

CHAPTER IV

RESULTS AND DISCUSSION

Reclaimed tire rubber and thermoplastics were mixed at ratio 30/70-70/30 (RTR/thermoplastic) by using a two-roll mill. In the two-roll mill, blends were cut diagonally from time to time and folded over several times during milling to ensure good mixing. Dynamic vulcanization of blends were performed by using three crosslinking systems, i.e., sulphur system, peroxide system and mixed system. In addition a compatibilizer was also applied. The recipes used for dynamic vulcanization and compatibilizer are given in Table 3.2. The notch-Izod impact strength and tensile strength measurements were performed in accordance with ASTM D 256 and ASTM D412, respectively, for each blend. Solvent swelling study indicates filler-matrix interaction makes the physical bonds at the interface to withstand the shear force. The phase structure of the RTR/thermoplastic blends at various compositions was assessed by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). Rheological behavior was also studied to understand the effect of shear rate on the flow behavior of materials.

4.1 RTR and HDPE Blends.

4.1.1 Impact Testing

It is observed that the impact strength of all blends increases with increasing RTR loading up to 50 pbw due to impact energy absorption of RTR. At higher loading, the impact strength of each blend system was dropped. This is probably attributed to the amount of carbon black that was already present in RTR that was critical point for the improvement. Thus at the critical carbon black concentration, the RTR/HDPE blend can have a split in the layer structure providing a shorter path for fracture propagation, thereby causing the sudden decrease in impact strength. Naskar et al. [23] also reported that properties of GRT/EPDM/acrylic modified HDPE blend depend on the relative proportion of total rubber and plastic. At high rubber content

(70:30 rubber/plastic and above), the blends show poor processability and physical properties. At high HDPE content (40:60 rubber/plastic and below), the blends behave as toughened plastics [23]. Tantayanon et al. investigated the impact strength of vulcanized RTR/PP blend and reported that the RTR/PP blend with sulfur crosslink agent had the highest impact strength at the ratio of 30/70. This could be attributed to the limitation of carbon black in the blend [36]. Phadke and De blended 100 pbw PP, 20 pbw NR and various GRT loading at 20-60 pbw. They found that the impact strength continued to increase up to 40 pbw GRT loading. At higher GRT loading, a decrease in impact strength was observed [38].

Figure 4.1.1 shows that RTR/HDPE blend with a compatibilizer exhibits the highest impact strength, suggesting that MB226D (or maleic anhydride grafted polyethylene) is a suitable compatibilizer for this blend. MB226D reduces the interfacial energy of both phases, therefore it improved the interfacial adhesion of RTR and HDPE.

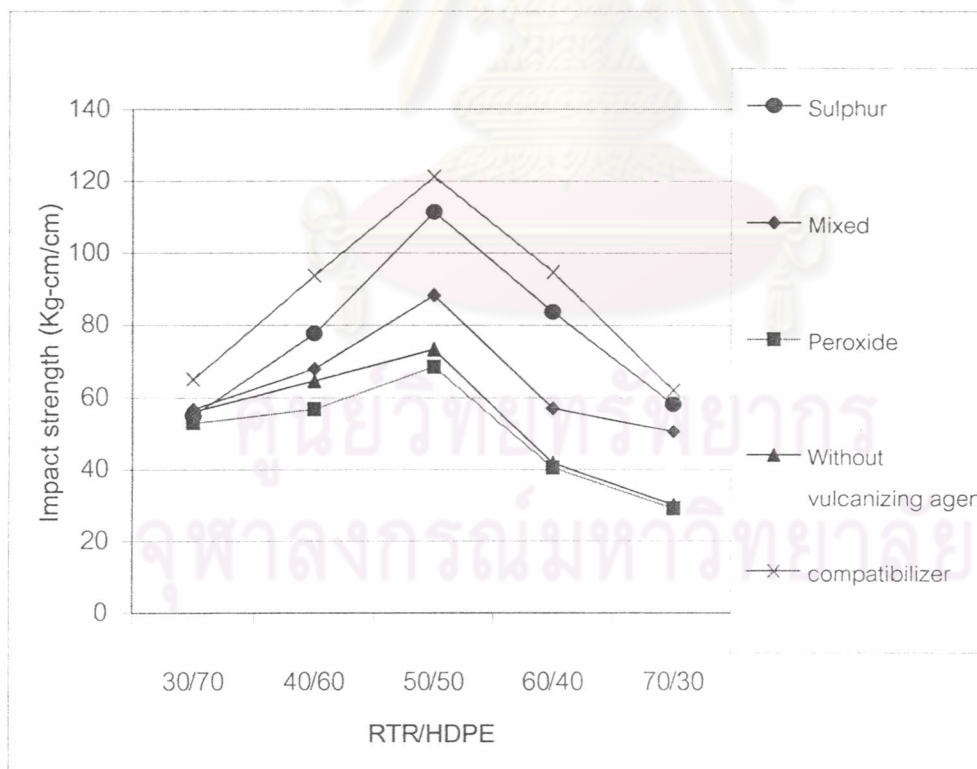


Figure 4.1.1 Impact strength of vulcanized RTR/HDPE blends.

