

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Gel fraction of TPEs

Degree of crosslinking of shoe sole scrap was determined by its gel fraction. Typically as the gel fraction decreases the degree of crosslinking decreases. Fig. 4.1 presents the gel fraction and swelling ratio of microwave devulcanized shoe sole scrap at various devulcanizing time as a function of microwave power. It can be seen that the gel fraction of SSS decreased with increasing microwave power. Similarly, an increase in the devulcanizing time of shoe sole scrap caused a decrease in the gel fraction. Particularly, a higher microwave power and devulcanizing time, more devulcanization obviously took place, as indicated by the lower in gel fraction simultaneously indication the reducing degree of crosslinking of shoe sole scrap. The decrease in gel fraction was because the large network structure of shoe sole scrap started to break down into a small network structure.

This result is in good agreement with the work studied by D.W. Kim et al. in 2002.[21] In their work, the effect of electron beam on the gel fraction of vulcanized rubber was investigated and the results should that electron beam irradiated at higher irradiation dose can reduce the gel fraction of low density polyethylene (LDPE)-ethylene vinylacetate copolymer (EVA) foam.

Based on this result (Fig 4.1), it was 450 watt for 60 or 90 sec that the devulcanized shoe sole scrap yielded the lowest gel fraction compared to the other conditions. Nevertheless, it was found that at these conditions the shoe sole scrap was degraded and burnt. Likewise at lower condition, 360 watt for 90 sec, the shoe sole scrap was also burnt. This was probably due to the overheating of shoe sole scrap at higher power and/or longer period of time. Therefore, the optimum condition of microwave energy for devulcanization of shoe sole scrap was 360 watt for 60 sec since this condition provided the shoe sole scrap with lowest gel fraction without degradation or burning.

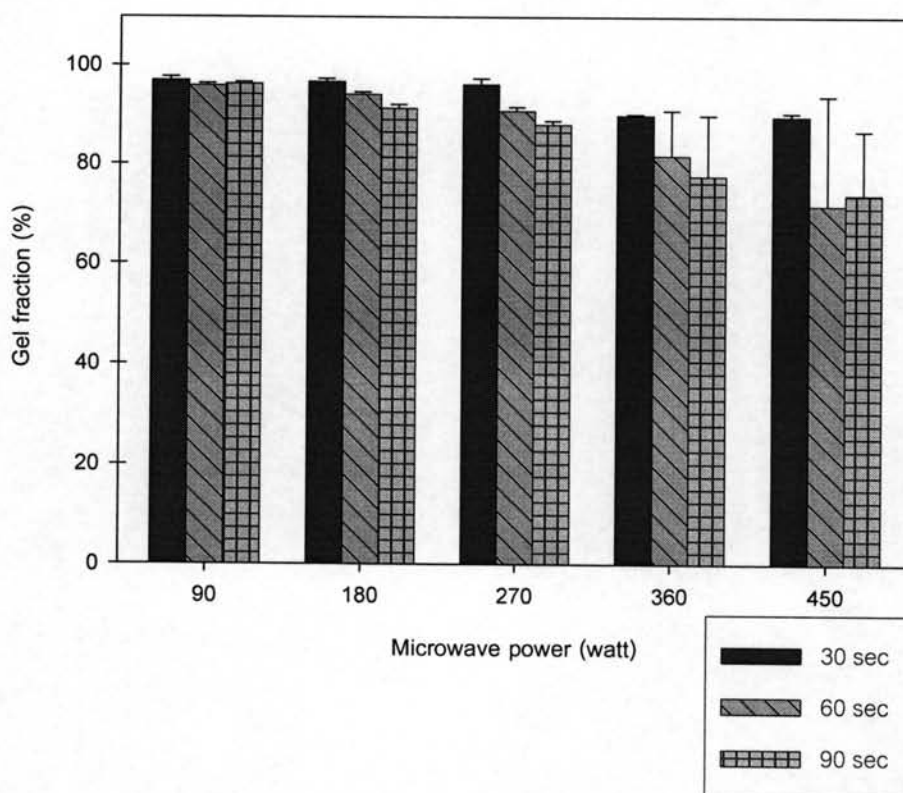


Fig. 4.1 The effects of microwave energy on gel fraction of shoe sole scrap was compounded with carbon black at various microwave power and devulcanizing time.

#### 4.2 Swelling ratio of TPEs

From Fig. 4.2, the swelling ratio of devulcanized shoe sole scrap as a function of microwave power at different devulcanizing time was presented. The swelling ratio is a direct measurement of the degree of crosslinking. Typically, as the swelling ratio increase the degree of crosslinking decreases, and vice versa. However, unexpectedly, it was observed from this figure that the swelling ratio slightly decreased with increasing microwave power. Even though it seemed to be that the swelling ratio increased when the devulcanizing time increased, particularly, at the lower microwave power. This result was similar to the work done by D. De et al[7] that the swelling ratio of reclaimed rubber increased with increasing milling time because of breakage of crosslinks bonds during milling time.

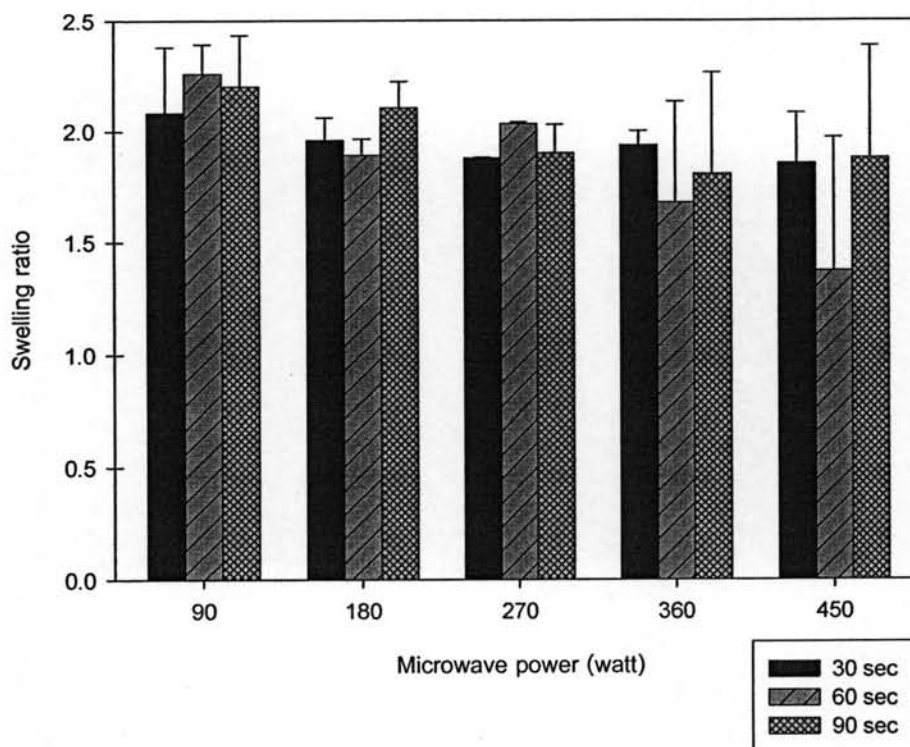
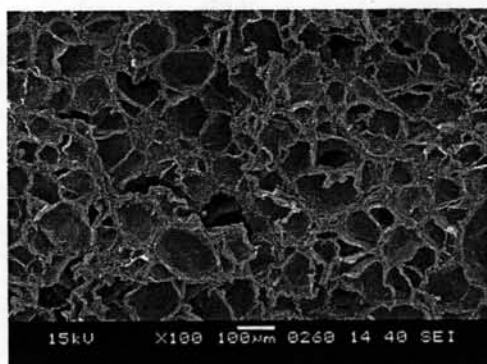


Fig. 4.2 The effect of microwave energy on swelling ratio of microwave power and devulcanizing time.

