พลาสติกเทอร์โมเซตชีวภาพเตรียมจากน้ำมันถั่วเหลืองอะคริเลตเตต-อิพ็อกซิไดซ์ พอลิเมอร์ไรซ์ร่วมกับพอลิเมทิวเมทาคริเลตโดยแสงยูวี

Bio-Based Thermoset Plastics Prepared from Acrylated Epoxidized Soybean Oil Copolymerized with Poly (Methyl Methacrylate) by UV Radiation

นาริต้า ขุนดำริ และ วราภรณ์ ตันรัตนกุล*
ภาควิชาวิทยาศาสตร์และเทคโนโลยีวัสดุ คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์
Narita Khundamri and Varaporn Tanrattanakul*
Department of Materials Science and Technology Faculty of Science, Prince of Songkla University.

บทคัดย่อ

พอลิเมอร์ที่ได้จากแหล่งปลูกทดแทนได้เรียกว่าพลาสติกชีวภาพ โดยพลาสติกเหล่านี้อาจจะมีทั้งชนิดย่อยสลายทางชีวภาพได้และไม่ได้ การสังเคราะห์พอลิเมอร์จากปิโตรเลียมมีการสร้างก๊าซเรือนกระจกและก่อให้เกิดภาวะโลกร้อน ในทางตรงกันข้าม การผลิตพลาสติกชีวภาพมีการปล่อยก๊าซเรือนกระจกน้อยกว่า พลาสติกชีวภาพที่ได้จากน้ำมันพืชมีการศึกษามานานกว่าสิบปีแล้ว วัตถุประสงค์ของการศึกษานี้คือการเตรียมและตรวจสอบสมบัติเชิงกลของพลาสติกชีวภาพ ด้วยการสังเคราะห์พอลิเมอร์ร่วมระหว่างน้ำมันถั่วเหลืองอะคริเลตเตตอิพ็อกซิไดซ์และพอลิเมทิวเมทาคริเลตด้วยการฉายแสงยูวีเป็นเวลา 7 นาที โดยที่น้ำมันถั่วเหลืองอะคริเลตเตตอิพ็อกซิไดซ์ เมทิวเมทาคริเลตมอนอเมอร์ และ 2% ของสารริเริ่มถูกผสมให้เป็นเนื้อเดียวกันก่อนเทลงบนเบ้ากระจกเพื่อนำไปฉายแสง น้ำมันถั่วเหลืองอะคริเลตเตตอิพ็อกซิไดซ์ที่มีปริมาณอะคริเลชันเท่ากับ 52 โมล% สังเคราะห์จากน้ำมันถั่วเหลืองอิพ็อกซิไดซ์ทางการค้าที่มีปริมาณอิพ็อกซิเดชัน เท่ากับ 100 โมล% ผสมกับกรดอะคริลิค อิทธิพลของอัตราส่วนระหว่างน้ำมันถั่วเหลืองอะคริเลตเตตอิพ็อกซิไดซ์และเมทิวเมทาคริเลต (30-70% โดยน้ำหนักของเมทิวเมทาคริเลต) ต่อสมบัติความทนต่อแรงดึงถูกตรวจสอบ การเกิดเป็นพอลิเมอร์ร่วมถูกตรวจสอบด้วยเทคนิคอินฟราเรดสเปคโตรสโกปี การเกิดเป็นเทอร์โมเซตยืนยันด้วยการทดสอบการบวมในตัวทำละลาย ค่ามอดุลัสของพอลิเมอร์ร่วมชีวภาพเพิ่มขึ้นตามปริมาณเมทิวเมทาคริเลตที่เพิ่มขึ้น ความเค้น ณ จุดขาดของพอลิเมอร์ร่วมชีวภาพมีค่าสูงกว่าพลาสติกชีวภาพจากน้ำมันถั่วเหลืองอะคริเลตเตตอิพ็อกซิไดซ์ และมีค่าสูงสุดเมื่อมีปริมาณเมทิวเมทาคริเลตเท่ากับ 40% ระยะยืด ณ จุดขาดมีค่าเพิ่มขึ้นเมื่อมีปริมาณเมทิวเมทาคริเลตเท่ากับ 30-40% และจะมีค่าลดลงเมื่อมีปริมาณเมทิวเมทาคริเลตเพิ่มขึ้น ความต้านทานต่อการฉีกขาดมีแนวโน้มเช่นเดียวกัน พลาสติกชีวภาพนี้ถูกวิเคราะห์ด้วยเทคนิคสแกนนิงคาลอริเมตตรี เทคนิคกลอุณหพลศาสตร์ และเทคนิคเทอร์โมกราวิเมตตรี ผลการทดลอง พบว่าพลาสติกชีวภาพมีอุณหภูมิแทรนซิชันค่าเดียว เป็นการยืนยันการไม่เกิดโฮโมพอลิเมอร์ของพอลิเมทิวเมทาคริเลต พลาสติกร่วมชีวภาพ มีความคงทนต่อความร้อนสูงกว่าพลาสติกชีวภาพจากน้ำมันถั่วเหลืองอะคริเลตเตตอิพ็อกซิไดซ์