Three types of crosslinking systems were compared. Vulcanization by sulfur produces predominantly polysulphide linkages, The peroxide system gives rise to C-C linkages. The mixed system produces both polysulphide linkage and C-C linkages. From the result in Figure 4.1.1 also showed that the blend obtained from sulfur vulcanization was found to exhibit the highest impact strength, and from the peroxide system was the lowest. That obtained from the mixed system showed an intermediate behavior.

RTR/HDPE blend without vulcanizing agent showed lower impact strength than the blends with sulphur system, mixed system and compatibilizer but it had close value to the blends with peroxide. This may be due to degradation of the HDPE phase by peroxide as reported by Yoon et al. [19].

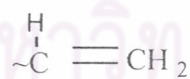
Degradation of peroxide



Generation of macroradical



Chain scission reaction



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4.1.2 Tensile Testing

It is observed that tensile strength decreases with higher RTR loading. This is probably attributable to the amount of carbon black that was already presented in RTR which may inhibit the molecular orientations and mobility of the rubber. The similar observation was reported by N. Sombatsompop et al. [35]. Figure 4.1.2 shows that without dynamic curing blend exhibits the lowest tensile strength at all blend ratios, whereas RTR/HDPE blends with the compatibilizer, peroxide, mixed system and sulphur show higher tensile strength, respectively. It evidenced that a compatibilization and dynamic vulcanization significantly improved the mechanical behavior of the blend.

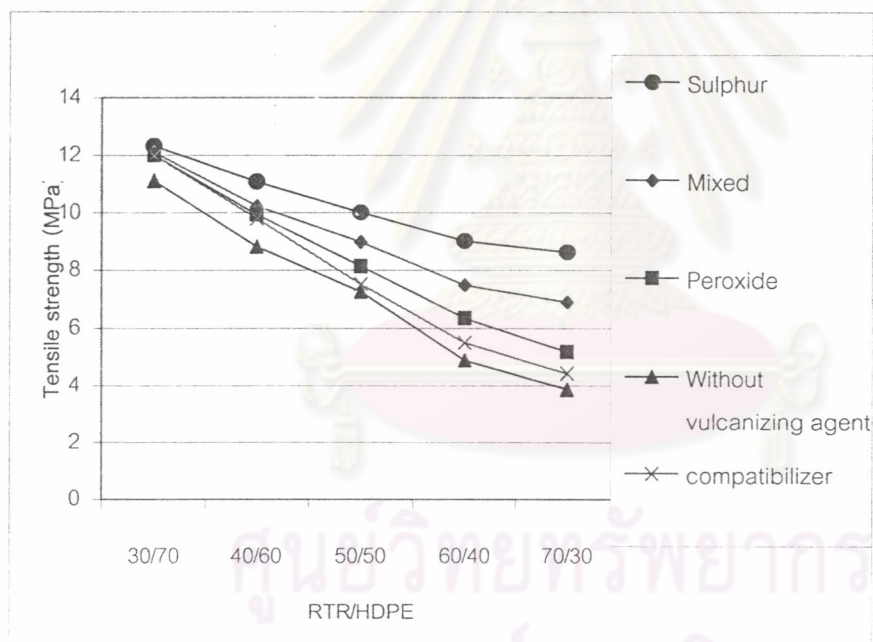


Figure 4.1.2 Tensile strength of vulcanized RTR/HDPE blends.

4.1.3 Solvent Swelling

Results of equilibrium swelling studies of the blends in toluene provide information about the filler-matrix interaction and crosslinking density. Swell ratio of

RTR/HDPE blended with sulphur and mixed system is lower than the ones with peroxide, compatibilizer and without dynamic curing agent. This indicates higher degree of crosslinking density and the filler-matrix interaction makes the physical bonds at the interface to withstand the shear force caused by swelling of polymer [31].

Table 4.1.1 Swell ratios of 50/50 RTR/HDPE blends.

Addition system	Swell ratio
Sulphur system	1.24
Mixed system	1.25
Peroxide system	1.40
Compatibilizer	1.38
Without vulcanizing agent	1.49

4.1.4 Thermogravimetric Analysis (TGA)

Generally, all commercial elastomers degrade between 300 and 550 °C in a usual TGA because of their hydrocarbon nature and each degradation step can be attributed to the characteristic feature of the individual polymer. In the TGA run, with the increase in temperature, the thermal degradation of filled polymer systems takes place through various steps. Low boiling materials decompose first, followed by the decomposition of plasticizers, polymers and fillers, respectively. The crystalline polar polymer degrades later than the amorphous one. We studied the TGA scans of RTR/HDPE blends at very low heating rate of 2 °C/min (Figure 4.1.3). The TGA scan shows sharp peak at 400 and 500°C. It was found that the degradation at 400°C increased but at 500 °C decreased with increasing RTR content in the RTR/HDPE blend. The TGA scan of RTR/HDPE blends with different vulcanizing agents shows no different decomposition pattern.