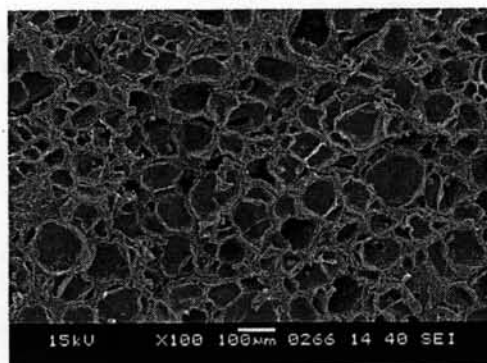
#### 4.3 Morphology of devulcanized shoe sole scrap

The SEM micrographs of the SSS, and SSS devulcanized at 270 watt and 360 watt for 60 sec are presented in Fig. 4.3(a), (b), and (c), respectively. As seen in Fig. 4.3(a), the structure of shoe sole scrap is a foam composite consisting of natural rubber (NR), low density polyethylene (LDPE), and ethylene vinyl acetate (EVA). The bound cells of SSS showed plastic fracture that is act ribbon-like, which implied that SSS is tough material. From Fig. 4.3(b), the cellular structures of devulcanized SSS at 270 watt 60 sec was smaller than those of the SSS due to the melting of thermoplastic phase(LDPE and EVA). Moreover, the bound cell at this condition had lower amount of ribbin-like than SSS because the elasticity of devulcanized SSS was reduced. Fig. 4.3(c) represented the micrograph of devulcanized SSS at 360 watt 60 sec. It can be seen that the overall of cell diameter was reduced. Also, the bound of cell shown no ribbin-like. The surface was smooth like a brittle material. From those results, it can be said that microwave power, resin in SSS was melt because this resin has poor high temperature extensibility resulting in the lower in the degree of crosslinking.

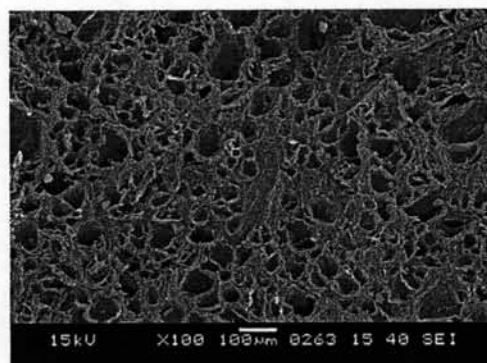
Besides the influence of microwave power, the SEM micrographs of SSS and devulcanized SSS at 360 watt for 30, 60, and 90 watt are presented in Fig. 4.4(a), (b), (c) and (d). Similar to the effect of microwave power, when the devulcanizing time increased, the overall of cell diameter was reduced, although it was not as obvious as compared to the effect of microwave energy. In addition, the devulcanized SSS at 360 watt for 60 and 90 sec(Fig. 4.4(c) and (d)) had some small particles in the structure because microwave energy damaged SSS resulted in the reduction of the degree of crosslinking. These micrographs can confirm the results of the gel fraction as described in the previous section.



(a)



(b)



(c)

Fig. 4.3 Morphology of (a) non-devulcanized SSS and microwave-devulcanized SSS at 270 watt 60 sec (b) and (c) 360 watt 60 sec.

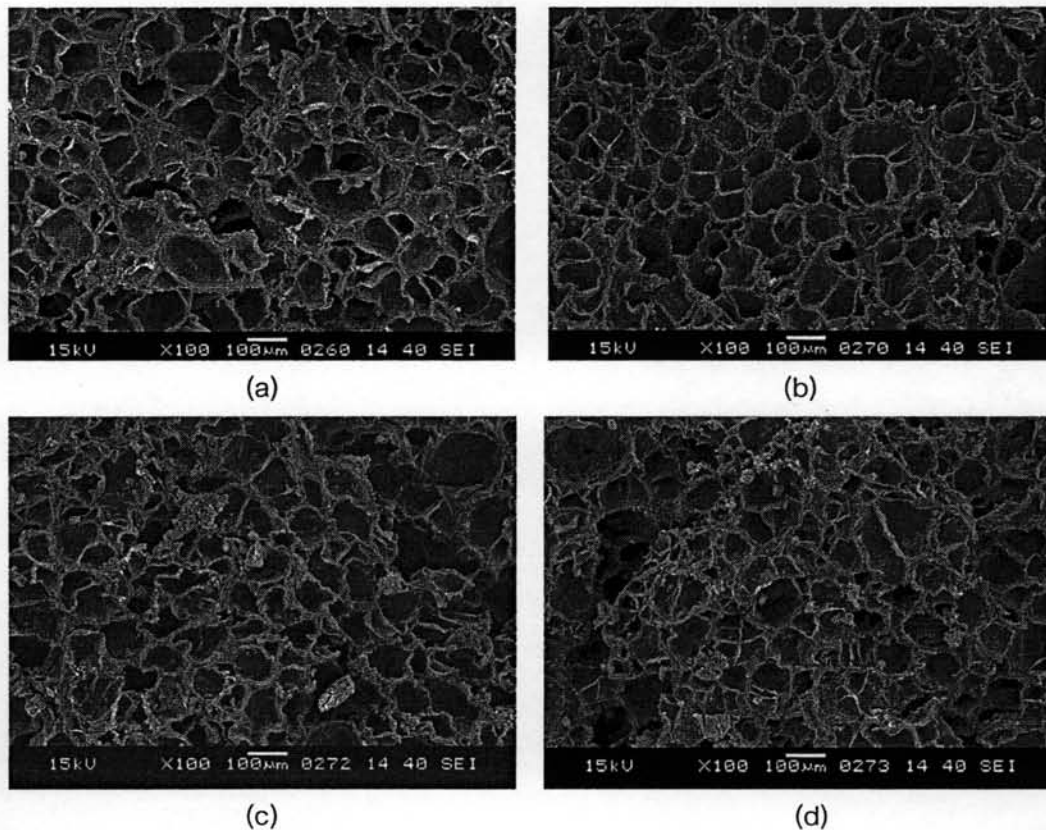


Fig. 4.4 Morphology of shoe sole scrap (a) non-devulcanized SSS (b) devulcanized SSS at 360 watt 30 sec (c) devulcanized SSS at 360 watt 60 sec and (d) devulcanized SSS at 360 watt 90 sec.

#### 4.4 Mechanical properties

##### 4.4.1 Tensile properties

Tensile properties of materials, primarily yield strength and tensile strength, are generally considered the most fundamental mechanical properties.

Tensile testing is performed by elongating a specimens and measuring the load carried by the specimen. From a knowledge of specimen dimensions, the load and deflection data can be translated into a stress-strain curve. A variety of tensile properties can be extracted from the stress-strain curve. The data is often used to specify material, to design parts, to determine elongation and tensile modulus.