คำสำคัญ : อะคริเลชัน พลาสติกชีวภาพ พอลิเมทิวเมทาคริเลต น้ำมันถั่วเหลือง

***Corresponding author.** E-mail: varaporn.t@psu.ac.th

Abstract

Polymers derived from renewable resources are referred to as bioplastics. They may or may not be biodegradable. Polymerization of petroleum-based polymers produces green house gases and contributes to the problems of global warming. In contrast, the preparation of bioplastics generates lesser green house gases. Bioplastics derived from vegetable oils have been studied more than 10 years. The objective of this study was to prepare and examine the mechanical properties of the bioplastic produced by a copolymerization between acrylatedepoxidized soybean oil (AESO) and poly (methyl methacrylate) (PMMA) using ultra violet (UV) radiation for curing over a period of 7 min. AESO, MMA and a 2 wt% of a photo-initiator were well mixed and poured into a glass plate. AESO was synthesized from a commercial ESO that had been converted to a 100 mol% epoxidation, and acrylic acid. AESO consisted of 52 mol% acrylation. The effect of the AESO:MMA weight ratio (30-70 wt% MMA) on the tensile properties was investigated. The formation of a copolymer between AESO and PMMA was verified by its FTIR spectra and its thermoset characteristics were proven by the swelling test. The initial modulus (Young's modulus) of the AESO-co-PMMA bioplastic increased with an increasing MMA. The stress at break of the AESO-co-PMMA bioplastic was higher than that of the AESO bioplastic and at a 40 wt% MMA the highest value was obtained. The synergistic behavior of the strain at break was derived from the bioplastic containing 30-40 wt% MMA. The strain at break decreased significantly when the MMA content > 40 wt%. The tear resistance also showed a similar behavior. These bioplastics were characterized by using a differential scanning calorimeter (DSC), a dynamic mechanical thermal analyzer (DMTA) and a thermogravimetric analyzer (TGA). A single glass transition temperature in the bioplastics was observed from both the DSC and the DMTA. This confirmed that there was no PMMA homopolymer in the bioplastics. The AESO-co-PMMA bioplastic had higher thermal stability than the virgin AESO bioplastic based on the TGA result.

Keywords : Acrylation, Bioplastics, Poly (methyl methacrylate), Soybean oil

Introduction

Polymers derived from renewable resources are referred to as bioplastics or bio-based polymers. They may or may not be biodegradable. Polymerization of petroleum-based polymers produces green house gases contributing to the problem of global warming. In contrast, the preparation of bioplastics generates less green house gases. Vegetable oil is a promising material for synthesis of bioplastics because not only is it abundant and is from a renewable resource but it can also act as a reactive monomer. Bioplastics prepared from vegetable oils have been studied for more than 10 years. Triglyceride is a major component of the vegetable oil. Triglyceride molecules consisted of three fatty acids joined to a glycerol unit. The numbers of double bonds in fatty acids, their degree of unsaturation, control the reactivity of the vegetable oil. Chemical modification of triglyceride has been reviewed by Khot *et al*. (2001). Epoxidized soybean oil (ESO) has been patented and commercialized. The high reactivity of the epoxide ring makes ESO able to crosslink with a suitable hardener. An ESO-based bioplastic has been developed and shows a relatively low tensile strength although it is a thermosetting polymer (Tanrattanakul & Saithai, 2009). In order to improve the mechanical properties of ESO polymer, ESO has been chemically modified to be acrylated ESO (AESO) and then copolymerized with a stronger polymer. There are many publications on AESO copolymerized with polystyrene (Khot *et al*., 2001; Donnell, Dweib *et al*., 2004; Lu *et al*., 2005; Dweib *et al*., 2006; Çolak & Küsefoğlu, 2007; Altuntaş *et al*., 2008; Zhan & Wool, 2010; Tasooji *et al*., 2010; Campanella, Scala, Wool, 2010). Copolymerization between AESO and poly (methyl methacrylate) by using benzoyl peroxide has also been reported (Li *et al*., 2010; Saithai *et al*., 2011; Saithai *et al*., 2012). Other polymers that have been used to copolymerize with AESO include a *p*-tertiary butyl phenol furfural resin (Çayli & Küsefoğlu, 2010), a polyester urethane acrylate (Oprea, 2010) and a styrene crosslinkable vinyl ester (Grishchuk & Kocsis, 2011). The AESO-co-PMMA polymers synthesized by free radical polymerization were crosslinked polymers (Saithai *et al*., 2011; Saithai *et al*., 2012). They reported that the mechanical properties and polymer characteristics of this copolymer were strongly dependent on the molar ratio of AESO:MMA and the degree of acrylation in AESO. The higher the MMA content and the higher degree of acrylation provided a polymer with higher mechanical properties and a higher glass transition temperature. Titanium dioxide in the nanoscale form has also been added to the AESO-co-PMMA to increase its mechanical properties (Saithai *et al*., 2012).

Recently, an AESO polymer has been prepared via photopolymerization under ultraviolet (UV) radiation (Pelletier *et al*., 2006; Kahraman *et al*., 2006; Habib & Bajpai, 2011, Rengasamy & Mannari; 2012). UV radiation has been applied to AESO-based copolymers such as copolymerization with poly(ethylene glycol) diacrylate or poly (ε-caprolactone) diacrylate (Kim *et al*., 2010). AESO grafted onto polypropylene has also been reported by Liliana *et al*. (2011). The advantages of UV curing are the speed of the process and the absence of solvent. The UV-curing technology has been employed for various applications such as coatings, adhesives, printing and electronic resists. UV-cured AESO-based polymers have been studied for coatings (Habib & Bajpai, 2011), biomedical applications (Kim *et al*., 2010), immobilization of hormones (Kahraman *et al*., 2006), membrane applications (Liliana *et al*., 2011) and film applications (Rengasamy & Mannari; 2012). To the best of our knowledge, there has been no previous report on UV-cured AESO copolymerized with poly (methyl methacrylate).

The objectives of this study were to investigate the mechanical properties of the AESO-co-PMMA copolymers prepared using UV irradiation. The resulting copolymers were characterized for their thermal properties, dynamic mechanical thermal properties and thermal degradation.

Materials and Methods

An epoxidized soybean oil (Vikoflex®7170) has an epoxy functionality of 4.6 epoxy rings per triglyceride which is equivalent to 100 mol% epoxidation. All chemicals were AR grade including acrylic acid, methyl methacrylate (MMA), hydroquinone, triethylamine and solvents. A photo-initiator (Darocur®1173) was kindly provided by BASF Chemical Co. Ltd. All chemicals were used as received, except MMA from which an inhibitor had to be removed by treatment with an aqueous sodium hydroxide solution then washed well with water until a pH of 7 was obtained. Then MMA was dried by adding anhydrous sodium sulfate and filtered through a filter paper.

