

Blends of LNR with Unsaturated Polyester Resin from Recycled PET: Comparison of Mechanical Properties and Morphological Analysis with the Optimum Blend by Commercial Resin

(Adunan LNR dan Resin Poliester Tak Tepu daripada Hasil Kitar Semula PET: Perbandingan Sifat Mekanik dan Morfologi dengan Adunan Optimum daripada Resin Komersil)

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ABSTRACT

In this study, poly(ethylene terephthalate) (PET) wastes bottle was recycled by glycolysis process using ethylene glycol. The unsaturated polyester resin (UPR) was then prepared by reacting the glycolysed product with maleic anhydride. The blend of UPR based on recycled PET wastes with liquid natural rubber (LNR) was carried out by varying the amount of LNR from 0 to 7.5 wt%. Mechanical tests such as tensile and impact were conducted to investigate the effects of LNR on the mechanical properties. Scanning Electron Microscopy (SEM) was used to analyze the morphology of the breaking area resulted from the tensile tests on the UPR and blend samples. From the results, the blend of 2.5 wt% LNR in UPR based recycled PET wastes achieved the highest strength in the mechanical properties and showed a well dispersed of elastomer particles in the sample morphology compared to other blends concentrations. This blend sample was then compared to the optimum blend of LNR with commercial resin through the glass transition temperature value T_g , mechanical strength and morphology properties. The comparison study showed that the T_g for UPR based recycled PET was higher than the value represented from commercial resin due to the degree of crystallinity in the molecular structure of the materials. LNR was found to be an effective impact modifier which gave a greater improvement in UPR from recycled PET wastes structure but not to the commercial one which needs 5% LNR to achieve the optimum properties. Thus, the compatibility between the UP resin based recycled PET and LNR was much better than with the commercial resin.

Keywords: Glycolysis; liquid natural rubber (LNR); recycled PET; unsaturated polyester resin (UPR)

ABSTRAK

Dalam kajian ini, bahan buangan botol minuman poli(etilena tereftalat) (PET) telah dikitar semula melalui proses glikolisis menggunakan etilena glikol. Kemudian, hasil glikolisis telah ditindak balas dengan malik anhidrida bagi menghasilkan resin poliester tak tepu (UPR). Adunan cecair getah asli (LNR) dengan UPR daripada hasil kitar semula PET disediakan dengan mengubah amaun penambahan LNR ke dalam UPR daripada 0 hingga 7.5% mengikut berat. Ujian mekanik seperti ujian tegangan dan hentaman telah dijalankan untuk mengkaji kesan penambahan LNR ke atas sifat mekanik UPR manakala Mikroskopi Elektron Imbasan (SEM) digunakan untuk menganalisis morfologi pada kawasan putus bagi sampel UPR dan adunan selepas melalui ujian regangan. Kajian ini menunjukkan adunan dengan 2.5% LNR dalam UPR daripada hasil kitar semula PET telah mencapai sifat mekanik yang paling tinggi dan mempunyai morfologi partikel getah yang tersebar dengan sekata ke seluruh bahagian matrik berbanding sampel dengan komposisi yang lain. Komposisi adunan ini kemudiannya dipilih untuk dibandingkan dengan sampel optimum adunan LNR dengan UPR komersil melalui nilai suhu peralihan kaca T_g , kekuatan sifat mekanik dan sifat morfologi. Hasil daripada perbandingan menunjukkan, UPR daripada hasil kitar semula PET mempunyai nilai T_g yang lebih tinggi daripada resin komersil kerana dipengaruhi oleh faktor darjah kehabluran dalam struktur molekul bahan tersebut. Penggunaan LNR sebagai bahan modifikasi dalam meningkatkan kekuatan hentaman adalah lebih efektif ke atas resin daripada hasil kitar semula PET berbanding penggunaannya ke atas resin komersil yang memerlukan sebanyak 5% LNR untuk mencapai sifat optimum. Tambahan lagi, keserasian adunan LNR dengan resin UPR daripada hasil kitar semula PET adalah lebih baik berbanding dengan adunan cecair elastomer tersebut bersama UPR komersil.

