คุณสมบัติทางกายภาพของเทอร์โมพลาสติกสตาร์ชจากแป้งข้าวเหนียวเสริมแรงด้วยเส้นใยเซลลูโลสจากกระดาษหนังสือพิมพ์รีไซเคิล

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

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บทคัดย่อ

ไบโอคอมโพสิทเป็นวัสดุที่เป็นมิตรต่อสิ่งแวดล้อม เนื่องด้วยผลิตจากทรัพยากรหมุนเวียนและสามารถย่อยสลายได้โดยธรรมชาติ งานวิจัยนี้ผู้วิจัยสกัดเส้นใยเซลลูโลสจากกระดาษหนังสือพิมพ์รีไซเคิล เพื่อใช้เสริมแรงในเทอร์โมพลาสติกสตาร์ชเพื่อที่จะปรับปรุงคุณสมบัติทางกลและการต้านทานความร้อนของเทอร์โมพลาสติสตาร์ช ไบโอคอมโพสิทถูกเตรียมจากแป้งข้าวเหนียวโดยใช้กลีเซอรอลเป็นพลาสติกไซเซอร์ในปริมาณ 30% โดยน้ำหนักของกลีเซอรอลต่อแป้ง เรียกว่าเมตริกซ์ ซึ่งจะถูกเสริมแรงด้วยเส้นใยเซลลูโลสปริมาณ 0 ถึง 8% โดยน้ำหนักของเส้นใยเซลลูโลสต่อเมตริกซ์ คุณสมบัติเชิงกลของไบโอคอมโพสิทถูกศึกษาโดยการทดสอบแรงดึงทางกล และคุณสมบัติทางกายภาพถูกศึกษาโดยเครื่องวิเคราะห์ทางความร้อนโดยดิฟเฟอเรนเทียลแสกนนิ่งแคลอริเมทรีและเทอร์โมแกรวิเมทริก และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด ผลการศึกษาแสดงให้เห็นว่าปริมาณเส้นใยเซลลูโลสเพิ่มขึ้นจะเพิ่มค่าความต้านทานแรงดึงสูงสุด (6.69 ± 0.29 MPa) และค่ามอดุลัสยืดหยุ่นสูงสุด (137.40 ± 3.84 MPa) ถึง 305% และ 546% ตามลำดับเมื่อเปรียบเทียบกับเทอร์โมพลาสติกสตาร์ชที่ไม่มีการเสริมแรง ความเสถียรภาพทางความร้อนและอุณหภูมิการย่อยสลายทางความร้อนของไบโอคอมโพสิทเพิ่มขึ้นจากการเสริมแรงด้วยเส้นใยเซลลูโลส นอกจากนั้นภาพจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดแสดงถึงการติดยึดกันอย่างดีระหว่างเมตริกซ์และเส้นใยเซลลูโลส

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Abstract

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 (Forssell *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 pulpfibers 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

in the range of 20-35% without adding water; however, lower and higher glycerol content led to samples that were too brittle to be cut or to exudation phenomena of glycerol, respectively. For this reason samples used within this work contained 30% wt/wt of glycerol to starch.

Cellulose fibers were extracted from used newspaper by a deinking-washing process. The newspaper, collected from waste containers at Faculty of Engineering, University of Trento, was firstly shredded to small pieces. Shredded paper (100 g) and equal amounts of deinking chemicals, i.e. sodium hydroxide (NaOH, 6 g) and sodium silicate (Na_2SiO_3, 6 g), were mixed with distilled water until reaching 2 L and ground with a grinder with totally 5.6% consistency. They were performed at 45 °C under 800 rpm mechanical stirring for 20 min with pH of 12. Then, after washed with running tab water (about 30 L) and subsequently with distilled water (1 L) until pH reached 7 through a 16-mesh screen, the fibers pulp was dispersed in distilled water with about 1% consistency and treated by ultrasonic disruptor (Elma-S30H, Elmasonic), conditioning at 275 W power and 50/60 Hz frequency for 5 min. After washing with distilled water (2 L) followed by drying in oven at 100 °C for 24 h and a last grinding (Kika-M20, Labortechnik), the final fibers with wool character were kept in desiccators.