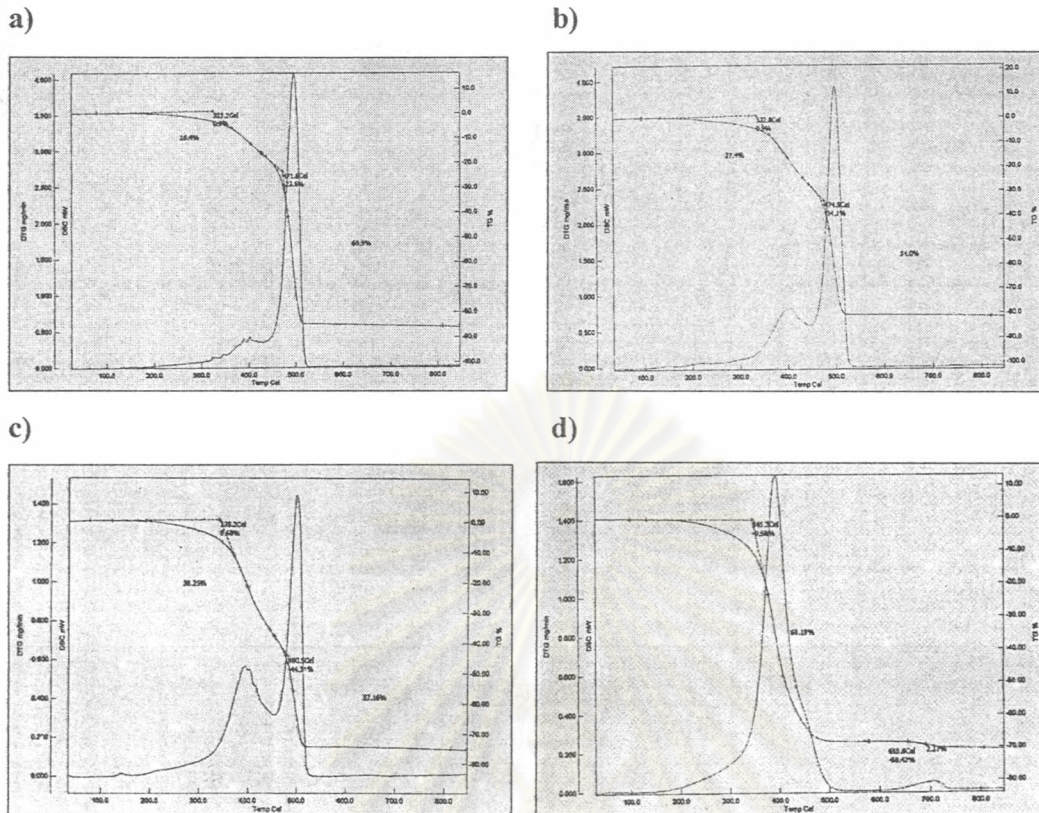


Figure 4.1.3 TGA thermograms of RTR/HDPE blends using sulphur vulcanizing system; a) 30/70 RTR/HDPE, b) 50/50 RTR/HDPE, c) 70/30 RTR/HDPE, d) 100/0 RTR/HDPE.

4.1.5 Differential Scanning Calorimetry Analysis (DSC)

Glass transition temperature (T_g), melting temperature (T_m) and degree of crystallinity of RTR/HDPE blends, as measured by DSC, are shown in Table 4.1.2.

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Table 4.1.2 Thermal analysis of RTR/HDPE blends

Blend (RTR/HDPE)	T _g (°C)	T _m (°C)	ΔH _f (J/g)	Crystallinity(%)
30/70 sulphur system	-42.84	131.26	116.43	39.66
50/50 sulphur system	-44.73	130.87	89.07	30.34
70/30 sulphur system	-46.36	129.46	61.11	20.81
50/50 mixed system	-45.90	131.35	81.62	27.80
50/50 peroxide system	-57.28	131.24	89.16	30.37
50/50 compatibilizer	-58.10	130.01	95.13	32.40
50/50 without vulcanizing agent	-57.05	131.73	74.15	25.26

It is found that the addition of RTR affected the T_g by shifting it towards lower temperatures with higher RTR loading. At 50/50 ratio, RTR/HDPE blends using sulphur and mixed system have higher T_g's than the ones with peroxide, compatibilizer and without vulcanizing agent. This indicates that sulphur and mixed system effectively increased the interfacial adhesion between RTR and HDPE. The low T_g obtained in the presence of RTR and without vulcanizing agent, peroxide and compatibilization indicated an increased segmental mobility of the rubber chains [32]. For the melting of RTR/HDPE blends using sulphur system, the T_m decreased with a decrease in concentration of the plastic phase (30/70 to 70/30 RTR/HDPE). Due to the fact that RTR has less ordered structure than the HDPE. Also, the inclusion of the more flexible phase of RTR could disturb the packing of HDPE chains [36].

4.1.6 Phase Morphology of Blends

The phase morphology of unvulcanized and vulcanized RTR/HDPE blends were studied (Figures 4.1.4-4.1.5). RTR/HDPE blend without vulcanizing agent (Figure 4.1.4d) appears to have larger RTR aggregates particle size than the blend with sulphur system (Figure 4.1.4b). This result can be explained that better dispersion apparently occurs from the effective role of crosslink in resisting rubber reagglomeration. Among sulphur system, RTR/HDPE blend (30/70-70/30), show

RTR aggregates increase when the RTR content in the blends increases (Figure 4.1.4 a-c). This probably due to the limitation of the amount of carbon black in the blend since carbon black can partially immobilize the chain segment of rubber. This observation is consistent with the sudden drop of impact and tensile strength of RTR/HDPE blend at 70/30.

