

## Material Properties

## Rubber toughening of nylon 6 with epoxidized natural rubber

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## ABSTRACT

This paper focuses on the use of epoxidized natural rubber (ENR) as a toughening agent for nylon 6 (PA6). Natural rubber (NR) was used to compare with ENR. Polymer blends were prepared by using a twin-screw extruder and pressing as a sheet in a compression molding machine. It was found that NR and ENR decreased yield stress and tensile strength but slightly increased elongation at break of PA6. NR slightly decreased impact strength of PA6, whereas this property increased up to sixfold by blending with ENR. This phenomenon could be explained in terms of blend morphology. Too large a particle diameter of NR was a cause of the premature failure. The impact strength of the blends increased with increasing ENR content. Rubber particle diameter also increased but was still much smaller than natural rubber particles. Phenolic resin was employed for crosslinking ENR. Compounded ENR increased tensile properties but decreased impact strength of the blends. This was because the morphology of ENR was changed from small particles to large patches of rubber after vulcanization.

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## 1. Introduction

It is well established that nylon 6 (polyamide 6, PA6) is a notch-sensitive plastic. It is sensitive to crack propagation and becomes embrittled at low temperature. Therefore, its impact resistance is poor and it tends to fail in a brittle manner at low temperature. Many attempts have been made to improve the impact strength of PA6 by adding low modulus toughening agents in order to produce a rubber toughened plastic. These low modulus materials decrease notch-sensitivity and also increase toughness at low temperature.

There are many publications reporting on rubber toughened nylon 6. Various different types of rubber have been used, including styrene–ethylene/butylene–styrene block copolymer (SEBS) and/or SEBS grafted with maleic anhydride (SEBS-g-MA) [1–15] (EPR) and/or (EPR-g-MA) [4–7,10,11,13–26], styrene–acrylic acid copolymer [3], acrylonitrile–butadiene–styrene copolymer (ABS) [26–31],

polyethylene–octene copolymer (EOR) and/or EOR grafted with maleic anhydride (EOR-g-MA) [7,15,32–34], epoxidized ethylene propylene diene rubber [35], ethylene propylene diene rubber grafted with maleic anhydride (EPDM-g-MA) [7,36,37], EPDM grafted with styrene acrylonitrile copolymer [26], core-shell impact modifier [3,38,39], polyvinyl acetate blended with ethylene–acrylic acid copolymer [40], ethylene–acrylic acid copolymer [3,41], polybutadiene [42], natural rubber with maleic anhydride (NR-g-MA) [43], carboxylated styrene–butadiene rubber [44], acrylonitrile–butadiene copolymer [45,46], carboxylated nitrile rubber [47], ultra-fine fully-vulcanized acrylate powdered rubber [48], and carboxylic styrene–butadiene ultra-fine full-vulcanized powdered rubber [49]. Effective toughening agents must be functionalized or polar rubber because PA6 is a polar material. Therefore, it is plausible to increase interfacial adhesion or to obtain reactive blending between PA6 and functionalized/polar rubber. Maleated rubber has been selected for this application, as reviewed by Paul et al. [4]. The grafted maleic anhydride reacted with the end group of PA6 yielding an *in situ* graft copolymer on the interface between the two phases. In theory, this graft copolymer acted as an emulsifier, leading to

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a decrease in interfacial tension, particle–particle coalescence rate and rubber particle size. As a result, improvement in mechanical toughness was achieved. Although natural rubber (NR) could be used as a toughening agent for many thermoplastics, it is deficient in that role for PA6 because of dissimilarity in polarity. To increase polarity and decrease unsaturation of NR, epoxidized natural rubber (ENR) is commercialized and used in many applications. Based on our knowledge, the application of ENR as a toughening agent for PA6 has not been reported yet. However, ENR was used as a compatibilizer for PA6/EPDM and PP/PA6 blends [50]. In that article, the authors showed that the *in situ* graft copolymerization between PA6 and ENR occurred during melt blending. There was an assumption that the epoxy group could react with the terminal amino group of PA6 [35,51] and the terminal carboxylic group [51].