Kata kunci: Cecair getah asli (LNR); glikolisis; kitar semula PET; resin poliester tak tepu (UPR)

INTRODUCTION

Post consumer PET bottles are left as “plastic waste”, causing an environmental problem since they cannot be degraded by natural processes. One of the effective

solutions to solve this problem is to recycle these plastics via chemical reactions. In regard to PET, it can be depolymerized by glycolysis in excess glycols. The glycolyzed products then can be used as reactants for the

preparation of other polymers such as unsaturated polyester resins (Pimpan et al. 2003).

In order to improve the fracture resistance of UPRs, these resins are usually blended or reacted with different additives or modifiers, which generally form a second dispersed phase after the resin cured. The most frequently used modifiers are liquid rubbers. These rubbers must be blended with the base resin before the curing process and then made to precipitate in a second phase, during the cure from the solution to produce the desired toughening action. The presence of elastomeric domains in the UP resin can increase the absorption and dissipation of mechanical energy. Benny and Eby (2003) reported a research on blends of unsaturated polyester resin with functional elastomer. They had modified the UP resin with various types of elastomer and interestingly, the increase in toughness had been observed with simultaneous increase in tensile strength for all elastomers compared to unmodified resin. This is because during the growth of the crack, the elastomeric particles can cause energy dissipation.

This paper reports a study on the effect of adding liquid natural rubber on the mechanical properties and morphology of UP resin from recycled PET waste bottle. The comparison between the optimum properties of blend samples that was prepared by UP resin from recycled PET waste and commercial UP resin was also reported.

MATERIALS AND METHODS

MATERIALS

PET mineral bottles wastes were collected from a disposal company. Ethylene glycol and zinc acetate were purchased from R&M Chemicals and Riedel-de haën respectively. All reagents were used without further purification. Glycolised product, maleic anhydride (Merck), hydroquinone (Merck) and styrene (Merck) were used for the synthesis of resin from recycled PET. General purpose grade of unsaturated polyester resin was purchased from Revertex Sdn. Bhd. for preparation of blends by commercial resin. Methyl ethyl ketone peroxide (MEKP) (catalyst) and cobalt octoate (accelerator) from the Aldrich Co were used to cure the resin. Liquid natural rubber was prepared from SMR-L grade natural rubber by photochemical oxidation in our laboratory (Ibrahim & Zuriati 1989).

METHODS

The poly(ethylene terephthalate) (PET) wastes bottles was recycled by glycolysis process using ethylene glycol (EG) with the molar ratio of PET:EG of 1:4 (w/w) with 0.5% zinc acetate based on weight of PET as catalyst. The reaction was carried out in nitrogen gas atmosphere at 190-200°C for 8 h (Ahmad et al. 2008). Unsaturated polyester resin (UPR) was then prepared by reacting the glycolised product with maleic anhydride at a fixed molar ratio of 1:1 in nitrogen gas atmosphere at 200°C until the acid value 29-34 (mg KOH/g) achieved in the product. The liquid resin

was then cooled to 12°C and hydroquinone was added in 0.45% by weight of PET in order to prevent premature gelation. Finally the liquid resin was dissolved in styrene monomer at 70°C to achieve a 40% (wt/wt) styrene in the resin (Dayang 2006). Unmodified resin sample (without LNR addition as a control sample) was prepared by methyl ethyl ketone peroxide (MEKP) as a catalyst and by the accelerator cobalt octoate in concentrations of 1.5% (wt) and 0.75% (wt) of the resin respectively to obtain a reasonable gel time. The resin was then poured into the mould and curing was done at room temperature for 24 h, followed by post curing at 60°C for 6 h. The preparation of UP resin/LNR blend was done by adding the LNR to the resin and then the mixture was stirred well for 1 h to produce a homogeneous blend. Curing of the blend was done by following the same procedure for pure UP resin. The amount of LNR was varied from 0 to 7.5% (Benny & Eby 2003). The same methods were applied for the preparation of the blend samples that used commercial UP resin.