In this research, tensile dumbbell specimens were cut from the 2 mm thick sheets and tested by a Lloyd universal testing machine model LR 100K according to the ISO 37 standard at a crosshead speed of 500 mm/min. The processing parameters during reclaiming



(i.e., the amount of LDPE content, microwave energy (360 watt 60 sec), and TMTD as reclaiming agent (2.75 phr)) are found to have a pronounced effect on the tensile properties of TPEs and the results are as follows.

#### 4.4.1.1 Effect of low density polyethylene (LDPE) content.

The stress-strain curves of TPEs at various LDPE contents are shown in Fig. 4.5. It is evident from the figure that, at 100:0 SSS/LDPE TPEs behaved like a weak brittle material as the large SSS particle made an easy way for the propagation of cracks and led to a lower in the mechanical properties compared to the others. [26] Upon the addition of LDPE, the deformation pattern changes drastically, particularly for the strain or elongation at break. The weak brittle material gradually changed to a strong tough one as a result of characteristic properties of LDPE. The addition of LDPE resulted in the incorporation of LDPE into TPEs and thereby the co-continuous phase in TPEs. This result proved that polymer blending can improve deficient properties of some traditional polymers, namely reclaim rubber in this case.

The effects of LDPE content on tensile strength, elongation at break, and 50% modulus of TPEs are shown in Figs. 4.6, 4.7, and 4.8, respectively. The tensile properties improved rather continuously as the LDPE content increased. This result was expected because as more LDPE content was incorporated into the rubber matrix, the plasticity of the rubber chain was increased, resulting in the improved toughness of TPEs.

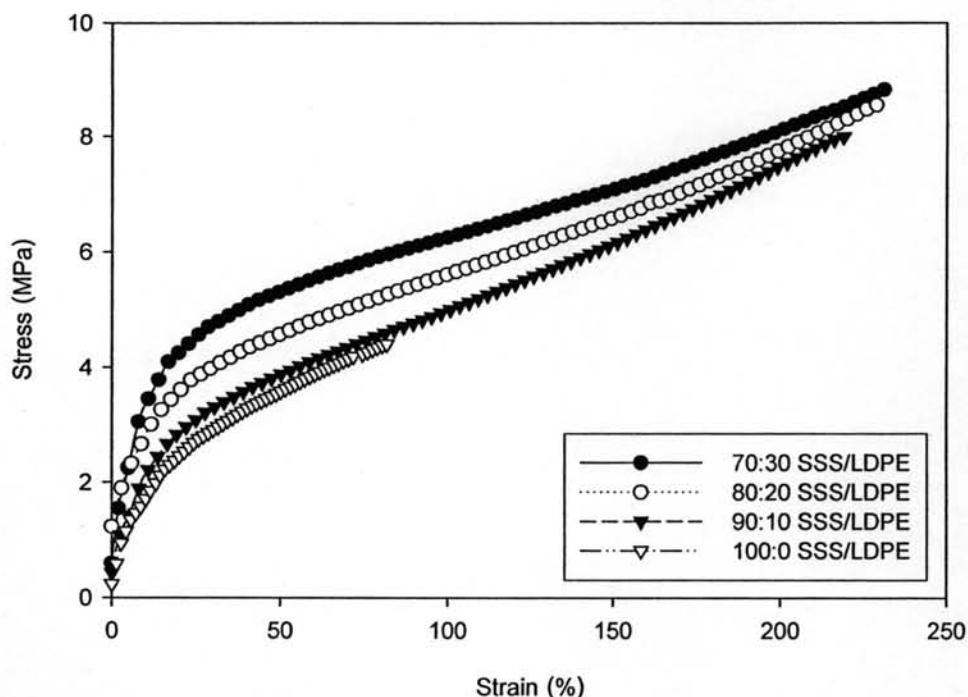


Fig. 4.5. Stress-strain plots of SSS/LDPE TPEs at various LDPE content.

#### 4.4.1.2 Effects of microwave devulcanization.

The effects of microwave power on tensile properties of TPEs are shown in Fig. 4.6, 4.7, and 4.8, respectively. The tensile strength and elongation at break of non-devulcanized shoe sole scrap(SSS/LDPE) TPEs is higher than those of microwave devulcanized shoe sole scrap(M-SSS)/LDPE TPEs. However, the change in 50% modulus was not significant; in other words, microwave energy seemed to have no effect on the tensile modulus of TPEs. The lower in the tensile strength and elongation at break of M-SSS/LDPE TPEs may be due to the decrease in the degree of crosslinking of shoe sole scrap at higher microwave energy. That is, plasticity of SSS increased when the degree of crosslinking decreased resulting in lower extensibility. In addition, the SSS particles in TPEs had poor interfacial adhesion with the LDPE phase because SSS was degraded by microwave energy.



#### 4.4.1.3 Effects of TMTD

The influence of TMTD as a reclaiming agent on the tensile properties of SSS/LDPE TPEs is presented in Fig. 4.6, 4.7, and 4.8, respectively. The tensile strength and 50% modulus of SSS/LDPE TPEs filled TMTD as a reclaiming agent were higher than those of unfilled TMTD-SSS/LDPE TPEs. The increase in both tensile strength and 50% modulus with TPEs filled TMTD was due to crosslinking reaction occurring during process when TMTD was added as a reclaiming agent into SSS. TMTD formed crosslink bonds between polymer chains during reclaiming process and consequently increased the tensile strength and 50% modulus. In addition, TMTD can generate free radical and breakdown the long polymer chain into the shorter ones.

Reaction in Fig. 4.9 shows the proposed mechanism to explain crosslinking reaction. During milling, vulcanized rubber samples undergo tremendous mechanical shearing, resulting in random polymer chain breakdown. Then the TMTD also breaks into radicals as the temperature rises due to mechanical shearing. These radicals combine with broken polymer chain radicals and thereby prevent the recombination of polymer radicals. When reclaiming of SSS was carried out in the presence of TMTD on an open two-roll mill, the tremendous mechanical shearing forces broken both polymer chain and crosslink bonds simultaneously with breaking of TMTD to form thiocarbamate radicals shown in Scheme 1.

Simple aliphatic disulfide have bond strengths of the order of -70 kcal/mol in the central S-S bond as well as in the C-S bond, which is too high for appreciable thermal dissociation into radicals at moderate temperatures.

In thiuram disulfides, potential resonance stabilization of the radicals should appreciably weaken the central bond and facilitate the formation of the thiocarbamate radical.

Initially this thiocarbamate radical may combine with a broken polymer radical (shown in Scheme 2). But with progress of milling no more thiocarbamate radicals are available to combine with broken polymer radicals.

As a result, end capping of the shear generated low molecular weight radicals by the thiocarbamate radicals gradually decreases with milling. Therefore, such

fragmented uncapped polymer radicals may couple themselves, leading to chain extension (molecular weight increases) during final part of milling (shown in Scheme 3).