Synthesis of acrylatedepoxidized soybean oil (AESO)

The molar ratio between ESO and acrylic acid was 1:15. ESO, 0.04 wt% hydroquinone and 0.1 wt% triethylamine were well mixed before increasing the temperature to 110°C. Acrylic acid was slowly added and the reaction maintained at 110°C for 7 h. The reaction was stopped by cooling the reactor. Water from the reaction was removed using a separation funnel. The residues of acrylic acid were removed by washing with distilled water until a pH of 7 was obtained. Water was removed using a separation funnel and the final product was purified by evaporation. The resulting AESO was examined by ^{1}H-NMR (Varian®INOVA, 500 Hz) and deuterated chloroform was used as a solvent. The degree of acrylation in AESO ($N_{acrylated}$) was determined from equation (1) based on a ^{1}H-NMR spectrum (Campanella *et al.*, 2011).

$$N_{acrylated} = \frac{9_{I5.8}}{I_{0.9}} \qquad (1)$$

$I_{5.8}$ is the intensity of a signal at δ 5.8 ppm and this corresponding to the acrylated protons (-CH), and $I_{0.9}$ is an intensity of a signal at δ 0.9 ppm that corresponded to the methyl protons ($-CH_3$).

Synthesis of AESO-co-PMMA

AESO was blended with MMA in various ratios (30-70 wt% MMA). The initiator content (2 wt%) was based on the total weight of the AESO plus MMA. The mixture was casted into a glass mold. The ultraviolet (UV) radiation was applied using a UV lamp (OSRAM ULTRA-VITALUX®, 300 W) at a wavelength of 365 nm for 7 min. The distance between the UV lamp and the glass plate was 10 cm. The formation of the copolymer was verified by FTIR analysis (BRUKER®TENSOR27) in the ATR mode.

Testing of mechanical properties

The tensile and tear testing were carried out at a crosshead speed of 50 mm/min and a sample sheet was die-cut according to ASTM D412 die C and ASTM D264 (right angle), respectively. Five to eight specimens were tested. Testing was performed at room temperature using alnstron®5569 universal testing machine.

Polymer characterization

Dynamic mechanical thermal analysis (DMTA) was conducted in a Rheometric Scientific®DMTA V at a frequency of 1 Hz with the tension mode from -50°C to 180°C and a heating rate of 2°C/min. Thermogravimetric analysis (TGA) was performed in the Perkin Elmer®DSC7 with a heating rate of 10°C/min from 50°C to 600°C under a nitrogen atmosphere. A Perkin Elmer®DSC7 was used for measurement of the thermal properties at a heating scan of 10°C/min from 0°C to 300°C. A solubility test was executed in tetrahydrofuran and chloroform which are good solvents for AESO and PMMA. A rectangular specimen (1 cm x 1 cm) was immersed in 10 ml of each solvent for 3 days at room temperature. A specimen was taken from the solvent and any remaining solvent was evaporated to obtain the soluble polymer. The degree of the soluble fraction was calculated according to equation (2). W_1 and W_2 were the weight of the specimen before testing and the weight of the soluble polymer, respectively. Three specimens were tested for every sample. A swelling test in ethanol was carried out at room temperature. A swelling index was calculated according to equation (3), where W_B and W_A were the specimen weight before and after swelling, respectively. W_A was determined when a constant weight of the swollen sample

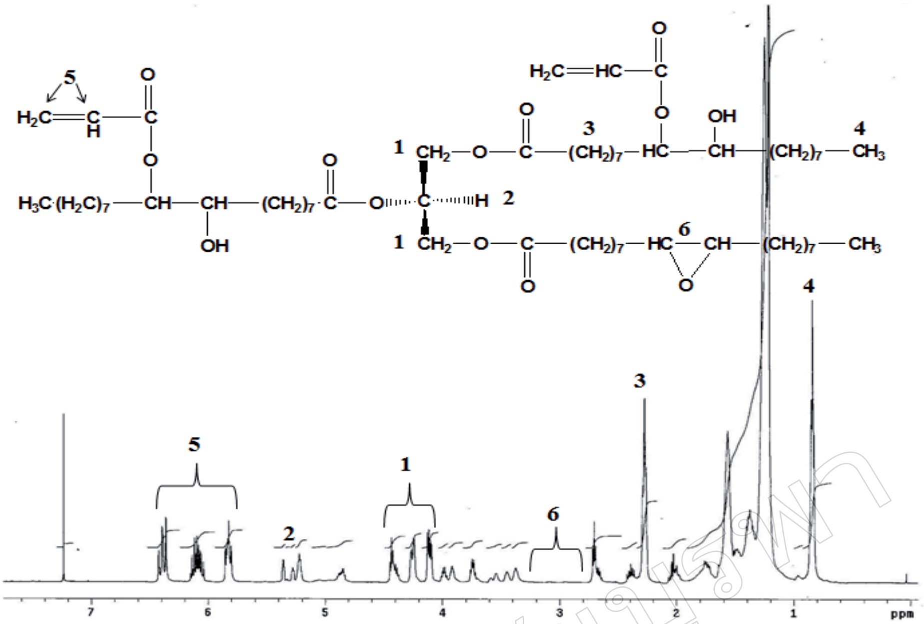

Figure 1 The ^{1}H-NMR spectrum of the AESO showing the acrylate group at position 5.

was obtained.

$$\text{Degree of soluble fraction (\%)} = \frac{W_2}{W_1} \times 100 \qquad (2)$$

$$\text{Swelling index (\%)} = \frac{W_A - W_B}{W_B} \times 100 \qquad (3)$$

Results and Discussion

Copolymer formation

Figure 1 represents the ^{1}H-NMR spectrum. The selected condition for synthesis of the AESO provided 52 mol% acrylation. The obtained AESO-co-PMMA copolymers were crosslinked materials based on a soluble test in which all copolymers were slightly dissolved in a good solvent of AESO and PMMA such as chloroform and tetrahydrofurane as shown in Table 1. The PMMA homopolymer (100% sample) prepared by UV radiation showed a very high degree of soluble fraction, i.e., ≥ 58%, indicating a thermoplastic behavior. In contrast, the AESO homopolymer (0% sample) dissolved slightly in both solvents due to its molecular network structure. The degree of the soluble fraction of all copolymer samples was in the same range: 2% - 3%, in a similar way to the