Biocomposites fabrication

Biocomposites were prepared from the TPS matrix and varying contents of cellulose fibers (0, 2, 4, 6, and 8% wt/wt of fibers to matrix). Firstly, the matrix and proper amounts of fibers were manually pre-mixed in a polyethylene bag for 15 min, stored in desiccators for 24 h for glycerol dispersion, and then successively melt compounded using an internal mixer Rheomix 600p (Thermo Haake) at 160 °C under 100 rpm rotor speed for 6 min. Secondly, the resulting mixtures were hot pressed by a compression molding machine (Fred S. Carver Inc.) at 160 °C to prepare 1 mm thick sheets with consecutive times-applied pressures of 10 min-no pressure, 10 min-0.74 MPa and 10 min-1.48 MPa. Lastly, they were cut into specimens for the following tests and then stored at 23-25 °C and relative humidity (RH) of 45-55% for 2 weeks. Glycerol losses were negligible because the processing temperature was operated under the glycerol boiling point (290 °C) and no exudation was observed during performance.

Mechanical tensile test

Mechanical tensile tests were carried out to measure ultimate tensile strength (UTS) and elastic modulus (*E*) according to ISO 527 standards (1993) by a tensile testing machine (Instron 4520) equipped with clamps of 100 N and operated with the crosshead speed of 5 mm/min. The tests were performed on 5 specimens dumbbell shaped with 30 mm gauge length after stored for 2 weeks at 23-25 °C and 45-55% RH.

Thermal analysis

DSC was carried out using a Mettler DSC 30 (Mettler Toledo) to determine thermal transition. Samples, cut to a square form and weighed approximately 15-20 mg, were placed in aluminum pans. The analyses were performed from -140 to 140 °C under the nitrogen flow of 100 mL/min with a heating rate of 5 °C/min. DSC data were analyzed by STARe software v.6.10; in particular, glass transition temperatures were taken from the midpoint of the changes in heat capacity (Myllarinen *et al.*, 2002).

TGA was performed using a Mettler TG 50 thermobalance (Mettler Toledo) to study thermal degradation. Samples were cut to a square form and weighed approximately 20-25 mg. The analyses were performed with a heating rate of 10 °C/min from 40-800 °C in nitrogen atmosphere with 100 mL/min flow rate.

Scanning electron microscopy and optical microscopy

Scanning electron microscope (Supra 40, Zeiss) was employed to study the morphologies of fibers and composites. In the first case, the fibers were also investigated by optical microscope (HAL 100, Zeiss) at 500X magnification. In the last case, the composites were fractured in liquid nitrogen and the fractured surface

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)

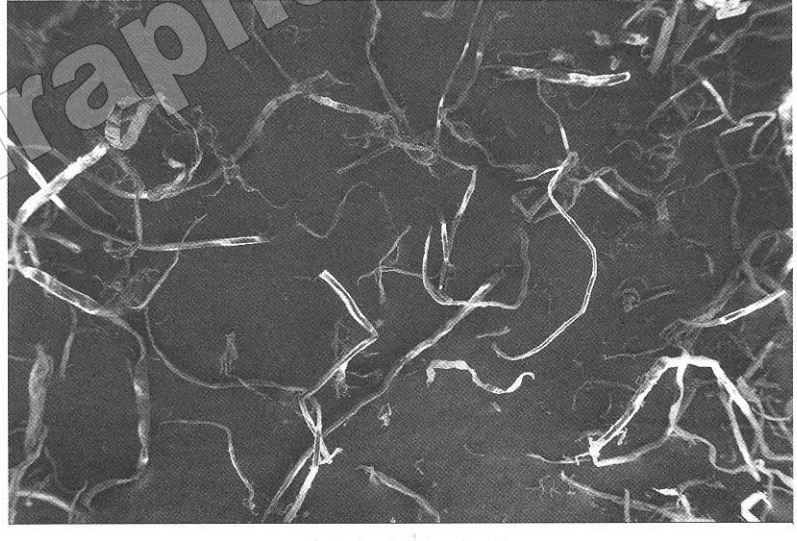

Fig. 2 SEM micrograph of cellulose fibers from used newspaper (scale bar: 100 µm)