The objective of this study is to develop rubber toughened PA6 by using ENR as the toughening agent. Comparison between blends containing NR and ENR is described in terms of mechanical properties and morphology. The effect of vulcanization in ENR on mechanical properties of the blends was also investigated.

## 2. Experimental

### 2.1. Materials

The Nylon 6 used was Ultramide™ B36 produced by BASF Co. Melting temperature was 219 °C and melt index at 230 °C was 5 g/10 min under a mass of 2160 g. Natural rubber, constant viscosity grade (STR5L CV60), was produced by Chalong Latex Industry, Co. Ltd., Thailand. Epoxidized natural rubber containing 50 mol% of epoxidation (Epoxyprene™ 50) was produced by Muang Mai Guthrie Public Co. Ltd., Thailand. Irganox™ B1171 produced by Ciba Specialty Chemicals Co was added to nylon as an antioxidant. Phenolic resin (SP1045) was produced by Schenectady International Inc. Saret™ SR75EPM2M produced by Sartomer Co. was used as a co-agent. All curatives for rubber compounding were commercial grade and used as received.

### 2.2. Polymer blends preparation

PA6 was dried in a vacuum oven at 90 °C for 24 h before using. One phr (per hundred of PA6) of Irganox™ B1171 was blended with PA6 prior to melt blending with rubber. Rubber compounds were prepared by using an internal mixer (Brabender™ Mixer 350E) at 80 °C and rotor speed of 60 rpm, and then sheeted by using a two-roll mill. Rubber sheet was cut into small pieces and dry blended with PA6 prior to melt blending. Formulations of rubber compounds are listed in Table 1. Uncompounded rubber was also sheeted by using the two-roll mill and cut into small pieces prior to blending with PA6. Melt blending was performed in a twin-screw extruder (Prism™ TSE16TC) at temperatures of 190 °C (zone 1), 220 °C (zone 2) and 230 °C (die). Screw speed was determined based on ease of processing and mechanical properties of the blends. The extrudate was subsequently quenched in a water bath at room temperature and pelletized. The blends were dried in a vacuum

**Table 1**  
Formulation of ENR compounding

Chemical	I	II
ENR	100	100
Wingstay™ L	1	1
Stearic acid	2	2
Zinc oxide	5	5
Phenolic resin	8	8
SR75EPM2M	–	3

oven and re-extruded using the previous extrusion conditions. The blends were again dried in the vacuum oven and kept in a desiccator at room temperature.

### 2.3. Mechanical properties and morphology investigation

A sheet was produced by compression molding (Kao Tieh™ KT7014) at 230 °C for 8 min under a pressure of 450 kg/cm<sup>2</sup>. Dumbbell-shaped specimens and V-notched specimens were prepared for tensile testing and charpy impact testing according to ISO 527 and ISO 180, respectively. Tensile properties were tested at speed of 50 mm/min by using a LLOYD™ LR10K machine. Mechanical properties were tested under ambient conditions. Eight to 10 specimens were tested for every sample. Freeze fractured surfaces of the blends were photographed by a scanning electron microscope (JEOL™ JSM5800LV) to determine size of rubber particles. The surface of specimens was etched with toluene for 2 h in order to remove rubber particles on the fractured surface. The specimens were dried in a vacuum oven at 60 °C for 4 h before coating with gold. Approximately 500 particles selected randomly were counted using an image analyzer to measure particle diameter and reported as a number-average diameter.

## 3. Results and discussion

### 3.1. Comparison between NR and ENR

To verify the hypothesis that ENR is more compatible with PA6 than NR due to the polarity effect and plausible reactive blending of PA6/ENR blend, PA6/NR and PA6/ENR blends were prepared under the same method with a blending speed of 150 rpm. Tensile properties and impact strength of the blends are given in Table 2. The addition of rubber (30 wt%) decreased yield stress ( $\sigma_y$ ), yield strain ( $\epsilon_y$ ) and stress at break ( $\sigma_b$ ) of PA6. Elongation at break ( $\epsilon_b$ ) of the blends was higher than that of neat resin. NR did not improve impact strength of PA6. In contrast, 30% ENR increased impact strength up to sixfold. This was attributed to the particle size of the rubber phase in the blends. The number-average particle diameter of NR and ENR particles was  $7.28 \pm 4.72 \mu\text{m}$  and  $1.13 \pm 0.48 \mu\text{m}$ , respectively. Particle size distribution of NR particles in the blends was much broader than that of ENR particles as illustrated in Table 3. Fig. 1a and b represent SEM micrographs of the blends containing 30% NR and 30% ENR, respectively. The black holes represent rubber particles etched by toluene. Similar results have been shown in many articles, for example, the impact strength increased approximately