The morphology of 50/50 RTR/HDPE blends with compatibilizer and different vulcanizing agents are shown in Figure 4.1.5. This explains that RTR particles can better disperse in HDPE matrix of the blend with sulphur and mixed system than that added with compatibilizer, peroxide and without vulcanizing agent. It is seen that the distribution of rubber is fine and, hence, the crosslinking is more effective in these system causing improvement in physical properties. In peroxide system, the size of the dispersed RTR is large. This may be due to chain scission on HDPE matrix predominates over crosslinking reaction causing poor physical properties. George et al. investigated the effect of dynamic vulcanization of PP/NBR blend on the morphology. They also found that the morphology of the PP/NBR blends vulcanized with sulphur system showed the size of the dispersed NBR domains is larger than those of the peroxide and mixed systems [20]. Tantayanon et al. also investigated phase morphology of PP/RTR blends. They found that SEM micrographs of unvulcanized blends appear to have larger RTR aggregates than do the vulcanized blends at the same loading amount, indicating a worse distribution of RTR in the PP matrix for the unvulcanized blends. This result indicates that better dispersion apparently occurs from the effective role of crosslinking in resisting rubber reagglomeration [36]. Nevatia et al. studied phase morphology of unvulcanized and vulcanized reclaimed rubber and scrap polyethylene blends. They found that the size of the unvulcanized rubber particles (about 5-6 μm) is much larger than vulcanized rubber in the blends. A sulphur accelerator system was found to be better than a peroxide system. They also found that not much change in the mechanical properties was observed when compatibilizer was incorporated. This may be explained as being due to the high filler content in the system. The effect of compatibilizer on the rubber filler system and the plastic filler system becomes insignificant. Because the compatibilizer does not enhance the interaction in the rubber-filler or plastic-filler

system, the overall effect of these compatibilizer is not appreciated because of high filler content in the reclaimed rubber [39].

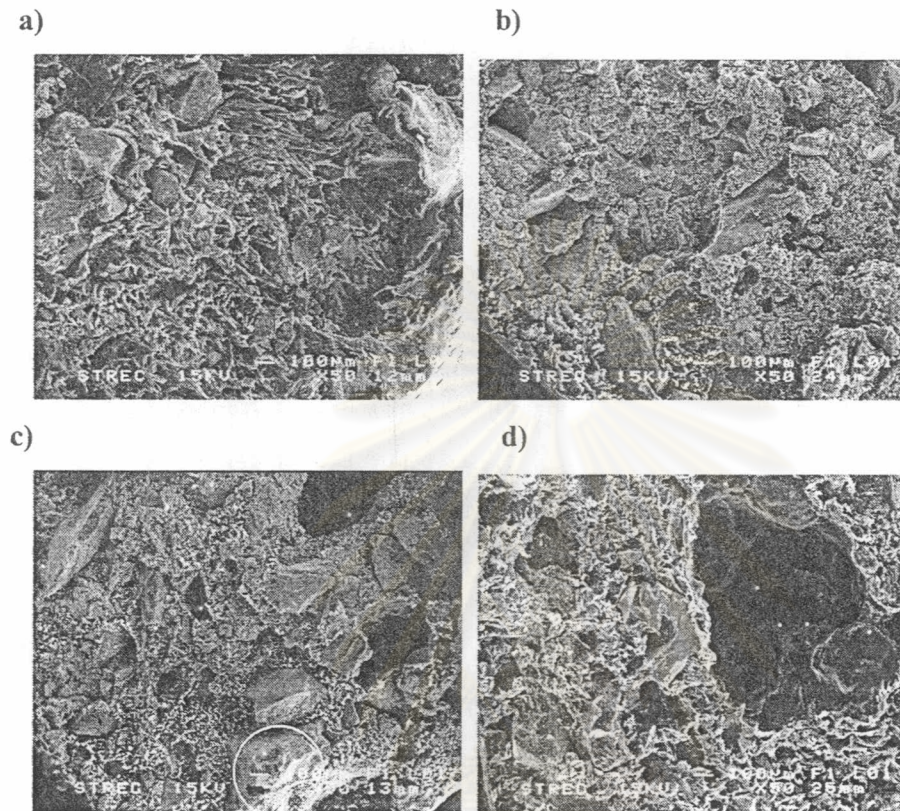


Figure 4.1.4 Scanning electron micrographs of RTR/HDPE blend with sulphur vulcanizing system; a)30/70, b)50/50, c) 70/30, d) 50/50 without vulcanizing agent.