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).

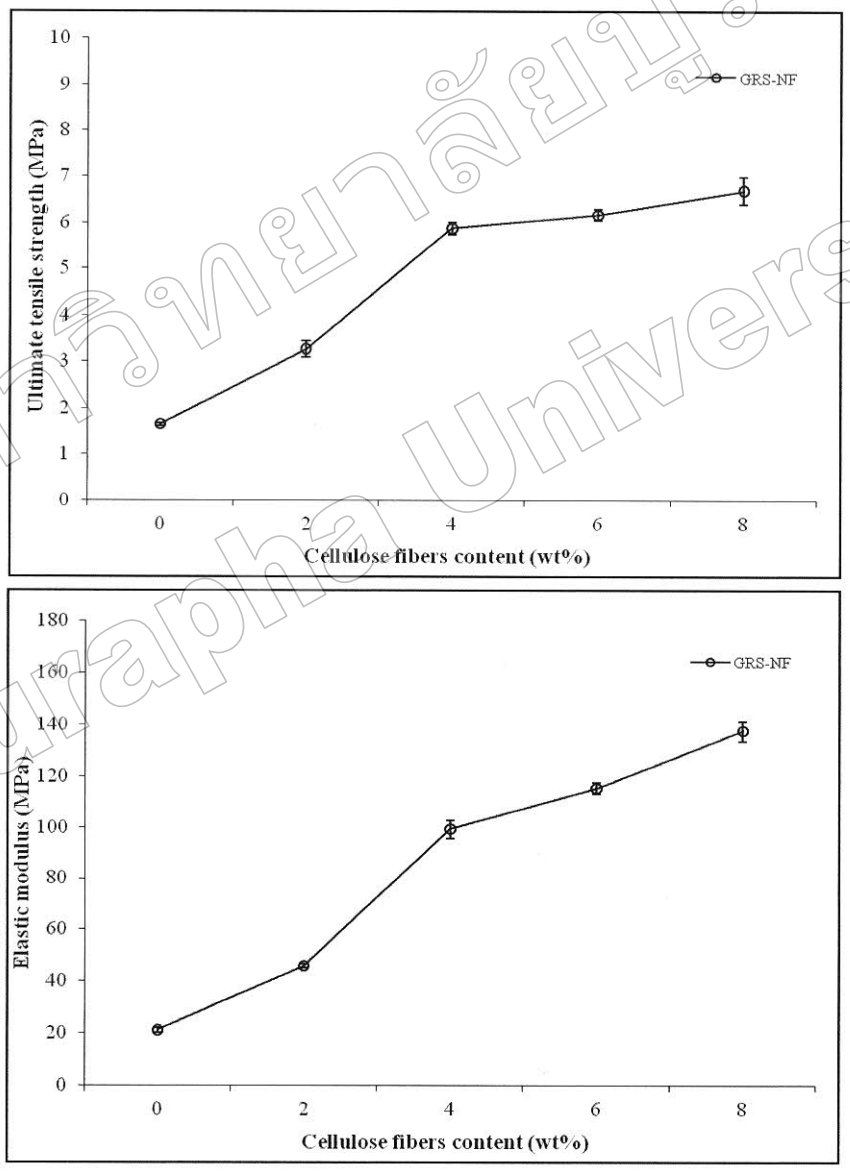

Fig. 3 Effect of cellulose fibers content on the mechanical properties, (a) ultimate tensile strength and (b) elastic modulus, of non-reinforced TPS and composites

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 (Forssell *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).