**Table 2**

Effect of rubber type on tensile properties and impact strength of the blends containing 30% un compounded rubber

Rubber	$\sigma_y$ (MPa)	$\varepsilon_y$ (%)	$\sigma_b$ (MPa)	$\varepsilon_b$ (%)	Impact strength (kJ/m <sup>2</sup> )
–	81.97 ± 4.56	19 ± 1	74.37 ± 11.59	45 ± 13	6.38 ± 2.43
ENR	23.64 ± 0.82	11 ± 1	28.35 ± 4.00	60 ± 10	34.51 ± 6.97
NR	39.47 ± 2.09	12 ± 1	45.26 ± 2.43	51 ± 8	6.80 ± 1.55

sixfold in a blend containing 20 wt% of EPR-g-MA [10], and functionalized EPR provided smaller rubber diameter and higher impact strength than EPR [13]. Large rubber particle diameter, 2–16  $\mu\text{m}$ , obtained from PA6/EPR blends was reported [16,24]. Additionally, epoxidation of EPDM was able to reduce rubber diameter in PA6/EPDM blends from 2–8  $\mu\text{m}$  to 0.7–2  $\mu\text{m}$  [35].

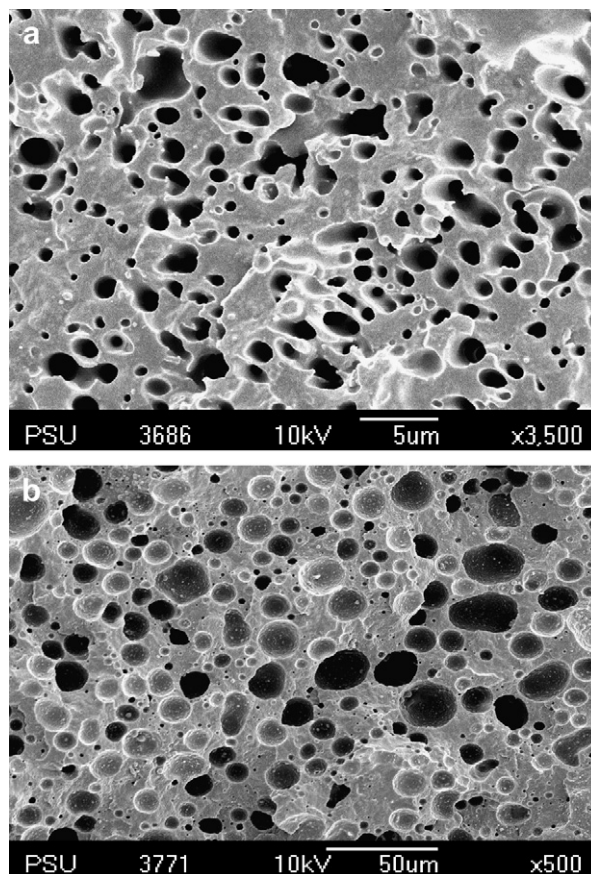
There are many factors involved in the effectiveness of rubber toughened plastics, i.e. type and concentration of rubber, rubber particle performance (size and shape), interfacial adhesion between rubber particles and matrix, blending method, rheological properties, processing conditions, etc. Furthermore, the efficiency of toughening agents may be high in some mechanical properties and low in others. Rubber particle size is critical for improving the toughness of the blends. Generally speaking, for the PA6/maleated rubber blends, the rubber particles should be below 1  $\mu\text{m}$  in order to increase mechanical properties of the blends. However, there were some contradictions among researchers as to the exact diameter, some said impact strength of the blends increased when the rubber particle diameter was in the range of 0.1–0.5  $\mu\text{m}$ , whereas the rubber diameter less than 0.2  $\mu\text{m}$  was preferred to optimize tensile properties [1], while others said impact strength of the blend did not increase when the rubber diameter was smaller than 0.05  $\mu\text{m}$  [1], <0.2  $\mu\text{m}$  [4] or <0.1  $\mu\text{m}$  [8,13].