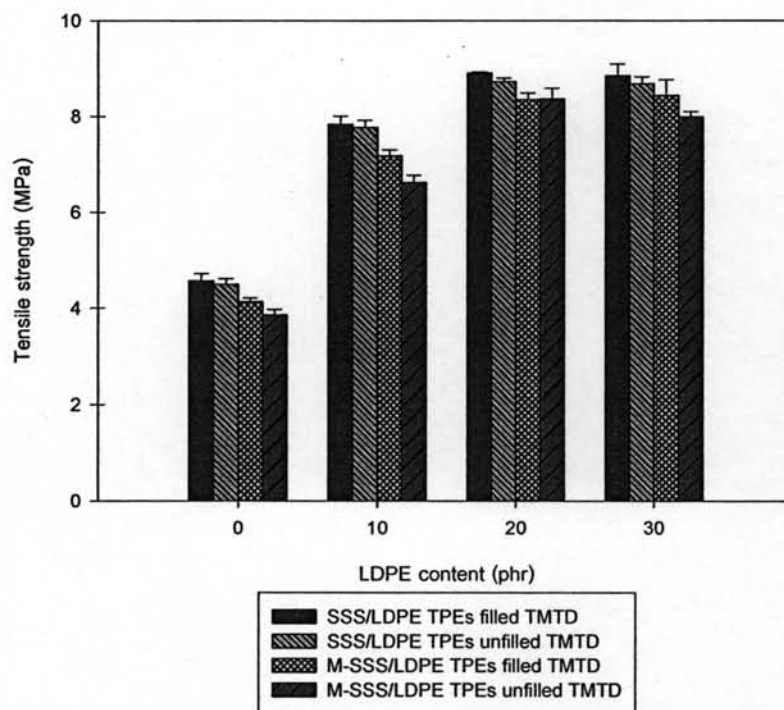


Fig. 4.6 Effects of microwave energy and TMTD as reclaiming agent on tensile strength of TPEs at various LDPE content.

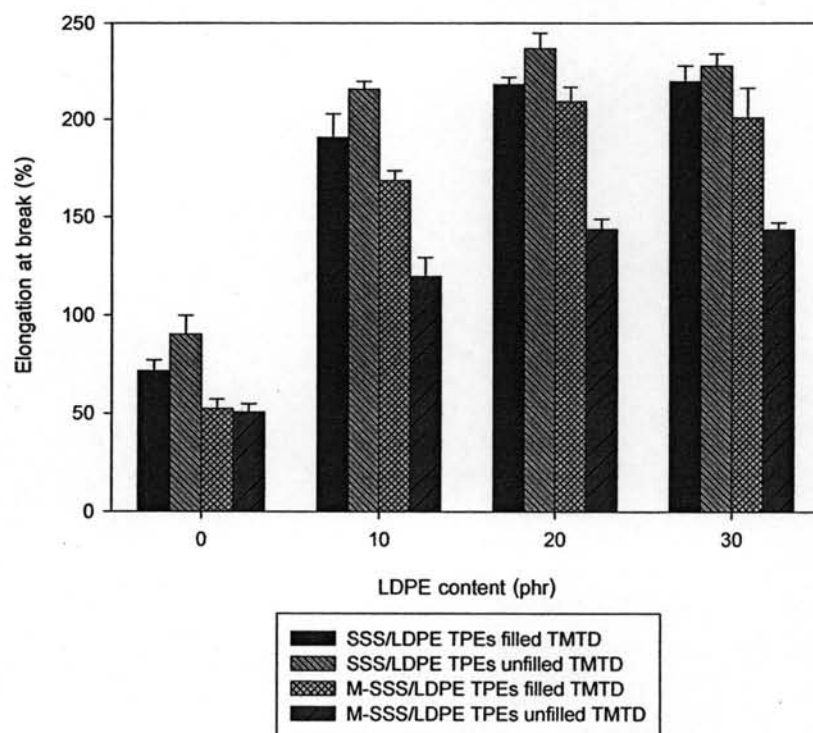


Fig. 4.7 Effects of microwave energy and TMTD as reclaiming agent on elongation at break of TPEs at various LDPE content.

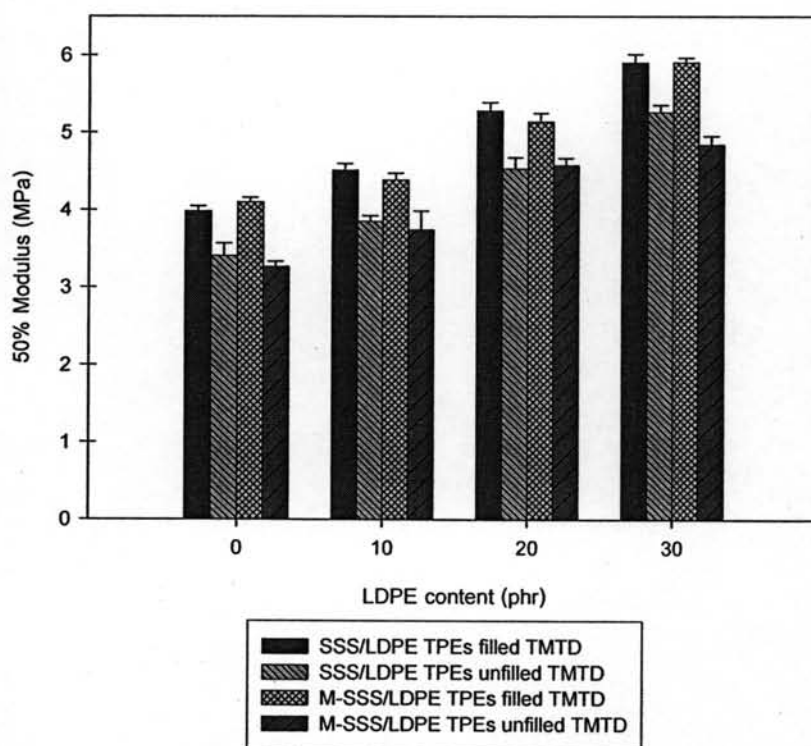
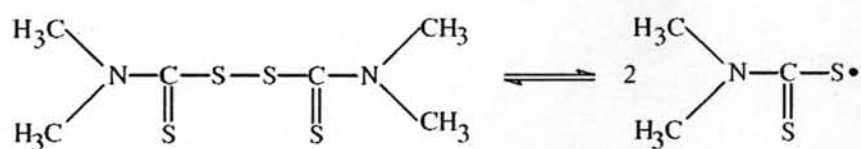
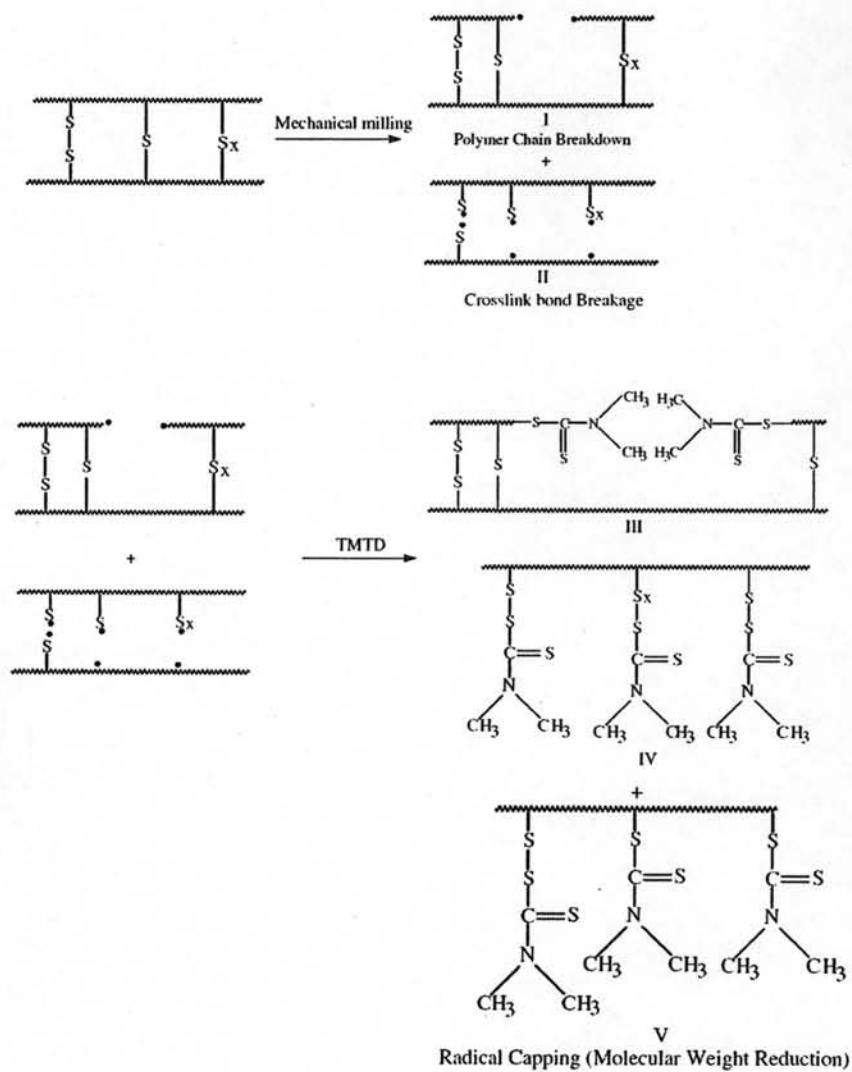