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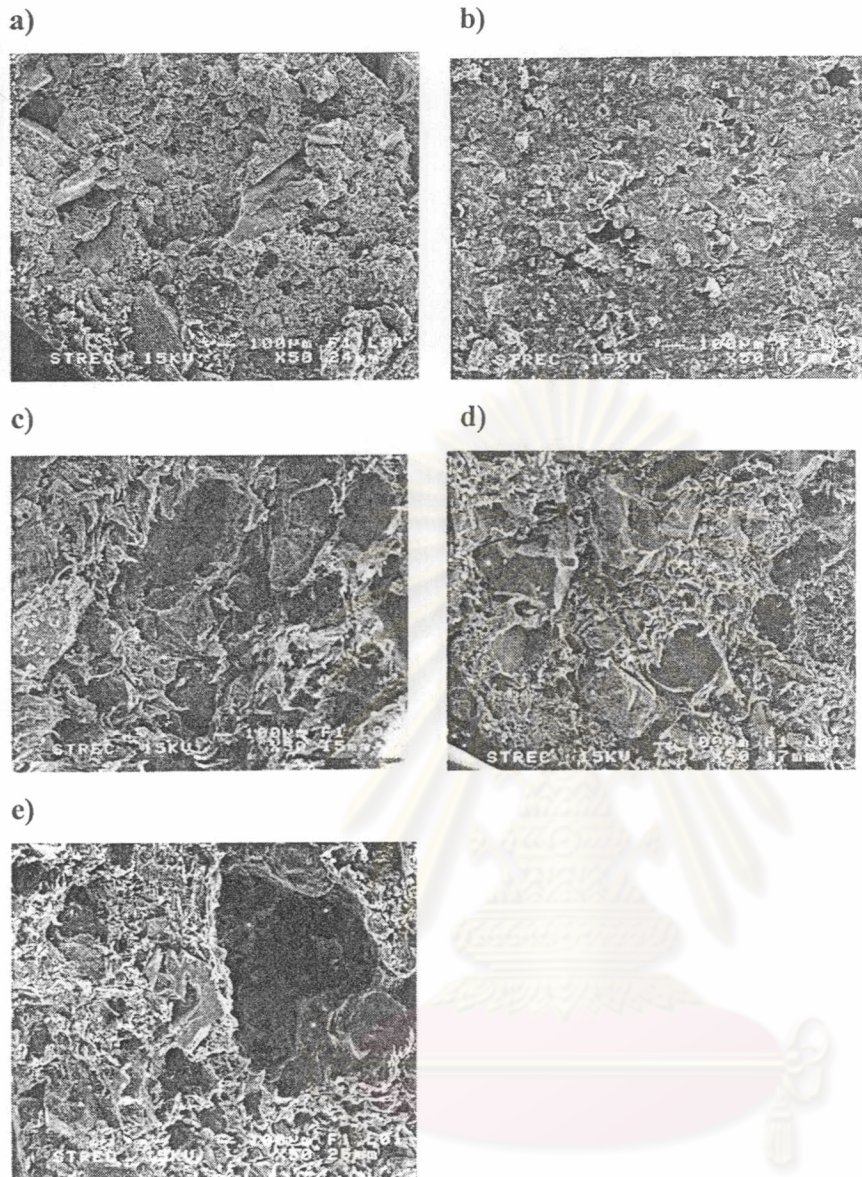


Figure 4.1.5 Scanning electron microscopy of 50/50 RTR/HDPE blends with a) sulphur system, b) mixed system, c) compatibilizer system, d) peroxide system, e) without vulcanizing agent.

4.1.7 Rheological Behavior

Melt rheological studies are useful for understanding the effect of shear rate on the flow behavior of materials. Figure 4.1.6 shows melt viscosities of RTR/HDPE blends with compatibilizer and different vulcanizing agents at different angular

frequency range from 0.1 to 100 rad/s at 5% strain. Rheological behavior indicates that the viscosity decreases with increasing angular frequency which indicates pseudoplastic behavior. From the Cox-Merz rule ($\eta^*[\omega] = \eta[\dot{\gamma}]$), angular frequency is equal value to shear rate [41,43]. The pseudoplastic nature of the blends implies that the required shear stress to cause flow becomes smaller as the rate of shear increases. Viscosity of RTR/HDPE blends with sulphur and mixed system show higher viscosity than peroxide and without dynamic curing system. This indicates that the high viscosity might be due to the influence of the vulcanization system which results in high degree of crosslink as an evident from the swelling ratio data reported earlier. Swelling ratio is a direct function of crosslink density, thus, the formation of intermolecular structure is expected to increase the frictional forces exerted during shearing as the polymer chains could not be easily deformed by the shearing action. It is interesting to see that viscosity of RTR/HDPE blends with compatibilizer is lower than the blends with peroxide at high angular frequency. This implies that the deformation rate of the blends with compatibilizer increase with increasing angular frequency. The lower deformation rate in the case of the cured samples could be due to the dispersed rubber particles into the HDPE matrix as a result of dynamic vulcanization. A. Mousa et al. [40] studied melt rheology of PVC/ENR TPEs with a special reference to the effect of dynamic vulcanization and apparent shear rate. They found that the apparent viscosity of the blend decreases with increasing apparent shear rate. The crosslink formation apparently slows down the flow properties which shows in high viscosity but does not hinder the flow of the vulcanized blends [40].

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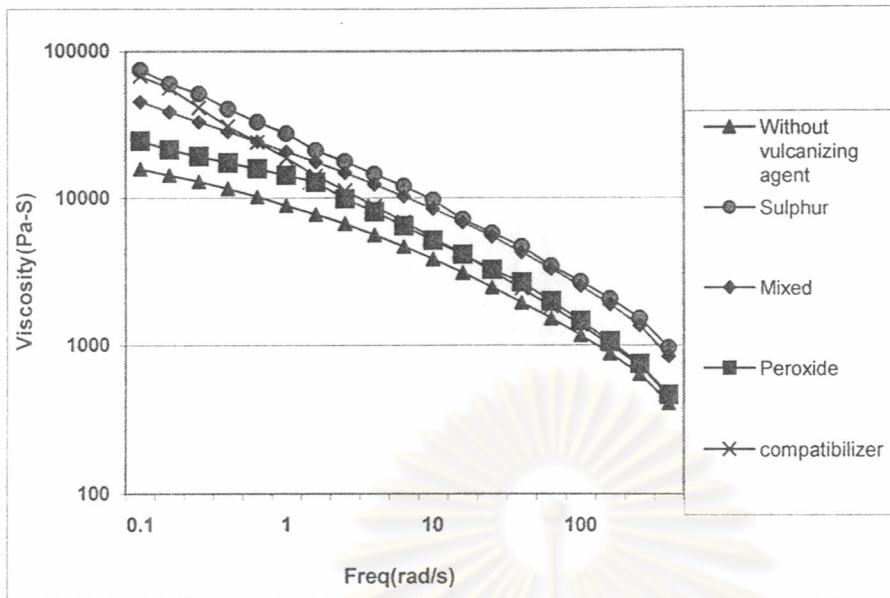