There is no doubt that the addition of NR and ENR reduced tensile strength of PA6, resulting from the low modulus of rubber. In general, it was expected to achieve higher impact strength in the plastic blended with rubber under appropriate conditions. Non-polarity of NR brought about low interfacial adhesion and gross phase separation resulting in poor impact strength in the present blend. The smaller particles of ENR enhanced impact strength of PA6 as a result of good interfacial adhesion, although the average particle diameter was larger than 1  $\mu\text{m}$ . To verify the presence of the interfacial graft copolymer between PA6 and ENR was beyond the scope of this study. Noticeably,

**Table 3**

The number-average diameter ( $D_{\text{avg}}$ ) and diameter range of un compounded rubber particles in the blends

Rubber	Screw speed (rpm)	Rubber content (%)	$D_{\text{avg}}$ ( $\mu\text{m}$ )	Diameter range ( $\mu\text{m}$ )
ENR	100	30	1.19 ± 0.32	0.20–3.34
ENR	150	20	0.67 ± 0.29	0.11–2.20
		30	1.10 ± 0.48	0.25–3.47
		40	1.93 ± 0.89	0.35–5.62
ENR	200	30	1.03 ± 0.37	0.14–3.03
NR	150	30	7.28 ± 4.72	0.20–25.50



**Fig. 1.** SEM micrographs of the blends containing 30% ENR (a) and 30% NR (b).

although the average particle diameter of ENR in this study was quite high (>1  $\mu\text{m}$ ), the blends still showed significantly improved impact strength. The diameter of NR particles in the present blends was very large compared to that reported by Carone et al. [43], in which PA6 blended with 25 wt% of NR showed submicron rubber diameters (0.8  $\mu\text{m}$ ). This may be due to the difference in blending conditions. The resident time in the internal mixer used in that work was much longer than that of the twin-screw extruder used in the present study. Another evidence of poor compatibility between NR and PA6 compared to NR and polypropylene (PP) [52] was that the average rubber diameter in the PP/NR blends was about 1.34  $\mu\text{m}$  when the blend containing 30% NR was prepared with the same twin-screw extruder.

### 3.2. Effect of blending speed

One disadvantage of NR and ENR as the toughening agent is their high tackiness, as they cannot be produced in pellet form. This makes it difficult to prepare a dry blend between plastic and ENR. Due to the limitation of the screw (24 cm – length), it was essential to re-extrude in order to obtain a homogeneous blend. Two parameters involved in blending conditions included screw speed and temperature. Only

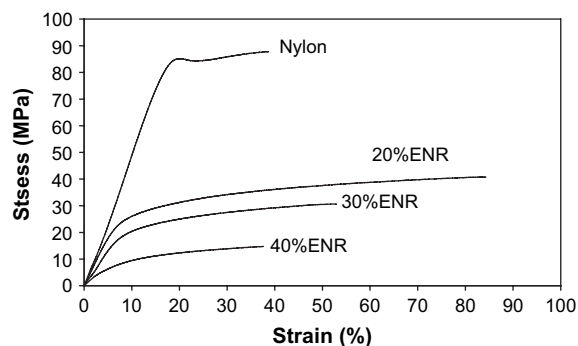
**Table 4**

Effect of speed of melt blending on tensile properties and impact strength of the blends containing 30% un compounded ENR