Table 1 Degree of soluble fraction of the AESO-co-PMMA sheets

MMA content (wt%)	Soluble fraction in THF (%)	Soluble fraction in chloroform (%)
0	2.04 ± 0.41	2.00 ± 0.22
30	2.68 ± 0.29	3.01 ± 0.16
40	2.47 ± 0.31	2.83 ± 0.42
50	2.51 ± 0.31	2.75 ± 0.26
60	2.44 ± 0.73	2.55 ± 0.36
70	2.41 ± 0.31	3.21 ± 0.06
100	58.53 ± 4.01	77.88 ± 9.75

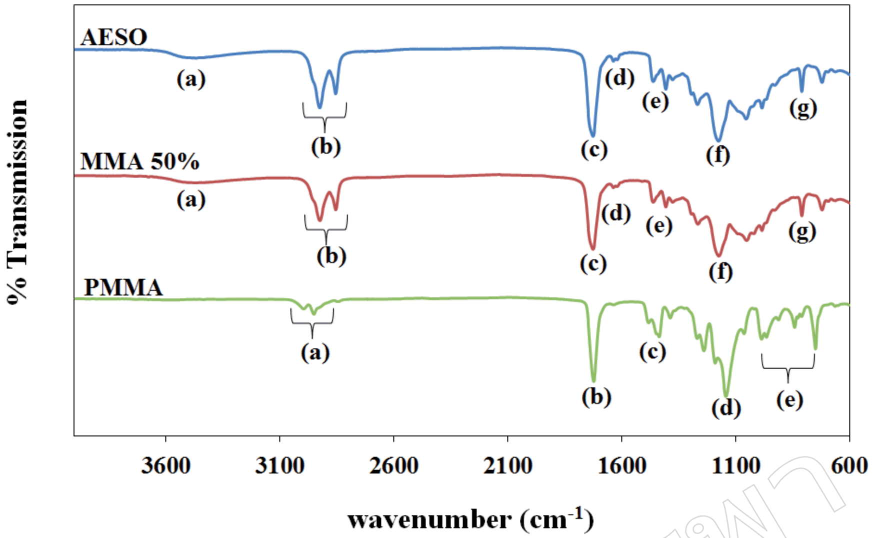

Figure 2 TThe FTIR spectrum of the AESO, PMMA and AESO-co-PMMA.

AESO. This result supported the view that the formation of the copolymer between the AESO and the PMMA was complete and there was no PMMA homopolymer. If the PMMA was not incorporated into the network structure of AESO, the degree of the soluble fraction would be higher due to the soluble PMMA. The occurrence of the copolymer was also identified by FTIR analysis. Figure 2 shows the FTIR spectra of AESO, PMMA and AESO-co-PMMA sheet, and the FTIR assignments of the copolymer are listed in Table 2. The presence of acrylate groups was noticed in the AESO-co-PMMA. This result substantiated the view that the product did form a copolymer in the resulting product. Because the AESO-co-PMMA was a thermosetting polymer, the molecular weight of the copolymers could not be determined.

Mechanical properties

The effect of the MMA content on the stress-strain behavior of the AESO-co-PMMA is illustrated in Figure 3. The AESO sample (0%) showed a low modulus and tensile strength although it was a thermosetting polymer. This may be due to the molecular structure of the triglyceride in AESO. The molecular chain length between the crosslink points depended on the molecular weight of the fatty acids. A typical composition of the soybean oil is 53.2% of linoleic acid (C = 18), 23.4% of oleic acid (C = 18), 11.0% of palmitic acid (C = 16) and 7.8% of linolenic acid (C = 18). This revealed that the network structure of the AESO was composed of short chain hydrocarbons, led to a weaker characteristic. The PMMA homopolymer was unable to be prepared for testing

Table 2 FTIR assignment of the AESO-co-PMMA copolymer

Position	Wavenumber (cm^{-1})	Assignment
(a)	3487	-OH stretching of AESO
(b)	2920, 2851	-CH2-stretching ofPMMA and–CHstretching of AESO
(c)	1722	-C=O carbonyl stretching
(d)	1456	CH_2=CH scissoring band of alkene at chain end of AESO
(e)	1169-1256	C-O-C stretching of PMMA
(f)	808, 723	C-C-O asymmetric bandof AESO and PMMA

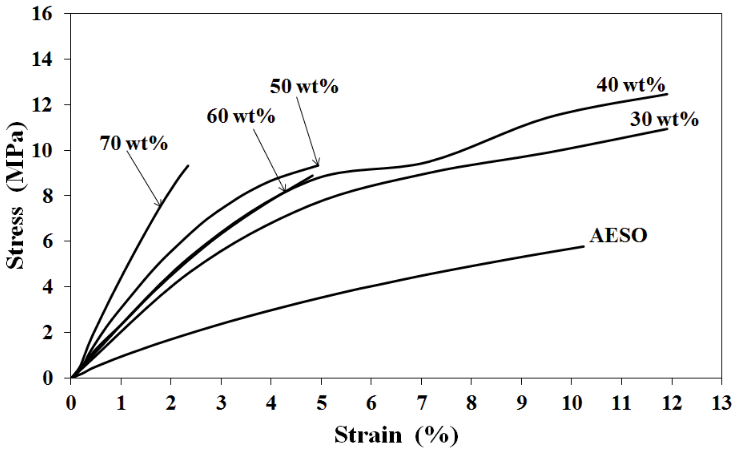

Figure 3 Stress-strain curves of the AESO, PMMA and AESO-co-PMMA copolymers containing different MMA contents.

specimens by die-cutting because it was too brittle for this preparation method. An injection molded specimen cannot be used for making a comparison because the preparation method strongly influences on the mechanical properties. The AESO-co-PMMA showed a different tensile behavior from the AESO. The MMA content had a big affect on the tensile behavior and that could be classified into 2 levels. A low MMA content (≤ 40%) improved all the tensile properties of the AESO whereas a high MMA content (≥ 50%) caused more brittleness. The tensile properties, i.e., the Young's modulus, the tensile strength (stress at break) and the strain at break, are illustrated in Figure 4a-4c, respectively. The Young's modulus increased with an increase of the MMA content, resulting from the more rigid structure of PMMA. All copolymers showed a higher tensile strength than the AESO and the maximum value was derived at 40% of MMA. A decrease in the tensile strength at a higher MMA content (≥ 50%) may be related to the lower ductility of the PMMA. An increase in the strain at break obtained at ≤ 40% MMA content owing to the brittleness of the PMMA.