Figure 4.1.6 The effect of angular frequency on the apparent melt viscosity of 50/50 RTR/HDPE blends.

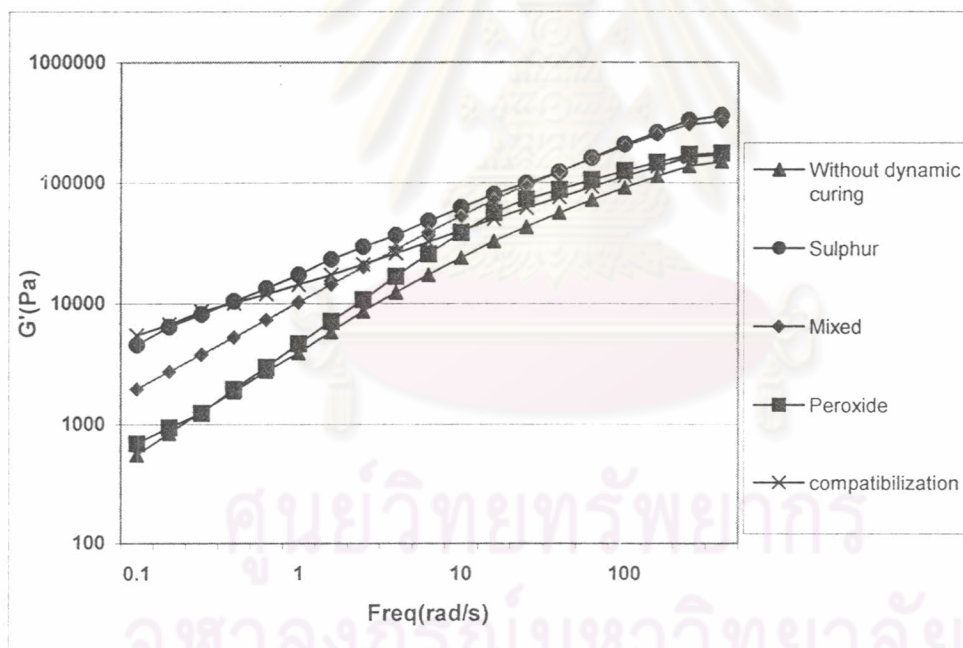


Figure 4.1.7 The effect of angular frequency on the storage modulus (G') of 50/50 RTR/HDPE blends.

Figure 4.1.7 show the frequency dependency of storage modulus (G') of the blends. G' value of the blends with sulphur system are the highest. It can be attributed to entanglement of the HDPE chain segment with RTR. It may also indicate positive

interaction between the two polymers. Similar observations were reported by Subhasish et al. for the polypropylene copolymer and a polyolefinic elastomer blend. They found that POE content increased, the storage modulus increased significantly. This indicates that the long chain branches present in POE molecules tend to produce entanglements and, thus, a higher elasticity can be observed [41].

4.2 RTR and LDPE blends.

4.2.1 Impact Testing

It is observed that impact strength of all blends increases with increasing RTR loading up to 50 pbw due to impact energy absorption of RTR. When the RTR was higher than 50 pbw, impact strength of the blend dropped. The RTR/LDPE blend without vulcanizing agent had lowest impact strength.

Three types of crosslinking systems and compatibilization have been used. From the result in the Figure 4.2.1 also showed that dynamic vulcanization by mixed system was found to exhibit the highest impact strength, and sulphur system the lowest. The peroxide and compatibilizer system showed an intermediate behavior.