ANALYSIS & TESTING

Tensile testing of the specimens had been carried out using an Instron Universal Testing Machine model 5567 according to ASTM D-638-91 at a cross-head speed of 5 mm/min. The impact strength was measured using impactometer model Ceast 6545/0000 according to ASTM 256-90b. To study the morphology of the samples, Scanning Electron Microscope (SEM) (Philips, Model XL30) was employed. Dynamical mechanical analysis (DMA) was used to measure the glass transition, T_g and the loss of rigidity ($\tan \delta$) for the unmodified and the best composition of LNR/UP resin blends samples that showed the optimum properties. The test was run by DMA 7e (Perkin Elmer) according to ASTM D 4065. Measurements were made in flexural geometry, at a 5°C min⁻¹.

RESULTS AND DISCUSSION

MECHANICAL PROPERTIES

The mechanical properties of the samples prepared by using UP resin from PET waste with liquid natural rubber are shown as the tensile strength (Figure 1), tensile modulus (Figure 2) and impact strength (Figure 3).

Tensile strength obtained after the addition of liquid natural rubber showed an increasing value at 2.5% rubber contained in the blend samples. Beyond this point, the addition of more rubber resulted in lowering of tensile strength. This is because LNR in this concentration showed better compatibility with the resin, where the rubber phase was homogeneously dispersed as particles of optimum size which are smaller compared with other samples in the polyester phase. It is known that the liquid natural rubber (LNR) which prepared by photochemical oxidation has functional groups such as hydroxyl (-OH), epoxy (C=O) and carbonyl (C-O) (Ibrahim & Sahrim 1992). These functional groups permit the compatibility through

