (b) 2%, (c) 4%, (d) 6% and (e) 8% (scale bar: 20 μm)

Fibers appear to be embedded in the matrix, organized in bundles and well adhering to the matrix as illustrated in Fig. 7. These phenomena indicated to strong interaction between the fibers and matrix

(Ma *et al.*, 2005). Furthermore, the absence of fibers' pullout indicated their good interfacial adhesion (Curvelo *et al.*, 2001).

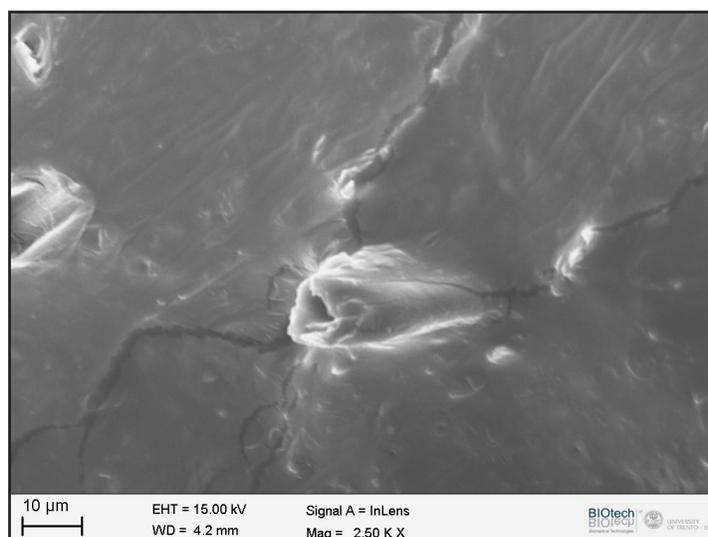


Fig. 7 SEM micrograph of fragile fractured surface of TPS reinforced with 8% wt/wt of fibers to matrix (scale bar: 10 μm)

Conclusion

Due to the poor mechanical tensile properties of TPS, the modification of the TPS was carried out using the recycled newspaper fibers. The addition of the cellulose fibers effectively improved the mechanical properties, i.e. both in UTS and E , and thermal stability. SEM micrographs showed good adhesion between TPS matrix and cellulose fibers. These biocomposites are an interesting approach to develop biodegradable plastics in order to increase the use of environmentally friendly materials in packaging.

Acknowledgements

This work was financially supported by the EU Bridging the Gap Erasmus Mundus Project, and partially supported by the Center of Excellence on Environmental Health, Toxicology and Management of Chemicals, Thailand. We acknowledge Prof. Dr. Claudio Migliaresi for supervisions, suggestions, and supports for convenient laboratories at Department of Materials Engineering and Industrial Technologies and BIOTech Research Center, University of Trento, Italy. We also express heartfelt thanks to Dr. Matteo Traina and Dr. Lorenzo Moschini for suggestions of experimental techniques.

References

- Angellier, H., Molina-Boisseau, S., Dole, P. & Dufresne, A. (2006). Thermoplastic-waxy maize starch nanocrystals nanocomposites. *Biomacromolecules*, 7, 531-539.
- Averous, L. & Boquillon, N. (2004). Biocomposites based on plasticized starch: thermal and mechanical behaviours. *Carbohydrate Polymers*, 56, 111-122.
- Averous, L., Fringant, C. & Moro, L. (2001). Plasticized starch-cellulose interactions in polysaccharide composites. *Polymer*, 42, 6571-6578.
- Carvalho, A.J.F.D., Curvelo, A.A.S. & Agnelli, J.A.M. (2002). Wood pulp reinforced thermoplastic starch composites. *International Journal of Polymeric Materials*, 51, 647-660.
- Curvelo, A.A.S., Carvalho, A.J.F.D. & Angelli, J.A.M. (2001). Thermoplastic starch-cellulosic fibers composites: preliminary results. *Carbohydrate Polymers*, 45, 183-188.
- Dufresne, A. & Vignon, M.R. (1998). Improvement of starch film performance using cellulose microfibrils. *Macromolecules*, 31, 2693-2696.

- Dufresne, A., Dupeyre, D. & Vignon, M.R. (2000). Cellulose microfibrils from potato tuber cells: processing and characterization of starch cellulose microfibril composites. *Journal of Applied Polymer Science*, 76, 2080-2092.
- Forsell, P.M., Mikkila, J.M., Moates, G.K. & Parker, R. (1997). Phase and glass transition behavior of concentrated barley starch-glycerol-water mixtures, a model for thermoplastic starch. *Carbohydrate Polymers*, 34, 275-282.
- Hulleman, S.H.D., Jansen, F.H.P. & Feli, H. (1998). The role of water during the plasticization of native starches. *Polymer*, 39, 2034-2048.
- ISO 527. (1993). *Plastics-determination of tensile properties*. Geneva: International Organization for Standardization.
- Janssen, L.P.B.M. & Moscicki, L. (2006). Thermoplastic starch as packaging material. *Acta Scientia Polonorum, Technica Agraria*, 5, 19-25.
- Lourdin, D., Bizot, H. & Colonna, P. (1997). "Anti-plasticization" in starch-glycerol films?. *Journal of Applied Polymer Science*, 14, 593-602.
- Ma, X., Chang, P.R. & Yu, J. (2008). Properties of biodegradable thermoplastic pea starch/ carboxymethyl cellulose and pea starch/ microcrystalline cellulose composites. *Carbohydrate Polymers*, 72, 369-375.
- Ma, X., Yu, J. & Kennedy, J.F. (2005). Studies on the properties of natural fibers-reinforced thermoplastic starch composites. *Carbohydrate Polymers*, 62, 19-24.
- Martins, I.M.G., Magina, S.P., Oliveira, L., Freire, C.S.R., Silvestre, A.J.D., Neto, C.P. & Gandini, A. (2009). New biocomposites based on thermoplastic starch and bacterial cellulose. *Composites Science and Technology*, 69, 2163-2168.
- Myllarinen, P., Partanen, R., Seppala, J. & Forsell, P. (2002). Effect of glycerol on behaviour of amylose and amylopectin films. *Carbohydrate Polymers*, 50, 355-361.
- Prachayawarakorn, J., Sangnitdej, P. & Boonpasith, P. (2010). Properties of thermoplastic rice starch composites reinforced by cotton fiber or low-density polyethylene. *Carbohydrate Polymers*, 81, 425-443.
- Rodriguez-Gonzalez, F.J., Ramsay, B.A. & Favis, B.D. (2010). Rheological and thermal properties of thermoplastic starch with high glycerol content. *Carbohydrate Polymers*, 58, 139-147.
- Teixeira, E.D.M., Pasquini, D., Curvelo, A.A.S., Corradini, E., Belgacem, M.N. & Dufresne, A. (2009). Cassava bagasse cellulose nanofibrils reinforced thermoplastic cassava starch. *Carbohydrate Polymers*, 78, 422-431.
- Thuwall, M., Boldizar, A. & Rigdahl, M. (2006). Extrusion processing of high amylase potato starch materials. *Carbohydrate Polymers*, 65, 441-441.
- Wollerdorfer, M. & Bader, H. (1998). Influence on natural fibers on the mechanical properties of biodegradable polymers. *Industrial Crops and Products*, 8, 105-112.