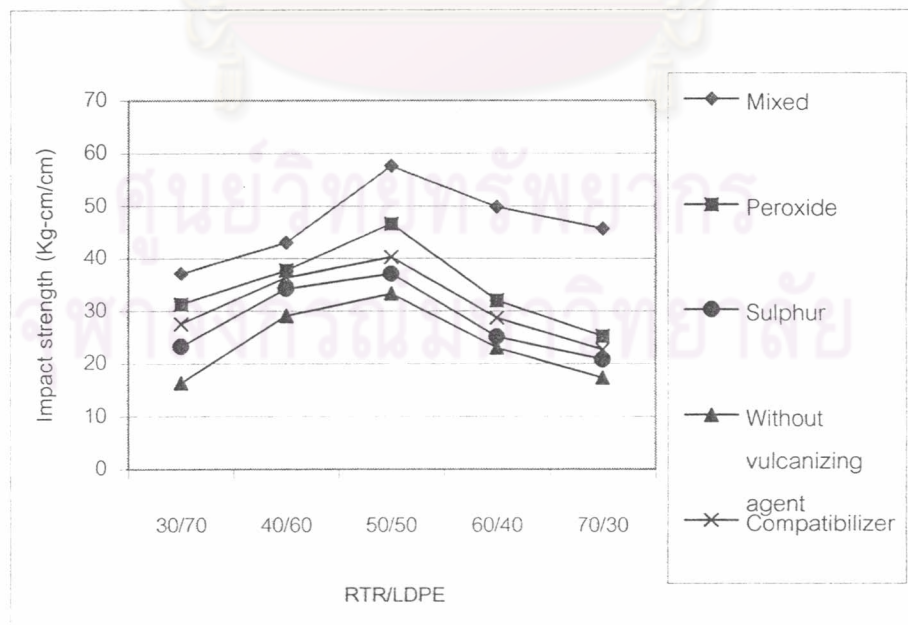


Figure 4.2.1 Impact strength of vulcanizing RTR/LDPE blends.

4.2.2 Tensile Testing

Figure 4.2.2 shows that without vulcanizing agent blend exhibits the lowest tensile strength at all blend ratios. In dynamic vulcanization, RTR/LDPE blends with mixed system show the highest tensile strength and sulphur system showed the lowest. The peroxide and compatibilizer system showed an intermediate tensile strength. RTR/LDPE blends with mixed system showed the highest tensile strength at every ratio. This is due to the interfacial crosslinking via the formation of sulfur bridges in RTR particles and compatibilizing action of MA/DCP induced by the dipolar interaction between the MA graft LDPE and NR, SBR components in RTR.

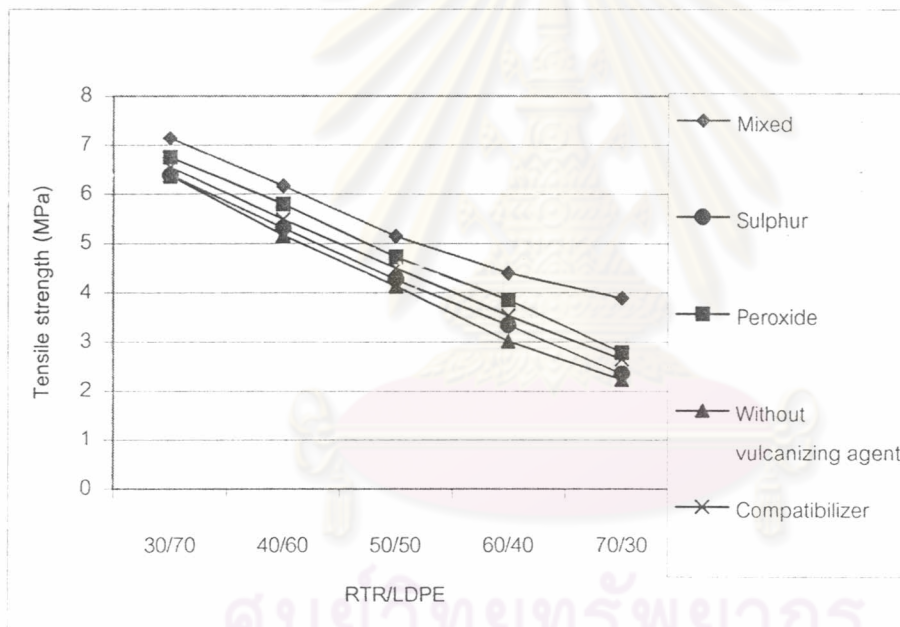


Figure 4.2.2 Tensile strength of vulcanized 50/50 RTR/LDPE blends.

4.2.3 Solvent Swelling

Swell ratio of RTR/LDPE blend with mixed system is the lowest whereas without vulcanizing agent is the highest. This indicates the highest degree of crosslinking density in RTR/LDPE blend with mixed system.

Table 4.2.1 Swell ratios of 50/50 RTR/LDPE blends

Addition system	Swell ratio
Sulphur system	3.68
Mixed system	2.72
Peroxide system	2.88
Compatibilizer system	3.29
Without vulcanizing system	4.30

4.2.4 Thermogravimetric Analysis (TGA)

Generally, all commercial elastomers degrade between 400 and 550 °C in a usual TGA because of their hydrocarbon nature and each degradation step can be attributed to the characteristic feature of the individual polymer. In the TGA run, with the increase in temperature, the thermal degradation of filled polymer systems takes place through various steps. We studied the TGA scans of RTR/LDPE blends at very low heating rate of 2 °C/min (Figure 4.2.3). The TGA scan shows sharp drop at 400 and 500°C. It was found that degradation at 400°C increased but at 500°C decreased with increasing RTR content in RTR/LDPE blend.