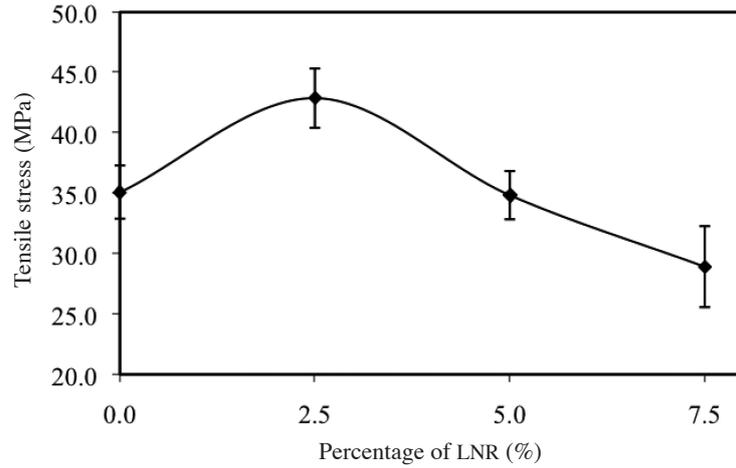


FIGURE 1. Tensile strength of liquid natural rubber modified resin

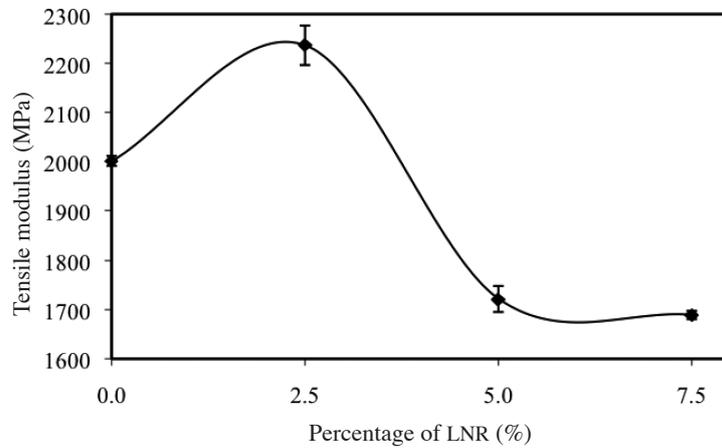


Figure 2. Tensile modulus of liquid natural rubber modified resin

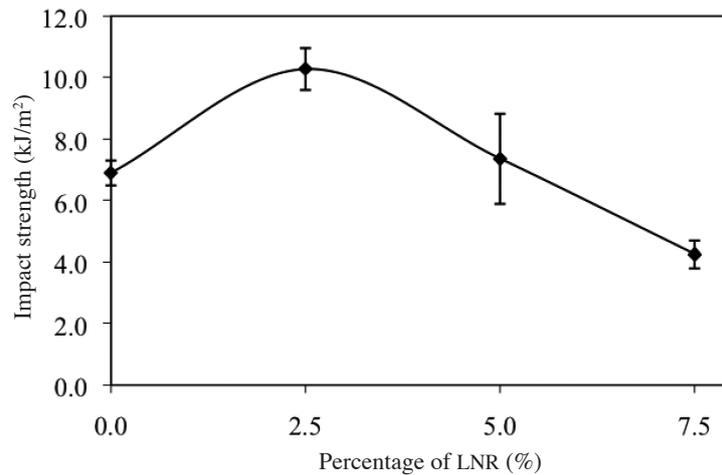


FIGURE 3. Impact strength of liquid natural rubber modified resin

the solubility of the elastomer in the uncured resin to form a homogenous distribution of discrete incompatible elastomeric particles during cross-linking. This rubber phase actually forms with microvoids which exist because of the resin shrinkage that happened during curing process.

The smaller size of microvoids is attributed to the smaller size of the cracking zone. Therefore the presence of large particles in the other samples leads to zones where cracking can pass through easily and reduce the value of the tensile stress (Suspene et al. 1993).

The addition of 2.5% LNR in the UPR also had the greatest value of tensile modulus among the blend samples. From the previous discussion, this LNR concentration had achieved a good adhesion and homogeneous distribution of rubber particles in the blend of UPR/LNR. During the deformation mechanism of the blend sample, there is combination of debonding occurred between internal cavitations of the rubber and the interface bonding of rubber particles with UP matrix interface. The microvoids will enlarge and leads to the cavitations of elastomeric particles before the matrix failure. When there are good interfacial bondings, the stress energy will be effectively transferred from the matrix and dissipated by rubber particles. Ragosta et al. 1999 showed that compatibility of UPR with polybutadiene rubber blend produced a finer and more homogeneous distribution of the particle size together with an improved adhesion between the components. They concluded that this type of morphology increased the fracture toughness because of the energy dissipation by rubber particles in the blend during deformation.

High tensile strength attributes to the increasing of the toughness of the sample's fracture. For the impact strength, blend of 2.5% LNR with UP resin also showed maximum value compared to other percentage of LNR addition. Suspene et al. 1993 had mention that generally, improvements in the fracture impact of thermoset resin can be obtained by dispersing elastomer particles with diameters from 0.5 to 5 μm in the blends. Based on the surface morphology of this sample, the size of elastomer

particles in this blend are less than 10 μm . Rubber which is flexible in fracture was able to act as load-bearing components favouring the initiation and the growth of shear-yielding deformations in the matrix (Huang et al. 1993). After the addition of LNR the deformation of the plastic had shifted from crazing to shier-yielding which contributed by the debonding mechanism as explain in previous discussion. Therefore, the presence of the compatibility elastomeric in the blend had increased the absorption and dissipation of impact energy which prevent the crack propagation in the matrix resin (Benny & Eby 2003).