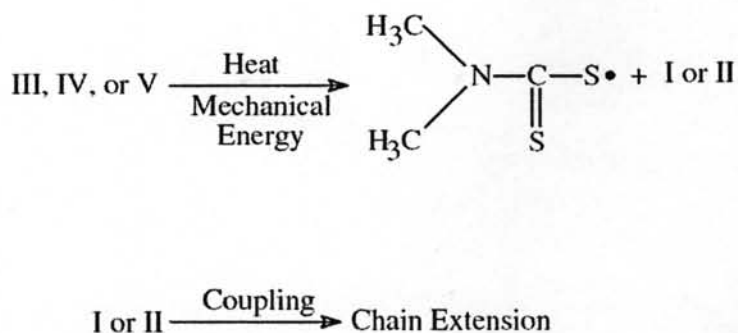
Fig. 4.8 Effects of microwave energy and TMTD as reclaiming agent on 50% modulus of TPEs at various LDPE content.



Scheme 1



Scheme 2



Scheme 3

Fig. 4.9 Mechanism of chain branching or crosslinking of TPEs during reclaiming process. [7]

For elongation at break, Fig. 4.7 shown that the elongation at break of TMTD-filled SSS/LDPE TPEs was lower than those of unfilled SSS/LDPE TPEs due to chain extension. This result meant that the SSS was more stiffer and harder. As a result, the lower elongation at break was obtained when mixing with TMTD 2.75 phr.

In contrast, microwave energy affected the elongation at break of M-SSS/LDPE TPEs in different way. The addition of TMTD helped promoting the elongation at break values of M-SSS/LDPE TPEs. Obviously, as seen in this figure M-SSS/LDPE TPEs filled TMTD had higher elongation at break than the unfilled ones. This observation might be due to the crosslink reaction of rubber-rubber. Because SSS was partially devulcanized before mixing with LDPE; thus, the amount of free radicals of SSS were increased. As a result, TMTD can highly react with those radicals, resulting in the increase crosslinking reaction into TPEs.

#### 4.4.2 Tear strength

Tear strength is the resistance to failure of a material when it is subjected to continuous stretching. [23] A great deal of effort has been devoted to understand the mechanism of tearing and to find various approaches to control it. In general, it is well known that higher tear resistance means better toughness. Table 4.1 showed the tear strength of TPEs at various LDPE content. It can be seen that the tear strength of TPEs increased with increasing LDPE content. This result implied that the toughness of TPEs increased with increasing the amount of LDPE which is due to the ductility from LDPE phase.

For the effect of microwave energy, it was shown that microwave energy directly affected on the tear strength of TPEs containing 0 phr of LDPE. Clearly, the tear strength of microwave-devulcanized shoe sole scrap (M-SSS TPEs) was lower than that of non-devulcanized shoe sole scrap TPEs. However, upon increasing LDPE content, it seemed that microwave energy had no effect on the tear strength. The lower in tear strength of microwave-devulcanized shoe sole scrap was attributed mainly to the degradation and reduction in elasticity of the shoe sole scrap caused by microwave energy. Nevertheless, when increasing the amount of LDPE, tear strength of both non-devulcanized and microwave devulcanized shoe sole scrap/LDPE TPEs were seemingly equal. This result implied that the LDPE phase predominantly influenced on the tear strength of TPEs.

The effect of TMTD as a reclaiming agent on tear strength of TPEs was also presented in Table 4.1. As shown, there was no effect of TMTD on tear strength of SSS/LDPE TPEs except for M-SSS/LDPE TPEs containing 0 phr of LDPE. The addition of TMTD caused a reduction in the tear strength of M-SSS/LDPE TPEs. This observation might be resulted from the chain scission of SSS chain due to microwave energy and TMTD.

From these results, it can be said that both microwave energy and TMTD had direct or synergistic effects on the tear strength of SSS. As seen, microwave energy can reduce the tear strength of unfilled TMTD-SSS from 31.50 kN/m to 28.59 kN/m. Then, with the addition of 2.75 phr TMTD, tear strength was further decreased to 25.59 kN/m. Thus, the lowest tear strength was obtained when microwave energy and a reclaiming agent were employed simultaneously.



Table 4.1 Tear strength of SSS/LDPE thermoplastic elastomers

LDPE content (phr)	Tear strength (kN/m)			
	Non-devulcanized SSS		Microwave-devulcanized SSS	
	unfilled TMTD	filled TMTD	unfilled TMTD	filled TMTD
0	31.50	31.61	28.59	25.59
10	36.77	36.18	36.07	36.81
20	46.10	44.74	44.20	43.65
30	49.52	48.56	49.63	48.30

#### 4.5 Physical properties of TPEs

##### 4.5.1 Hardness

Table 4.2 shows the effect of microwave energy and TMTD on the hardness of TPEs. Obviously, the hardness of the TPEs increased with increasing LDPE content. In other words, TPEs become stiffer and harder as the amount of LDPE content increased. This is because as more LDPE phase get into the shoe sole scrap, the elasticity of the rubber chain is reduced, resulting in more rigid TPEs.

For the effect of microwave energy, it was found that microwave energy had no effect on the hardness values of TPEs. The hardness values of TPEs containing non-devulcanized shoe sole scrap (SSS) and microwave devulcanized shoe sole scrap were similar. However, TMTD as a reclaiming agent had some effects on the hardness values of TPEs.