Screw speed (rpm)	$\sigma_y$ (MPa)	$\varepsilon_y$ (%)	$\sigma_b$ (MPa)	$\varepsilon_b$ (%)	Impact strength (kJ/m <sup>2</sup> )
100	29.07 ± 1.36	12 ± 1	29.35 ± 4.50	36 ± 6	32.78 ± 4.41
150	23.64 ± 0.82	11 ± 1	28.35 ± 4.00	60 ± 1	34.51 ± 6.97
200	26.37 ± 2.11	11 ± 1	29.64 ± 7.22	60 ± 6	34.72 ± 7.59

screw speed was varied to seek the optimal condition, whereas the screw temperature had to be maintained at the fixed temperature. The screw speed should not be too slow because the resident time will be too long causing thermal degradation. On the one hand, the screw speed should not be too fast because of limitations of ENR feeding rate. Three screw speeds were chosen for blending: 100, 150 and 200 rpm. Table 4 shows tensile and impact properties of the blend containing 30% ENR. Obviously, tensile properties of all blends were in the same range. Based on the ease of processability, the speed of 200 rpm was not appropriate for feeding. The speed of 100 rpm obviously meant longer resident time than at 150 rpm, hence there was higher risk of thermal degradation. As a result, the speed of 150 rpm was applied for other experiments. Particle size of rubber as listed in Table 3 was in the same range ( $\sim 1 \mu\text{m}$ ) for all blending speeds.

Insignificant change in rubber diameter with changing speed of blending had been reported. Increasing the rotor speed from 20 to 150 rpm did not have any major influence on rubber diameter in PA6/EPR blend [16]. This article also mentioned that there were many researchers reporting little effect of shear stress on rubber diameter in the blends. It was claimed that above a critical shear stress the blends were not sensitive to either shear stress or shear strain and there was an optimum shear rate where the finest dispersion was obtained for each blend. Oommen et al. [24] reported that rubber diameter in the skin of the extrudate (PA6/EPR blends) decreased with increasing shear rate, whereas no change with shear rate was observed in the center of the extrudate, where the shear rate was essentially zero. On the other hand, the blend containing EPR-g-MA showed morphology independent of shear rate, indicating stable morphology. One interesting result of the effect of processing conditions on rubber diameter was shown in PET blended with SEBS and SEBS-g-MA



**Fig. 2.** Stress–strain curves of nylon 6 (PA6) and the blends containing un compounded ENR.

**Table 5**

Effect of ENR content on tensile properties and impact strength of the blends containing un compounded ENR

ENR Content (%)	$\sigma_y$ (MPa)	$\varepsilon_y$ (%)	$\sigma_b$ (MPa)	$\varepsilon_b$ (%)	Impact strength (kJ/m <sup>2</sup> )
0	81.97 ± 4.56	19 ± 1	74.37 ± 1.59	45 ± 13	6.38 ± 2.43
20	29.54 ± 1.47	10 ± 1	38.22 ± 3.12	81 ± 15	26.29 ± 5.61
30	23.64 ± 0.82	11 ± 1	28.35 ± 4.00	60 ± 10	34.51 ± 6.97
40	12.11 ± 1.74	9 ± 2	14.83 ± 2.27	48 ± 9	59.69 ± 9.29

[53]. The blends containing SEBS and SEBS-g-MA with 1% MA showed increase in rubber diameter with increasing rubber content and insignificant change in rubber diameter with changing blending conditions. SEBS-g-MA with very high maleic anhydride content (4.5% MA) showed insignificant change in rubber diameter with both rubber content and processing conditions. The former case was similar to the present study.