It was unable to investigate the impact strength because of the high flexibility of the samples containing a low MMA content. An area under the stress-strain curve is frequently used to identify the tensile toughness. Figure 3 shows that the AESO-co-PMMA containing 40% MMA had the largest area under the curve or highest tensile toughness, and this was much higher than that of the AESO. The tensile toughness decreased and was lower than that of AESO when the MMA content was further increased. Therefore, the AESO-co-PMMA containing 40% MMA seemed to be the best sample in terms of its tensile properties. The effect of the MMA content of the tear resistance is demonstrated in Figure 5. The tear strength increased with an increasing MMA content. The rigidity of the PMMA played a major role on the tear resistance. Obviously, the addition of PMMA enhanced the mechanical properties of AESO.

Theoretically, the mechanical properties of thermosetting polymers are directly related to the crosslink density. The crosslink density is strongly dependent on functionality of the starting materials, the type of the curing and the curing conditions. In order to compare the effect of the curing technique (thermal curing vs. UV radiation curing), AESO should have the same degree of acrylation and the AESO-co-PMMA should have same MMA content. From this point of view, the present study could be compared with the study of Saithai *et al*. (2011). They synthesized AESO-co-PMMA by thermal curing and used AESO with 52 mol% of acrylation and the AESO:MMA weight ratio of 100:60 (38 % MMA). The Young's modulus, tensile strength, strain at break and tear strength of that

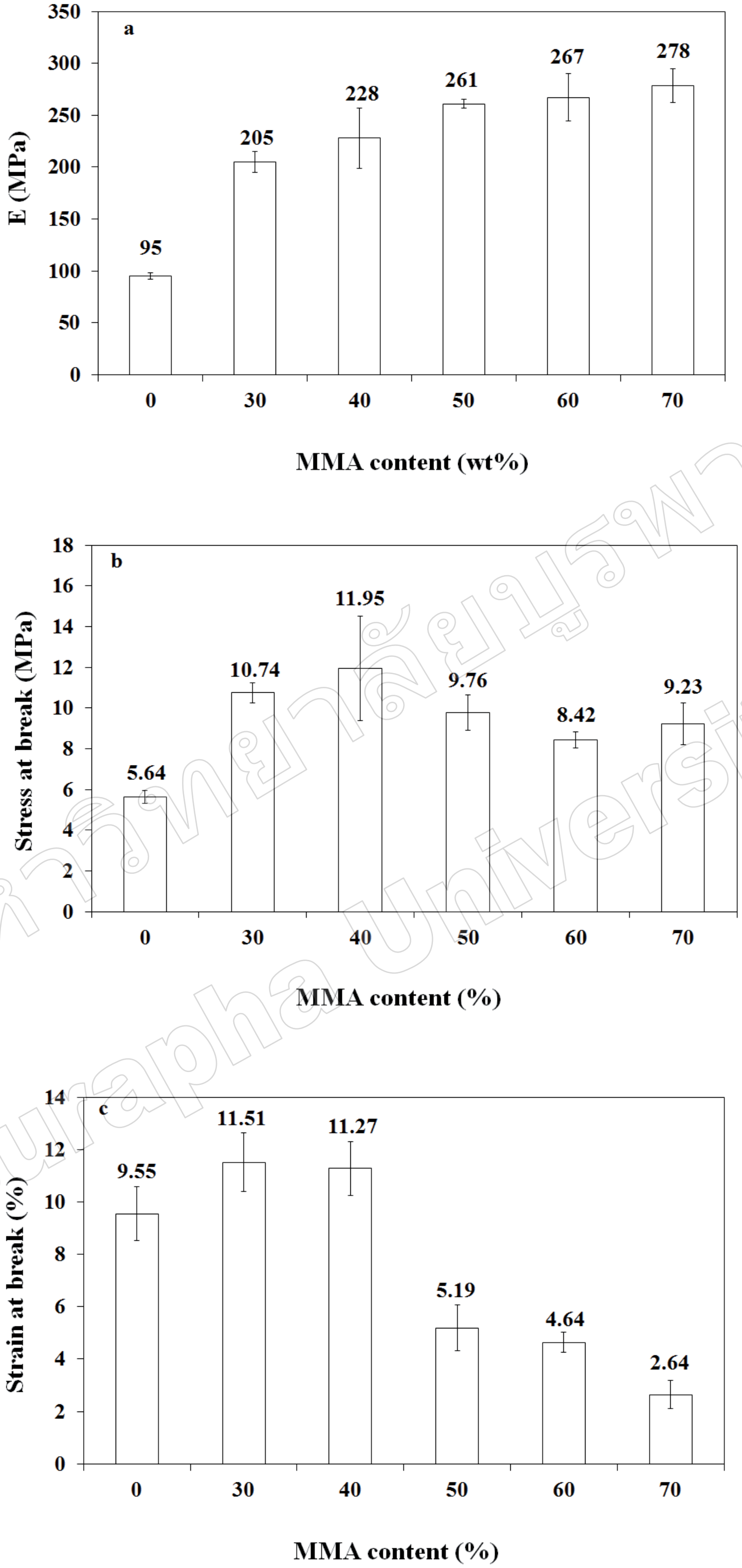

Figure 4 Effect of the MMA content on the tensile properties of the AESO-co-PMMA copolymers: (a) Young's modulus, (b) tensile strength and (c) strain at break.