The hardness value of TPEs filled TMTD was slightly greater than those of unfilled TPEs. This might be due to the crosslink formation between rubber-rubber and rubber-plastic. This result is similar to the work done by D. De et al. who investigated the effect of TMTD on hardness values of ground tire rubber [7]. From their work, it was found that the hardness value of ground tire rubber slightly increased with increasing the concentration of TMTD due to higher crosslink density of reclaim rubber vulcanizate.

Table 4.2 Hardness of SSS/LDPE thermoplastic elastomers

LDPE content (phr*)	Hardness (IRHD)			
	Non-devulcanized SSS		Microwave-devulcanized SSS	
	unfilled TMTD	filled TMTD	unfilled TMTD	filled TMTD
0	81.4	80.5	80.0	81.0
10	86.6	87.3	84.3	87.7
20	90.7	91.5	90.7	91.6
30	92.4	93.8	92.3	93.8

#### 4.5.2 Abrasion

The abrasion of elastomers involves complex processes such as microcutting and tearing, crack growth, fatigue, and thermal and oxidative degradation. Depending on the type of polymers and the conditions of abrasion, any one of the above factors may play a prominent role in the failure of the sample by abrasion. Hence, the abrasion resistance is related to the strength of the matrix, resistance to thermo-oxidative degradation, crack growth resistance under dynamic conditions, frictional force and the nature of the abrasive.[27]

The basis of fatigue wear is failure of the surface layer of rubber as a result of manifold deformations. The frictional wear of elastomers is characterized by vertical ridge formation and subsequent removal of the ridges in the course of abrasion.

According to the tensile strength and elongation at break, the TPEs containing 20 phr of LDPE was chosen to evaluate the abrasion resistance of SSS/LDPE TPEs. Abrasion resistance of TPEs at 20 phr of LDPE content, expressed as abrasion loss was presented in Table 4.3. The higher in the volumes mean higher abrasion loss or lower abrasion resistance of material. The results showed that abrasion resistance of SSS/LDPE TPEs tended to be better than M-SSS/LDPE TPEs. This observation might be due to the degradation of shoe sole scrap phase which reduced the matrix strength resulting in an increase in the rate of wear. In the case of M-SSS, the increase in abrasion resistance (lower abrasion loss) of the TMTD filled TMTD TPEs as compared to the unfilled TPEs was due to crosslinking reaction between rubber-rubber phase and rubber-plastic phase which increased the matrix strength.

For non-devulcanized SSS, however, the decrease in abrasion resistance (higher abrasion loss) of the TPEs filled TMTD comparing to the unfilled TPEs was observed. Similar reason to the elongation at break can be used to explain this result. Since TMTD can

break polymer chain of SSS into the shorter ones resulting in the decrease in the elasticity or increase in the stiffness and hardness of SSS; as a result, an increase in the abrasion loss can be obtained.

Table 4.3 Abrasion resistance of SSS/LDPE thermoplastic elastomers at 20% LDPE content

LDPE content (phr)	Abrasion loss (mg/1000 cycle)			
	Non-devulcanized SSS		Microwave-devulcanized SSS	
	unfilled TMTD	filled TMTD	unfilled TMTD	filled TMTD
20	108	114	118	115

## 4.6 Morphology

Morphology is a major determinant of the properties of heterogeneous polymer blends. For example, a large particle size and weak adhesion would result in poor mechanical properties in the blends. The main physical factors that determine the final morphology of the blends are component ratio, their intrinsic melt viscosity, rate of shear during melt mixing, and the presence of other ingredients.

### 4.6.1 Morphology of SSS/LDPE TPEs at various LDPE content.

Scanning electron micrographs (SEM) of tensile fractured surfaces of SSS/LDPE TPEs unfilled TMTD at various LDPE content are shown in Fig. 4.10. It is evident from the micrograph that the addition of LDPE increased the plastic deformation of SSS/LDPE TPEs. The failure surface of SSS/LDPE TPEs at higher LDPE content showed ductile failure with a high extent of plastic deformation, as evidenced by the presence of fibrillar structure and peaks. The presence of voids in the surface is associated with the detachment of the dispersed rubber phase from the plastic matrix.

On the basis of the above analysis, the incorporation of LDPE markedly promotes not only the plastic deformation of the matrix but also the deformation of the matrix around shoe sole scrap particles (i.e., non-devulcanized SSS part). [26] Therefore, greater toughness is expected with increasing the amount of LDPE in SSS/LDPE TPEs.

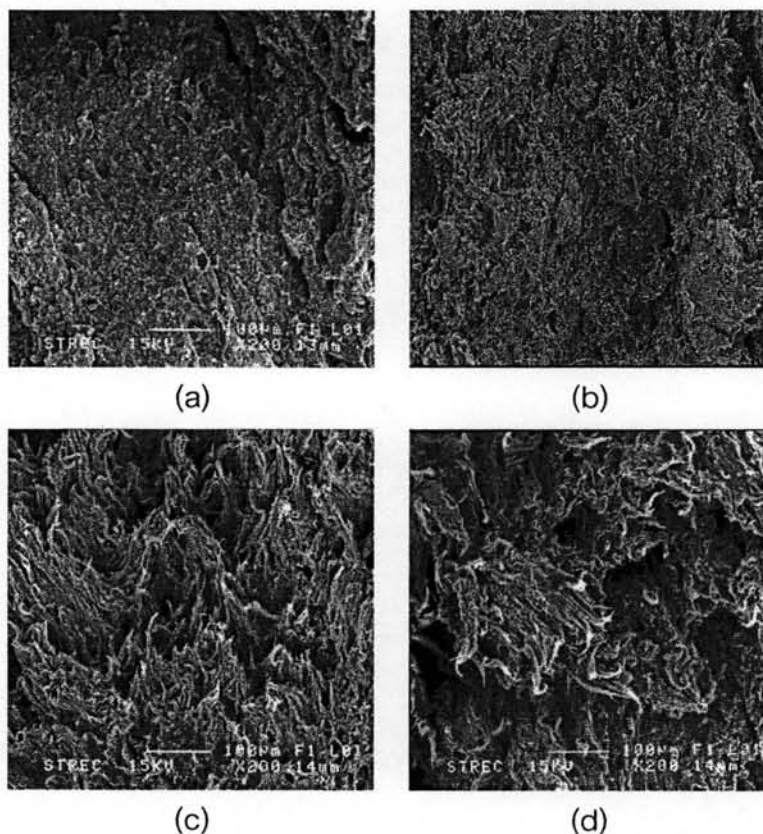


Fig. 4.10 SEM micrographs of tensile fracture surface of TPEs at various LDPE content (shoe sole scrap/LDPE) (a) 100:0 (b) 90:10 (c) 80:20 (d) 70:30

#### 4.6.2 Comparison morphology of TPEs between M-SSS/LDPE and SSS/LDPE

SEM micrographs of tensile fractured of the non-devulcanized TPEs (SSS/LDPE TPEs) and microwave devulcanized TPEs (M-SSS/LDPE TPEs) are shown in Fig. 4.11(a) and (b), respectively. There was greater amount of plastic deformation of the matrix in the SSS/LDPE TPEs than in the M-SSS/LDPE TPEs. In other words, the failure mechanism of non-devulcanized (SSS/LDPE) TPEs showed ductile behavior, whereas the microwave-devulcanized (M-SSS/LDPE) TPEs exhibited brittle failure. This result was in good agreement with the tensile properties as discussed previously. Microwave energy generated heat to shoe sole scrap, as a result its elastic properties were reduced or the plasticity properties were increased. Additionally, microwave-devulcanized shoe sole scrap can be melted into LDPE phase which then reduced the natural properties of LDPE resulting in the reduction of the extent of plastic deformation.