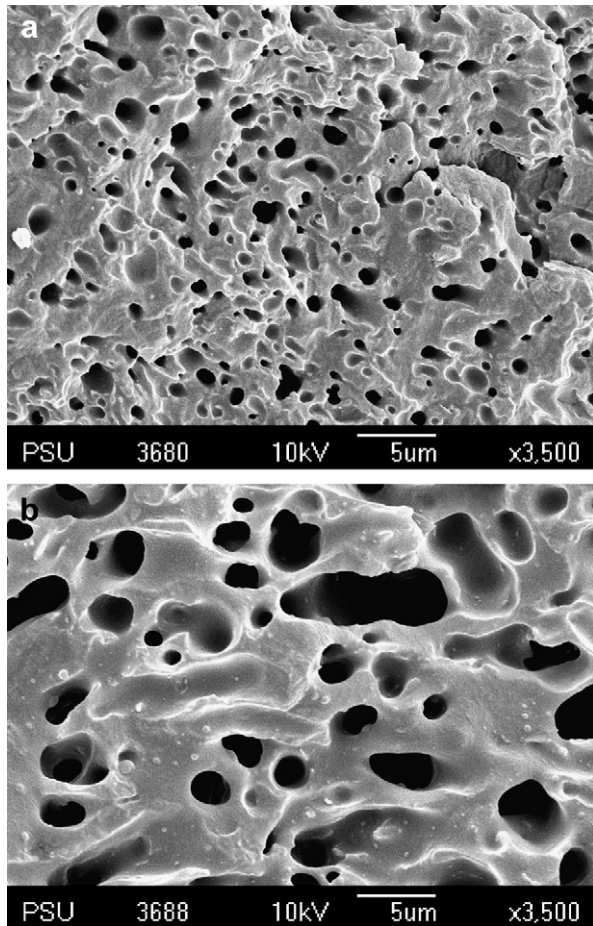
### 3.3. Effect of rubber content

Fig. 2 represents stress–strain curves of PA6 and the blends containing different ENR content. ENR increased ductility of PA6. In Table 5, all the blends showed lower yield stress, yield strain and stress at break than neat nylon, while the elongation at break and impact strength of the blends were higher, 4–10-fold. Remarkably, the impact strength of the blends significantly increased with increasing ENR content. On the other hand, yield stress and tensile strength of the blends decreased with increasing ENR content. Even though the maximum impact strength derived from the blend containing 40% ENR, this blend showed very low tensile properties. Particle size of ENR in the blends increased with ENR content as shown in Figs. 1b and 3a and b. The average diameters are tabulated in Table 3.

Compared to the blend containing EPR-g-MA [20], the present blend showed lower tensile properties due to larger diameter of ENR particles. The PA6/epoxidized EPDM blend [35] exhibited higher impact strength than the present blend and EPDM-g-MA was more effective than epoxidized EPDM [37]. The rubber diameter of EPDM-g-MA was about 0.4–0.5  $\mu\text{m}$  [37] while that of epoxidized EPDM was about 0.7–2  $\mu\text{m}$  [35]. The PA6/ENR blend in the present study displayed lower tensile strength and higher elongation at break than PA6 containing the ethylene–acrylic acid copolymer (EAA) reported by Valenza et al. [41]. The EAA diameter was smaller than the present ENR. Evidently, effect of ENR diameter on tensile properties contradicted that on impact strength. It agreed with theory that as the concentration of ENR increased the rubber particle size increased, leading to a reduction in tensile properties. However, it seems that rubber concentration, not rubber diameter, plays a major role in impact strength, or PA6/ENR blends may not require submicron particles for high toughness.

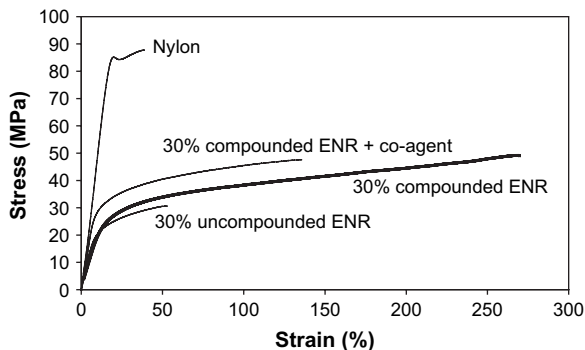
### 3.4. Effect of rubber compounding

As described in Section 3.3, un compounded ENR enhanced impact strength but decreased tensile strength of



**Fig. 3.** SEM micrographs of the blends containing un-compounded ENR: 20% (a) and 40% (b).

PA6. As we know, natural rubber must be used in the vulcanized form for engineering applications. For this reason, compounded ENR was applied to improve tensile properties of the blends. Two ENR compounds were prepared for the blend containing 70% PA6 and referred to as samples I and II (Table 1). Phenolic resin (SP1045) was used as a vulcanizing agent. The stress–strain curves and mechanical