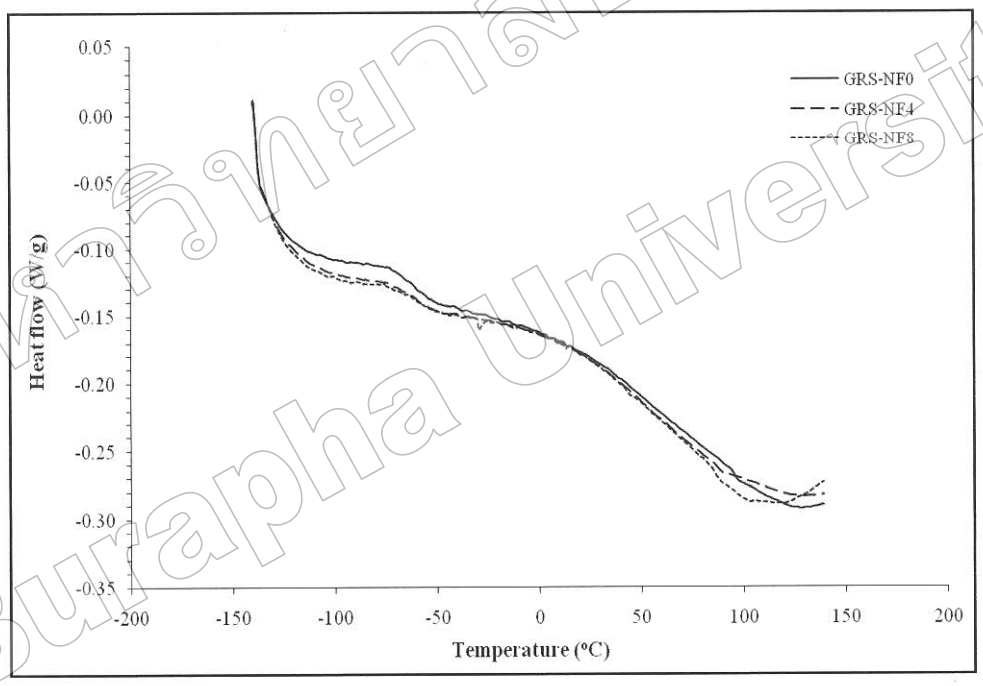

Fig. 4 DSC scans for non-reinforced TPS and composites

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).