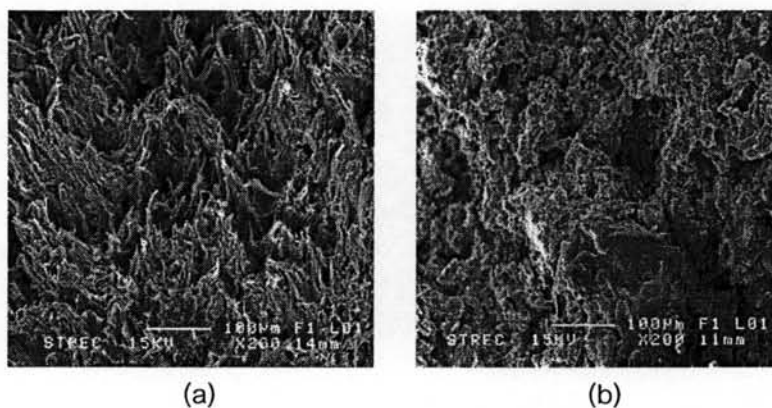


Fig. 4.11 SEM micrographs of tensile fracture surface of 80:20 SSS/LDPE TPEs (a) non-devulcanized TPEs (b) microwave-devulcanized TPEs.

#### 4.6.3 Comparison morphology of TPEs between SSS/LDPE filled and unfilled TMTD

Fig. 4.12(a) and (b) showed SEM micrographs of the SSS/LDPE TPEs unfilled and filled TMTD, respectively. Obviously, the addition of TMTD as a reclaiming agent affected to the morphology of SSS/LDPE TPEs. The fractured surface of SSS/LDPE TPEs filled TMTD was smoother and uniform in the continuous matrix in the blends. That is, TMTD can be used to improve compatibility of SSS phase and LDPE phase, as evidenced by the absence of fibrillar structure and peaks.[27]

Regarding the tensile properties, the compatibility between phases can be used to support the increment in tensile strength and 50% modulus (Fig. 4.6 and 4.8) of the SSS/LDPE TPEs filled TMTD compound to the unfilled TPEs. Nevertheless, similar to the effect of microwave power, TMTD caused the reduction in the elongation at break (Fig. 4.7), as evidenced by the brittle failure of the filled TMTD TPEs.



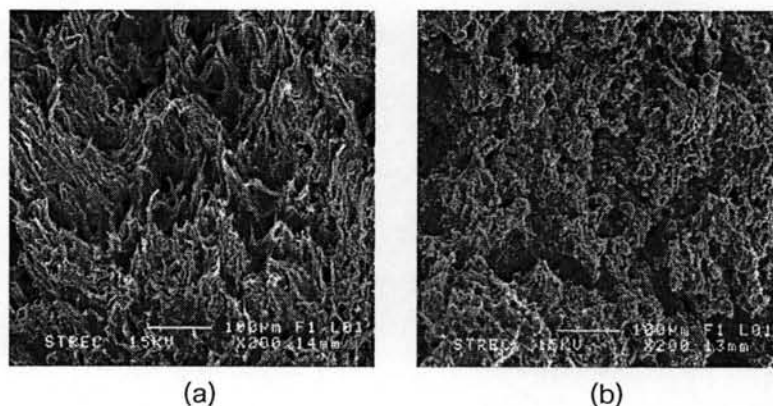


Fig. 4.12 SEM photographs of tensile fracture surface of 80:20 SSS/LDPE TPEs (a) unfilled TMTD (b) filled TMTD 2.75 phr.

#### 4.6.4 Comparison morphology of TPEs between M-SSS/LDPE filled and unfilled TMTD

Fig. 4.13 showed the morphology of the TPEs of M-SSS/LDPE filled and unfilled TMTD. The morphology of TPEs filled TMTD presented fibrillar structure due to crosslinking reaction between rubber and plastic phase resulting in a high mechanical properties. As discussed earlier, in contrast to the non-devulcanized SSS/LDPE TPEs, the addition TMTD certainly increased the tensile properties (Fig. 4.6-4.8). Thus, this SEM micrograph correlated well with tensile strength. In the case of M-SSS TPEs unfilled TMTD, SEM micrograph revealed shows elastic-type deformation with irregular tensile paths (Fig. 4.13 (a)). The lack of fibrils indicated elastic type failure.

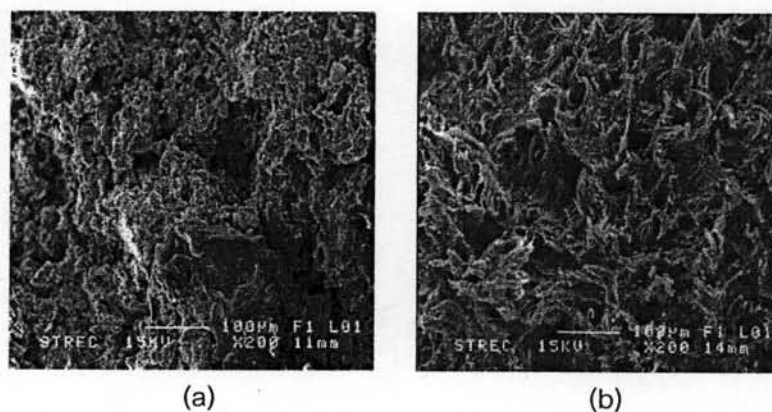


Fig. 4.13 SEM photographs of tensile fracture surface of 80:20 M-SSS/LDPE TPEs (a) unfilled TMTD (b) filled TMTD 2.75 phr.

#### 4.6.5 Comparison morphology of TPEs filled TMTD between SSS/LDPE and M-SSS/LDPE TPEs

Fig. 4.14 (a) and (b) showed morphology of TPEs filled TMTD between SSS/LDPE and M-SSS/LDPE TPEs, respectively. The failure surface of SSS/LDPE TPEs filled TMTD showed elastic-type deformation with irregular tensile paths (Fig. 4.14(a)). The lack of fibrils indicated elastic type failure which reduced toughness of TPEs. In contrast, M-SSS/LDPE TPEs filled TMTD displayed fibrillar structure that was associated with the crosslinking reaction of shoe sole scrap and LDPE phase, resulting in greater tensile properties than SSS/LDPE TPEs filled TMTD. By comparing these two micrographs with those presented in Fig. 4.11, it can be concluded that both microwave power and TMTD played an important role in the tensile properties of the prepared TPEs. When M-SSS was used to prepare TPEs, TMTD was needed in order to achieve the TPEs with greater tensile properties (Fig. 4.6-4.8 and Fig. 4.14(b)). On the other hand, if TPEs were prepared from non-devulcanized SSS, the existence of TMTD although increased the tensile strength and modulus, but at the same time it also decreased the elongation at break.