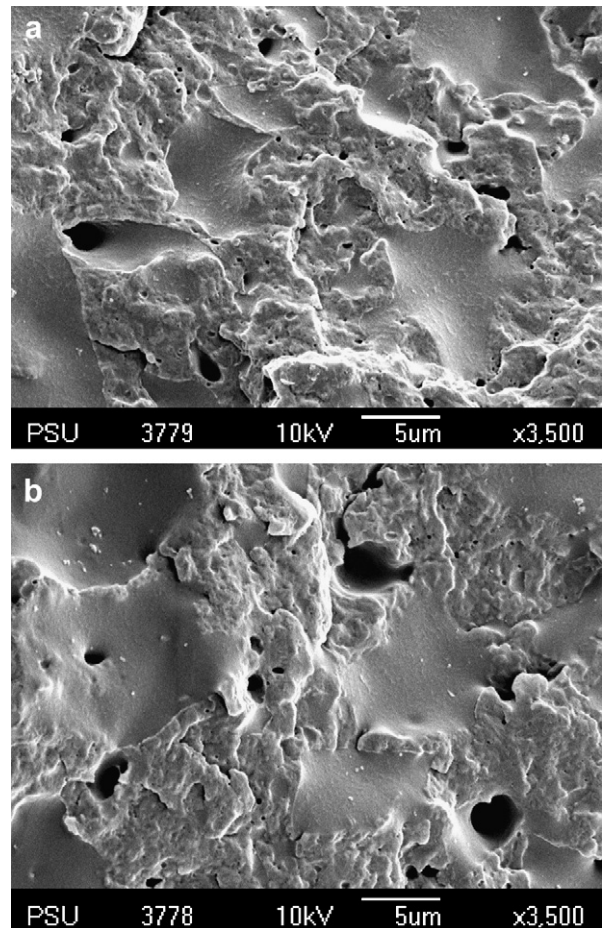
**Fig. 4.** Stress–strain curves of the blends containing un-compounded and compounded ENR.

**Table 6**

Effect of vulcanization on tensile properties and impact strength of the blends containing 30% ENR

Sample	$\sigma_y$ (MPa)	$\varepsilon_y$ (%)	$\sigma_b$ (MPa)	$\varepsilon_b$ (%)	Impact strength (kJ/m <sup>2</sup> )
Unvul. ENR	23.64 ± 0.82	11 ± 1	28.35 ± 4.00	60 ± 10	34.51 ± 6.97
I	30.19 ± 0.95	16 ± 1	48.94 ± 1.25	272 ± 13	19.32 ± 3.48
II	34.51 ± 1.66	13 ± 3	47.00 ± 1.26	154 ± 18	11.22 ± 1.56

properties of the blends are shown in Fig. 4 and Table 6, respectively. Rubber vulcanization improved tensile properties but lowered impact strength of the blends. The co-agent (SR75EPM2M) increased tensile strength but decreased strain at break. Undoubtedly, the co-agent should increase degree of crosslinking. Unexpectedly, the compounded ENR considerably decreased impact strength. This is because of a change in morphology of the blends after rubber vulcanization. A few dispersed ENR particles were observed and the rubber domain appeared as smooth patches, as shown in Fig. 5 (the rougher area belonged to PA6). Interfacial adhesion between nylon and compounded ENR seemed to be very good, contributing to improve



**Fig. 5.** SEM micrographs of the blends containing 30% compounded ENR: no co-agent (a) and 3 phr of co-agent (b).

tensile properties. Unfortunately, the large patches of rubber were unsuitable for good impact resistance.

#### 4. Conclusions

Toughness enhancement of nylon 6 with epoxidized natural rubber has been successfully achieved. The impact strength of the blends increased with ENR content whereas their tensile properties decreased with increasing ENR. Rubber content was the key factor for toughness enhancement. Morphology of ENR was changed from small particles to large patches of rubber after vulcanization. As a result, the compounded rubber provided superior tensile properties but inferior impact strength of the blends in comparison to the uncompounded rubber.

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