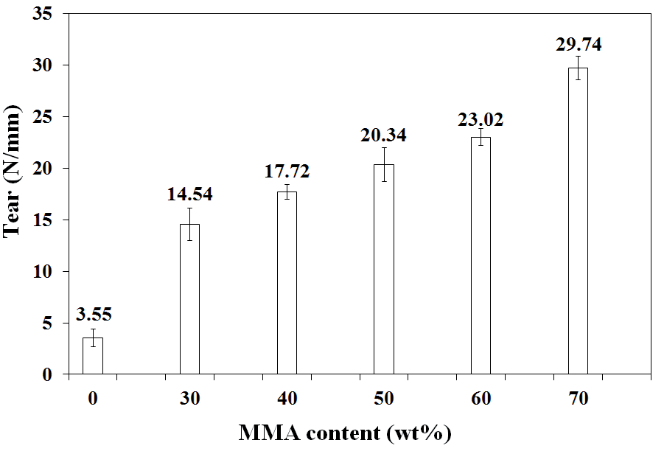

Figure 5 Effect of the MMA content on the tear resistance of the AESO-co-PMMA copolymers.

copolymer was 12.70 MPA, 1.60 MPA, 14% and 2.31 N/mm, respectively. Because the copolymer is a weak material they improved the curing condition and varied the degree of acrylation of AESO so as to increase the mechanical properties (Saithai *et al*., 2012). Their results showed that by having a 57 mol% acrylation and containing 38% MMA, the tensile strength and the strain at break of AESO-co-PMMA was 6.0 MPA and 30%, respectively. Although that strain at break was higher than found in the present study, but the tensile strength was still lower than the present one. The differences in the mechanical properties among these AESO-co-PMMA copolymers can be explained in terms of their glass transition temperatures.

Characterization

The swelling index of AESO, PMMA and AESO-co-PMMA are listed in Table 3. PMMA had a higher swelling index than AESO. The higher flexibility of the thermoplastic PMMA may contribute to higher swelling index. The presence of PMMA molecules in the AESO networks may enhance the chain length between the crosslinked points. As a result, the AESO-co-PMMA showed an increase in the degree of swelling as the MMA content increased, and their swelling index was lower than that of the PMMA homopolymer.

The DMTA results are described in terms of the storage modulus (E′), the loss modulus (E″) and the tan δ as a function of the temperature (Figure 6). The storage modulus, loss modulus and tan δ curves of AESO in the present study have a similar shape to those reported by Lu *et al*. (2005). The storage modulus at the glassy state increased with an increasing MMA content, in a similar

Table 3 Swelling index of the the AESO-co-PMMA sheets

MMA content (wt%)	Swelling index in ethanol (%)
0	8.98 ± 0.06
30	14.49 ± 0.63
40	13.17 ± 0.60
50	16.67 ± 0.27
60	19.37 ± 0.63
70	19.38 ± 1.06
100	36.68 ± 1.54

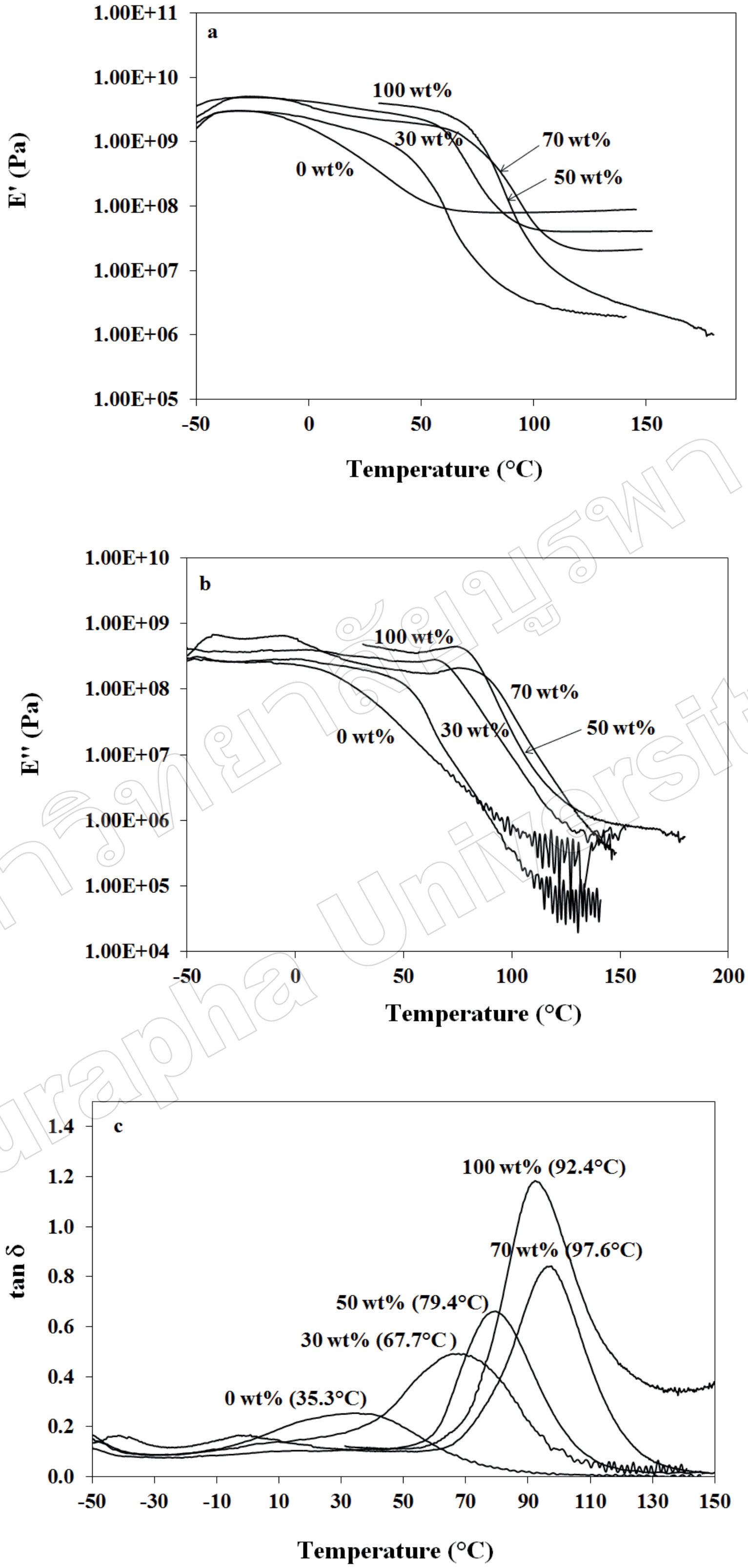

Figure 6 Effect of the MMA content on the dynamic mechanical thermal properties of the AESO-co-PMMA copolymers: (a) storage modulus, (b) loss modulus and (c) tan δ.