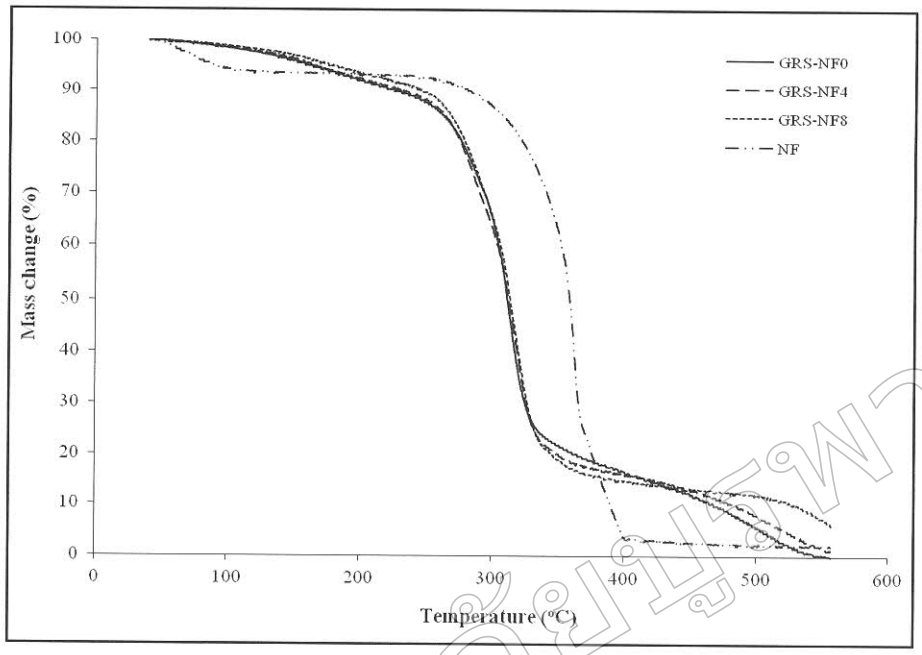

Fig. 5 TGA scans for non-reinforced TPS and composites

The composites degradation temperatures of the maximum rate, obtained from derivative thermogravimetry (DTG) peaks, gradually increased with higher fibers content as shown in Table 1. The results are ascribed by the higher thermal stability of the cellulose fibers, compared to starch, and specifically the good compatibility of both polysaccharides (Martins *et al.*, 2009). It seems that the degradation temperatures of composites were between the values of matrix and fibers with an additional effect (Averous & Boquillon, 2004). These results indicated that the addition of cellulose fibers improved the thermal resistance of non-reinforced TPS.

Table 1 DSC and TGA results

Composites	DSC		TGA	
	T_{t1} (°C)	T_{t2} (°C)	Degradation temperature (max DTG peak) (°C)	Weight loss at 320 °C (%)
GRS-NF0	-60.7	88.4	310.6	64.2
GRS-NF4	-58.4	94.3	312.2	61.0
GRS-NF8	-55.2	96.0	315.7	59.4
NF	N/A	N/A	361.3	18.6

Remark: N/A = not available

Morphologies

SEM micrographs of the fragile fractured surfaces of the non-reinforced TPS and composites are shown in Fig. 6. Fig. 6(a) shows the homogeneous matrix, processed by glutinous rice starch and glycerol, and Fig. 6(b,c,d,e) evidence the well dispersion of fibers in the matrix.