MORPHOLOGICAL ANALYSIS

Scanning electron microscope (SEM) was used to examine the fractured surface of the liquid natural rubber modified unsaturated polyester resin to reveal the texture and morphology of the phase separated system. It was reported that phase separation between elastomer and matrix resin during the curing is essential, as phase separated blends are tougher than homogeneous blends (Benny & Eby 2003). The fractured surface of all modified UPR showed a two-phase morphology consists of a rigid continuous phase represented by the resin and a dispersed rubbery phase of spherical particles (Thomas et al. 2007). The SEM micrographs for the morphology analysis of the blends that prepared with 0 to 7.5% addition of LNR in the resin from the recycled PET wastes are shown in Figure 4.

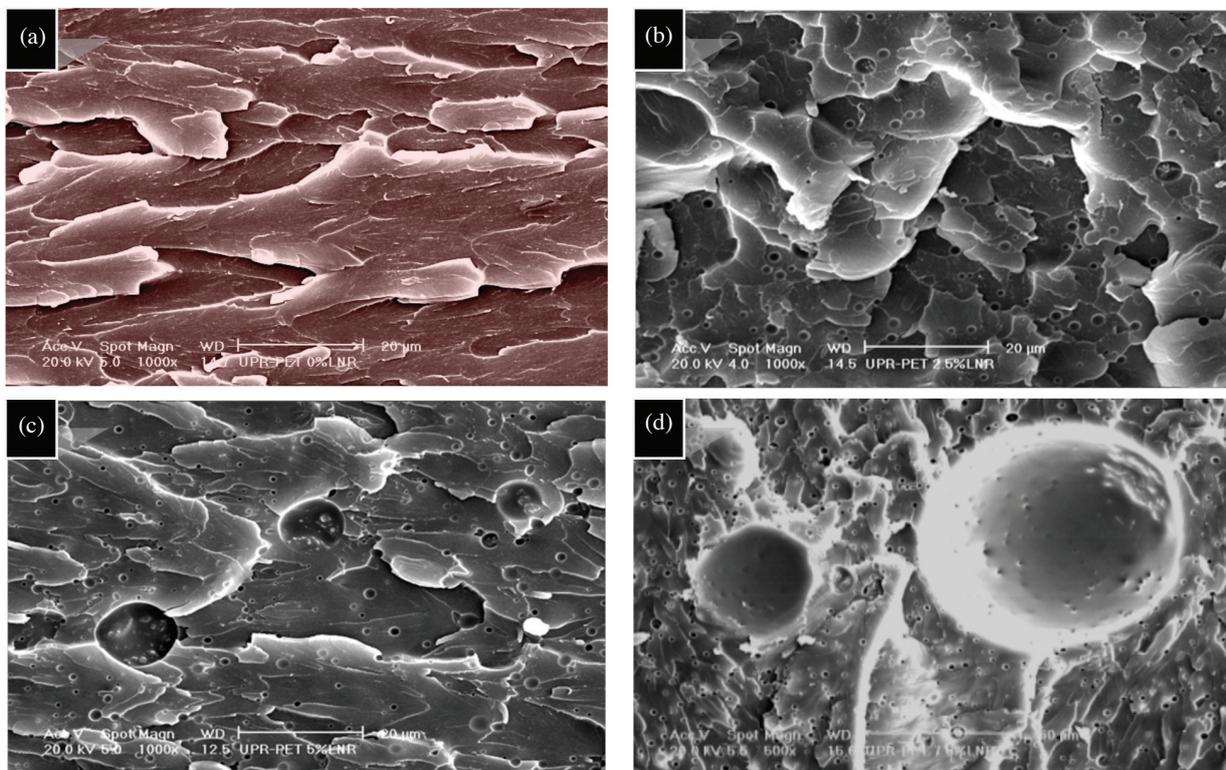


FIGURE 4. SEM micrographs with 1000x magnification for a) 100%UPR, (b) 97.5%UPR/2.5%LNR, (c) 95%UPR/5% LNR and (d) 92.7%UPR/7.5 %LNR

SEM micrograph for pure UPR matrix without addition of LNR is shown in Figure 4(a). The glassy fracture surface in the figure showed more flat ripples which was due to the brittle fracture (Thomas et al. 2007). It also showed that there was no two-phase exist in the morphology of the sample where the resin is completely cured.