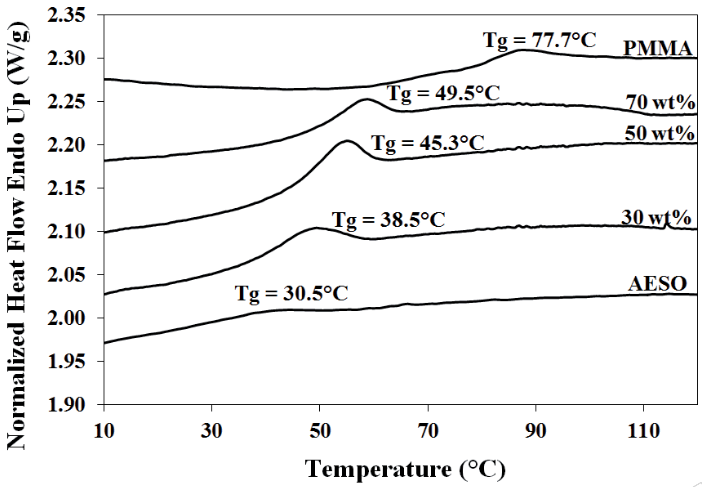

Figure 7 DSC thermograms of the AESO, PMMA and AESO-co-PMMA copolymers.

way to the effect on the Young's modulus. The tan δ peak (Figure 6c) represents the α relaxation temperature and is equivalent to the glass transition temperature (T_g). The AESO homopolymer showed the tan δ peak at 35.3°C whereas Lu *et al*. (2005) reported that the tan δ peak of AESO was at 71°C. This is because AESO in the present study contained a lower degree of acrylation (2.4 acrylates per triglyceride or 52 mol%) whereas their AESO contained 3.4 acrylates per triglyceride (75 mol%). Furthermore, the curing conditions were also different. The PMMA homopolymer synthesized by the UV radiation showed a tan δ peak at 92°C. All AESO-co-PMMA copolymers showed one tan δ peak or one T_g, and the peak shifted to a higher temperature when the MMA content increased. This caused the higher modulus, tensile strength and tear resistance and the lower strain at break. In the previous study (Saithai *et al*., 2011; Saithai *et al*., 2012), the tan δ peak of the AESO-co-PMMA copolymers were in the range of 34-42°C. Thus, their AESO-co-PMMA copolymers showed a lower modulus and strength than those in the present study.

The DSC is a typical measurement of T_g because only the thermal properties are involved. The DSC thermograms of AESO, PMMA and AESO-co-PMMA are pro-

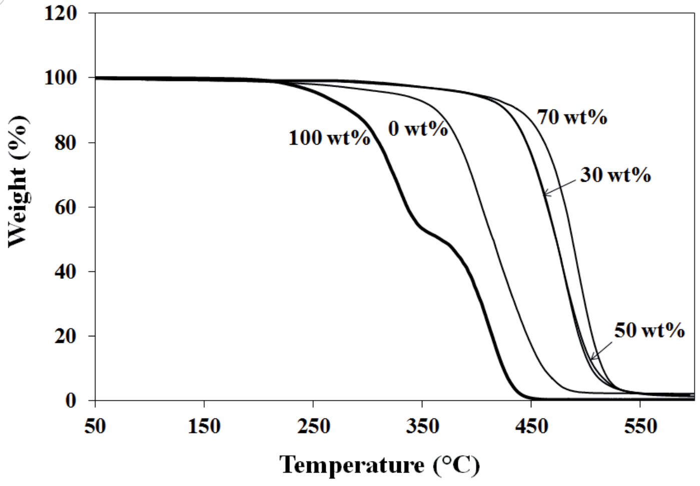

Figure 8 TGA thermograms of the AESO, PMMA and AESO-co-PMMA copolymers.

Table 4 Thermal degradation of the AESO-co-PMMA sheets

MMA content (wt%)	T_5 (°C)	T_{10} (°C)	T_{50} (°C)
0	306	359	414
30	378	423	472
50	376	424	472
70	381	434	487
100	248	278	362

vided in Figure 7. The Tgof AESO and PMMA was 30.5°C and 77.7°C, respectively. Theoretically, the T_g obtained from the DSC is lower than that from the DMTA because there is no force involved in the DSC measurement. The T_g of AESO-co-PMMA increased with an increasing MMA content. All copolymers also showed a single T_g, that was similar to the DMTA results. These results indicated that AESO-co-PMMA was a random copolymer.

The thermal degradation of AESO-co-PMMA was explained by the TGA thermograms (Figure 8). The thermoplastic PMMA showed the lowest thermal stability. The network structure of the AESO caused a higher thermal stability. A synergistic behavior was obtained as a result of the copolymerization. The degradation shifted to a higher temperature with an increase of the MMA content. All AESO-co-PMMA copolymers showed a single step degradation indicating that this was a characteristic of the random copolymer and not a PMMA homopolymer. The thermal degradation temperature was described in terms of the temperature at a certain weight loss as displayed in Table 4. For example, T_5 was the temperature at which the sample weight lost was approximately 5%. It showed that the degradation temperature was significantly increased by copolymerization with PMMA, and the degradation temperatures were in the same range of the copolymer containing 30% and 50% MMA. The degradation temperature slightly increased when the MMA content increased to 70%. The TGA results also indicated that the optimal MMA content should not more than 50%.