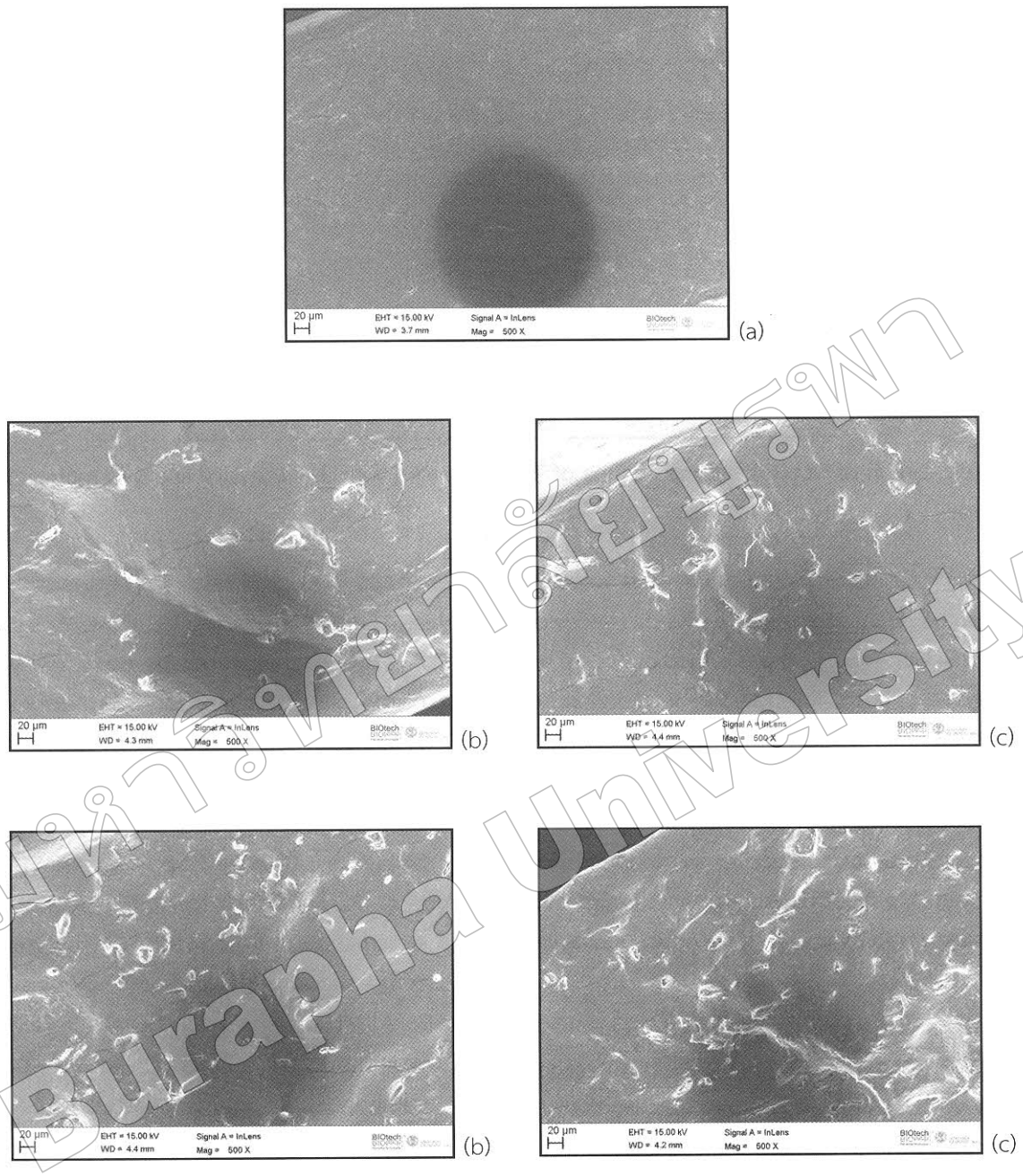

Fig. 6 SEM micrographs of fragile fractured surface of (a) non-reinforced TPS and composites filled with different fibers contents, (b) 2%, (c) 4%, (d) 6% and (e) 8% (scale bar: 20 µm)

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).

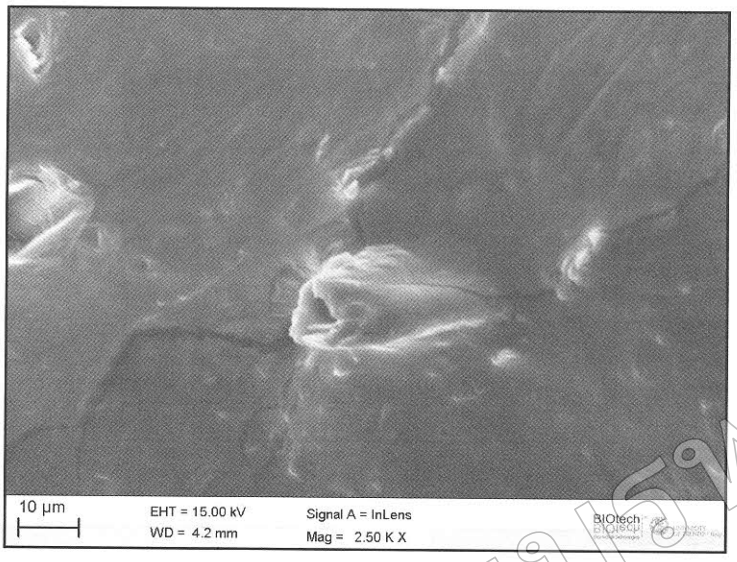

Fig. 7 SEM micrograph of fragile fractured surface of TPS reinforced with 8% wt/wt of fibers to matrix (scale bar: 10 µm)

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.

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