SEM micrograph for 2.5% LNR addition in the resin in Figure 4(b) showed a well dispersion of elastomer spherical particles with smaller size (less than 10 μm) compared to other modified UPR samples which show that LNR is compatible with UPR in this concentration. From the figure, there were also microvoids in the rubber phase which caused by the shrinkage during the curing resin process. The fracture for this LNR concentration sample showed a rough surface around the rubbery nodules and also the empty microvoids which resulted from rubber particles pull out and cavitations during the plastic deformation. This indicated that the 2.5% LNR in the UPR had more toughness fracture among the other samples.

The addition of LNR of more than 2.5% attributed to the reduction of the mechanical properties. High concentration of the LNR in the resin increased the size of the elastomer particles due to the further interfacial tension that exist between the phases. The SEM micrograph for 5% and 7.5% LNR blend samples (Figure 4(c) & (d)) revealed that the rubber phases were formed into very large size of microvoids with poor distribution of rubbery particles which attributed to more cracking zone. Moreover the UP matrix around the particles appears rather flat especially for the blend's surface with the addition of 7.5% LNR which indicates the occurrence of a very limited plastic deformation, in accordance with the observed lack of toughness (Ragosta et al. 1999).

COMPARISON WITH THE OPTIMUM SAMPLE BY COMMERCIAL RESIN

The same methods were applied to the commercial resin where the variation of LNR addition from 0 to 7.5 (wt%) had been done to the resin. The optimum blend which showed the highest value in the mechanical properties and compatibility based on morphological properties was chosen among the concentrations. Blend of LNR with commercial resin was found to be optimum at 5% of LNR addition compared to UPR from recycled PET which need

only 2.5% of LNR addition in the resin to achieve optimum properties. The comparison of analysis results between the samples from UPR commercial and UPR from recycled PET are shown in the Table 1.

From the table, dynamic mechanical analysis showed that samples for pure and optimum blend which were prepared by UPR from recycled PET has the highest temperature of glass transition, T_g and low value of damping $\tan \delta$ compared to those samples from UPR commercial. During the analysis, the loading sample experienced transition from a semi-crystalline network to a rubbery state and a maximum in the damping $\tan \delta$ and the temperature of the glass transition, T_g will appear in the DMA plot (Aslan et al. 1997).

Resin based recycled PET by ethylene glycol has a high degree of crystallinity which is due to the regularity of the unsaturated polyester molecules. This resin contained only EG segments that have most regular structure which is easier for the former to form more crystalline regions causing the sample to be opaque compare to the sample made by commercial resin which is translucent due to the amorphous properties (Pimpan et al. 2003). As a result, more heating energy is needed for UPR from recycled PET samples to achieve the glass transition point due to the high degree of semi-crystalline networks that exist in the resin. T_g also related to mechanical properties, such as impact resistance, toughness, loss of rigidity and relaxation. The higher of T_g in the UPR from recycled PET had been supported by the strength of the mechanical properties where the samples prepared by UPR from recycled PET are tougher than the samples made from UPR commercial.

Another factor that contributed to the toughness of the blend UPR from recycled PET with LNR is the compatibility between the two components. The comparison of morphological analysis for the optimum blends in the commercial resin and resin from recycled PET with LNR showed that LNR has achieved a homogenous distribution with small size of particles in the resin prepared from recycled PET. However, the optimum amount of LNR addition which is 5% (wt/wt) in the commercial resin create a large size of particle which reduced the toughness of the resin as mention in the discussion for tensile strength section.