Conclusion

A bioplastic polymer has been synthesized from acrylated epoxidized soybean oil and methyl methacrylate via photopolymerization under UV radiation for 7 min. The obtained polymer was a crosslinked random copolymer, an AESO-co-PMMA copolymer. A poly (methyl methacrylate) homopolymer was not obtained. The methyl methacrylate content showed strongly effect on the tensile properties, tear strength, glass transition temperature and thermal stability. The Young's modulus, tear strength, T_g and thermal degradation temperature of AESO-co-PMMA copolymer increased as the methyl methacrylate content increased. The tensile strength, strain at break and tensile toughness had their maximum value when the methyl methacrylate content was 40%; any further increase in the methyl methacrylate content decreased these properties. The optimal methyl methacrylate content was therefore 40%. The results showed that the mechanical properties of the soybean oil-based plastic by copolymerization were successfully enhanced by incorporation of methyl methacrylate under UV radiation.

Acknowledgements

The authors would like to acknowledge the financial support from the Research Development and Engineering (RD & E) fund through The National Nanotechnology Center (NANOTEC), The National Science and Technology Development Agency (NSTDA), Thailand (P-10-11333) to Prince of Songkla University.

References

Altuntas, E., Çayli, G., Küsefoglu, S. &Nugay, N. (2008). Renewable Polymeric Nanocomposite Synthesis Using Renewable Functionalized Soybean-Oil-Based Intercalant and Matrix. *Designed Monomers and Polymers, 11*, 371-381.

Campanella, A., Scala, J.J. & Wool, R.P. (2011). Fatty Acid-Based Comonomers as Styrene Replacements in Soybean and Castor Oil-Based Thermosetting Polymers. *Journal of Applied Polymer Science, 119*, 1000-1010.

Çayli, G. & Küsefoglu, S. (2011). Polymerization of Acrylated Epoxodized Soybean Oil with Phenol Furfural Resins via Repeated Forword and Retro Diels-Alder Reactions. *Journal of Applied Polymer Science, 120*, 1707-1712.

Çolak, S. & Küsefoglu, S.H. (2007). Synthesis and Interfacial Properties of Aminosilane Derivative of Acrylated Epoxidized Soybean Oil. *Journal of Applied Polymer Science, 104*, 2244-2253.

Dweib, M.A., Hu, B., Shenton III, H.W. & Wool, R.P. (2006). Bio-based composite roof structure: Manufacturing and processing issues. *Composite Structures, 74*, 379-388.

Grishchuk, S. & Kocsis, J.K. (2011). Hybrid thermosets from vinyl ester resin and acrylatedepoxidized soybean oil (AESO). *eXPRESS Polymer Letter, 5*, 2-11.

Habib, F. & Bajpai, M. (2011). Synthesis and Charaterization of AcrylatedEpoxidized Soybean Oil for UV cured coatings. *Chemistry and Chemical Technology, 5*, 317-326.

Kahraman, V.M., Apohan, N.K., Ogan, A. & GüngÖr, A. (2006). Soybean oil Based Resin: A New Tool for Improved Immobilization of α-Amylase. *Journal of Applied Polymer Science, 100*, 4757-4761.

Khot, S.N., Lascala, J.J., Can, E., Morye, S.S., Williams, G.I., Palmese, G.R., Kusefoglu, S.H. & Wool R.P. (2001). Development and Application of Triglyceride-Based Polymers and Composites. *Journal of Applied Polymer Science, 82*, 703-723.

Kim, H.M., Kim, H R. & Kim, B.S. (2010). Soybean Oil-Based Photo-Crosslinked Polymer Networks. *Journal of Polymers andthe Environment, 18*, 291-297.

Li, Y., Fu, L., Lai, S., Cai, X. & Yang, L. (2010). Synthesis and characterization of cast resin based on different saturation epoxidized soybean oil. *European Journal of Lipid Science andTeechnology, 112*, 511-516.

Liliana, M., Cortes, F., Alejandro, D. & María, R. (2012). Surface Modifition of Polypropylene Membrane by Acrylate Epoxidized Soybean Oil to be Used in Water Treatment. *Journal of Applied Polymer Science, 124*, 147-153.

Lu, J., Khot, S. & Wool, R.P. (2005). New sheet molding compound resins from soybean oil. I. Synthesis and characterization. *Polymer, 46*, 71-80.

O'Donnell, A., Dweib, M.A. & Wool, R.P. (2004). Natiral fiber composites with plant oil-based resin. *Composites Science and Technology, 64*, 1135-1145.

Oprea, S. (2010). Properties of polymer networks prepared by blending polyester urethane acrylate with acrylatedepoxidized soybean oil. *Journal of Materials Science, 45*, 1315-1320.

Pelletier, H., Belgacem, N. & Gandini, A. (2006). Acrylated Vegetable Oil as Photocrosslinkable Materials. *Jouranl of Applied Polymer Science, 99*, 3218-3221.

Rengasamy, S. & Mannari, V. (2012). Development of soy-based UV-curable acrylate oligomers and study of their film properties. *Progress in Organic Coatings, 76*, 78-85.

Saithai, P., Tanrattanakul, V., Chinpa, W., Kaewtatip, K. & Dubreucq, E. (2011). Synthesis and Characterization of Triglyceride-based Copolymer from Soybean Oil. *Material Science Forum, 695*, 320-323.

Saithai, P., Tanrattanakul, V., Dubreucq, E. & Lecomte, J. (2012). BioplasticNanocomposite Prepared from Acrylated Epoxidized Soybean Oil-PMMA Copolymer and Nano-Titanium Dioxide. *Advanced Science Letters, 19*, 862-865.

Tanrattanakul, V. & Saithai P. (2009). Mechanical Properties of Bioplastics and Bioplastic-Organoclay Nanocomposites Prepared from Epoxidized Soybean Oil with Different Epoxide Contents. *Journal of Applied Polymer Science, 114*, 3057-3067.

Tasooji, M., Tabarsa, T., Khazaeian, A. & Wool, R.P. (2010). AcrylatedEpoxidized Soy Oil as an Alternative to Urea-Formaldehyde in Making Wheat Straw Particleboards. *Adhesion Science and Technology, 24*, 1717-1727.

Zhan, M. & Wool, R.P. (2010). Biobased Composite Resins Design for Electronic Materials. *Journal of Applied Polymer Science, 118*, 3274-3283.