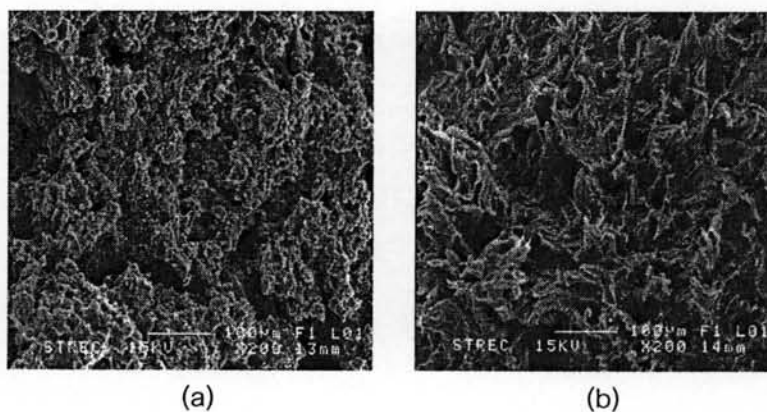


Fig. 4.14 SEM micrographs of tensile fracture surface of 80:20 TPEs filled TMTD (a) non-devulcanized TPEs (b) microwave-devulcanized TPEs.

#### 4.7 Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of polymers are highly dependent on the material structure. Thus, the molecular level changes that occur in polymer under the application of a sinusoidal stress is reflected in dynamic mechanical measurements.

The glass-rubber transition marks the onset of long range motions of amorphous polymer chain segments and is characterized by a large drop in modulus and a pronounced loss factor peak. The last region is the flow region, where the amorphous chains undergo net translatory motions relative to each other and a terminal fall off in modulus is accompanied by a continuous increase in loss factor. [26]

Fig. 4.15 and 4.16 present the DMA thermograms of the SSS/LDPE and M-SSS/LDPE TPEs, respectively. As seen, the  $\tan \delta$  peak of the TPEs filled TMTD was shifted to higher temperature, indicating greater  $T_g$  values. The  $T_g$  values of the selected TPEs are listed in Table 4.4. From this table, the results indicated that both SSS/LDPE and M-SSS/LDPE TPEs filled TMTD had higher  $T_g$  value than those of TPEs unfilled TMTD due to crosslinking reaction between rubber and plastic phase which can limit the movement of molecular chains to a great extent. Moreover, it might be due to some interfacial adhesion between shoe sole scrap particle and SSS/LDPE TPEs matrix.

In the case of microwave energy, the  $T_g$  values of M-SSS/LDPE TPEs unfilled TMTD was slightly lower than the  $T_g$  value of the SSS/LDPE TPEs unfilled TMTD because microwave energy broken crosslinking chain of the shoe sole scrap structure, implying that the flexibility of TPEs was improved. On the other hand, the  $T_g$  value of M-SSS/LDPE TPEs filled TMTD was slightly higher than those of the SSS/LDPE TPEs filled TMTD due to crosslinking between shoe sole scrap phase and LDPE phase.

**Table 4.4** Glass transition temperature ( $T_g$ ) of the 80:20 SSS/LDPE and M-SSS/LDPE TPEs unfilled and filled TMTD.

Blending	$T_g$ ( $^{\circ}\text{C}$ )
SSS/LDPE TPEs unfilled TMTD	-40.10
SSS/LDPE TPEs filled TMTD	-37.80
M-SSS/LDPE TPEs unfilled TMTD	-41.20
M-SSS/LDPE TPEs filled TMTD	-36.60

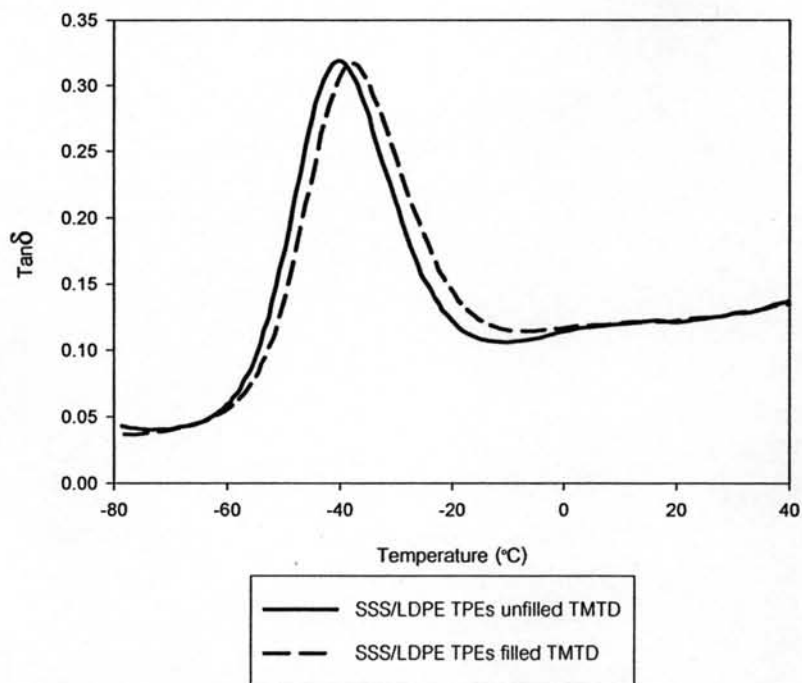


Fig. 4.15 Effect of TMTD on the  $\tan \delta$ -temperature of 80:20 SSS/LDPE TPEs.

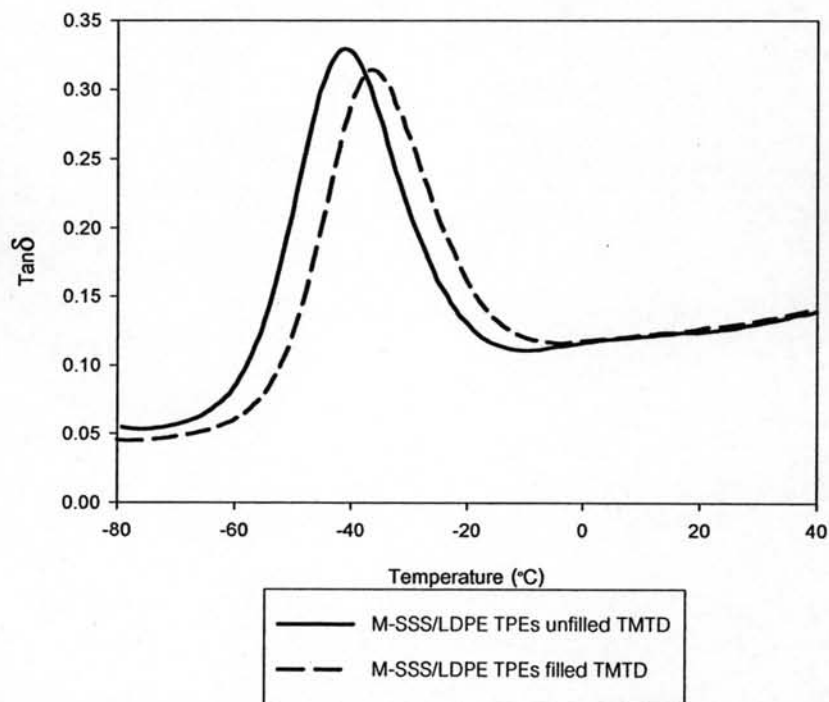


Fig. 4.16 Effect of TMTD on the  $\tan \delta$ -temperature of 80:20 M-SSS/LDPE TPEs.