TABLE 1. Comparison of analysis results between unmodified and optimum (%wt) of LNR addition in blend samples for UPR-PET and UPR-C

Analysis	UPR-PET		UPR-C	
	Unmodified resin	Optimum (wt%) LNR/UPR blend	Unmodified resin	Optimum (wt%) LNR/UPR blend
DMA				
T_g ($^{\circ}\text{C}$)	106.69	101.82	81.57	65.23
$\tan \delta$	0.248	0.224	0.368	0.390
Tensile Strength (MPa)	35.10	42.88	32.54	35.00
Impact Strength (kJ/m^2)	7.85	10.28	6.90	7.54

*UPR-PET: UP resin from recycled PET and UPR-C: Commercial UP resin

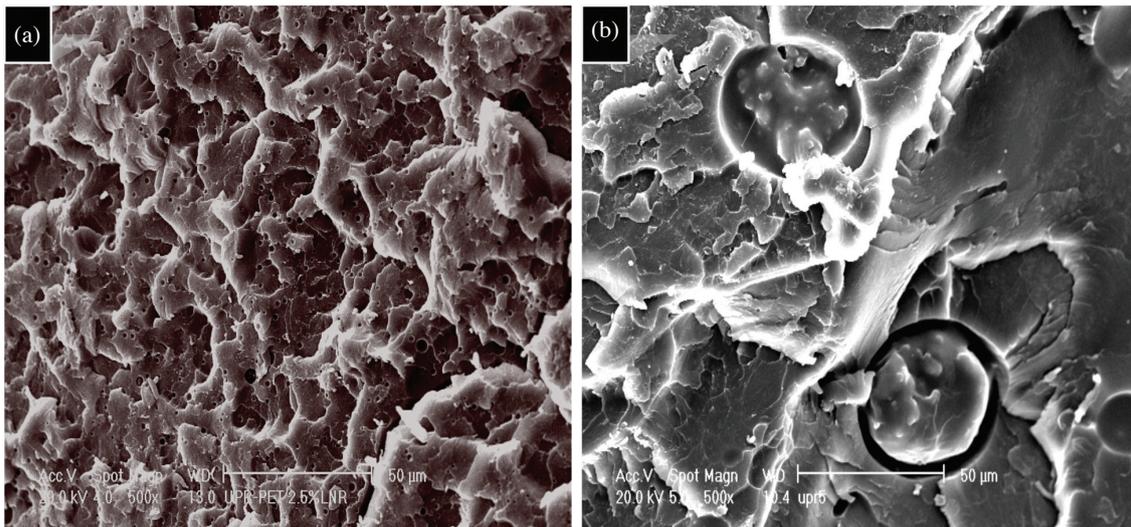


FIGURE 5. Comparison of morphological analysis between optimum (wt%) addition of LNR in (a) UP resin from recycled PET and (b) Commercial UP resin by SEM micrograph with 500x magnificant

CONCLUSIONS

The unsaturated polyester resin had been successfully prepared from PET waste which can be recycled by glycolysis process. The mechanical properties of the UPR can be improved by introducing the LNR. Based on the mechanical and morphological properties, 2.5% of LNR was the optimum composition in the blend sample for the resin from recycled PET while 5% of LNR is needed for the commercial resin. Different rubber content will result in different morphologies. The morphological analysis also showed that the addition of small amount of LNR produced a finer and more homogeneous distribution of the smaller particle together with an improved adhesion at the phase boundary. The comparison between the optimum blends which was based on the mechanical and morphological analysis from the resin prepared with the commercial one showed that LNR acts as an effective modifier for the UPR based on recycled PET but not in the commercial resin. Further study can be done to investigate in details the influence of the compatibility for blend of liquid natural rubber with unsaturated polyester resin through thermodynamics and kinetics study.

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