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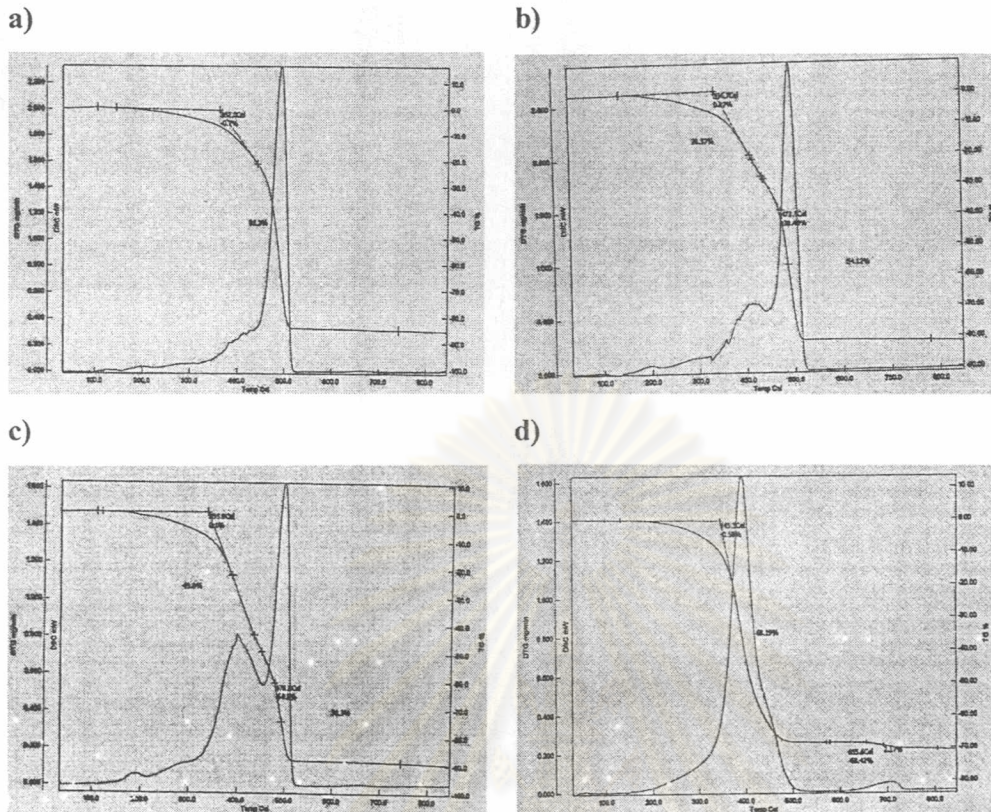


Figure 4.2.3 TGA thermograms of RTR/LDPE blends using mixed vulcanizing agents; a) 30/70 RTR/LDPE, b) 50/50 RTR/LDPE, c) 70/30 RTR/LDPE, d) 100/0 RTR/LDPE.

4.2.5 Differential scanning calorimetry analysis (DSC)

Glass transition temperature (T_g), melting temperature (T_m) and degree of crystallinity of RTR/LDPE blends, as measured by DSC, are shown in Table 4.2.2.

Table 4.2.2 Thermal analysis of RTR/LDPE blends

Blend (RTR/LDPE)	T _g (°C)	T _m (°C)	ΔH _f (J/g)	Crystallinity(%)
30/70 mixed system	-31.16	110.28	41.94	14.29
50/50 mixed system	-37.43	108.83	31.94	13.81
70/30 mixed system	-43.48	108.54	29.13	9.92
50/50 sulphur system	-58.25	108.81	40.64	13.84
50/50 peroxide system	-55.39	109.14	46.32	15.78
50/50 compatibilizer system	-58.84	108.64	40.37	13.75
50/50 without vulcanizing agent	-58.73	111.60	42.65	14.53

It found that the addition of RTR affected T_g by shifting it towards lower temperatures with higher RTR loading. At 50/50 ratio, RTR/LDPE blends using mixed system has the highest T_g. This indicates an effective crosslinking using mixed system for interfacial adhesion of RTR and LDPE blends[42]. The T_g reduction achieved in the presence of RTR and without vulcanizing agent, peroxide, compatibilizer, sulphur indicate an increased segmental mobility of the rubber chains and this hints at some disruption of the crosslinked structure [32]. For the melting of RTR/LDPE blends using mixed system, the T_m decreased with a decrease in concentration of the plastic phase (30/70 to 70/30 RTR/LDPE). This caused by the lower percentage crystallinity of LDPE due to more RTR present in the blends. The inclusion of the more flexible phase of RTR could disturb the packing of LDPE chains. [36].

4.2.6 Phase Morphology of Blends

The phase morphology of unvulcanized and vulcanized RTR/LDPE blends were studied (Figures 4.2.4-4.2.5). RTR/LDPE blend without vulcanizing agent (Figure 4.2.4d) appear to have larger RTR aggregates particle size than the blend with

mixed system (Figure 4.2.4b). This result can be explained that better dispersion apparently occurs from the effective role of crosslink in resisting rubber reagglomeration. Among mixed system, RTR/LDPE blend (30/70-70/30), show RTR aggregates increase when the RTR content in the blends increases (Figures 4.2.4 a-c). This probably due to the limitation of the amount of carbon black in the blend since carbon black can partially immobilize the chain segment of rubber. This observation is consistent with the sudden drop of impact and tensile strength of RTR/LDPE blend at 70/30. The morphology of 50/50 RTR/LDPE blends with compatibilizer and different dynamic curing systems are shown in Figure 4.2.5. This explains that RTR particles can better disperse in LDPE matrix of the blend with mixed system than that added with peroxide, compatibilizer, sulphur and without vulcanizing agent. It is seen that the distribution of rubber is fine and, hence, the crosslinking is the most effective in these system causing improvement in physical properties [20, 36, 39].

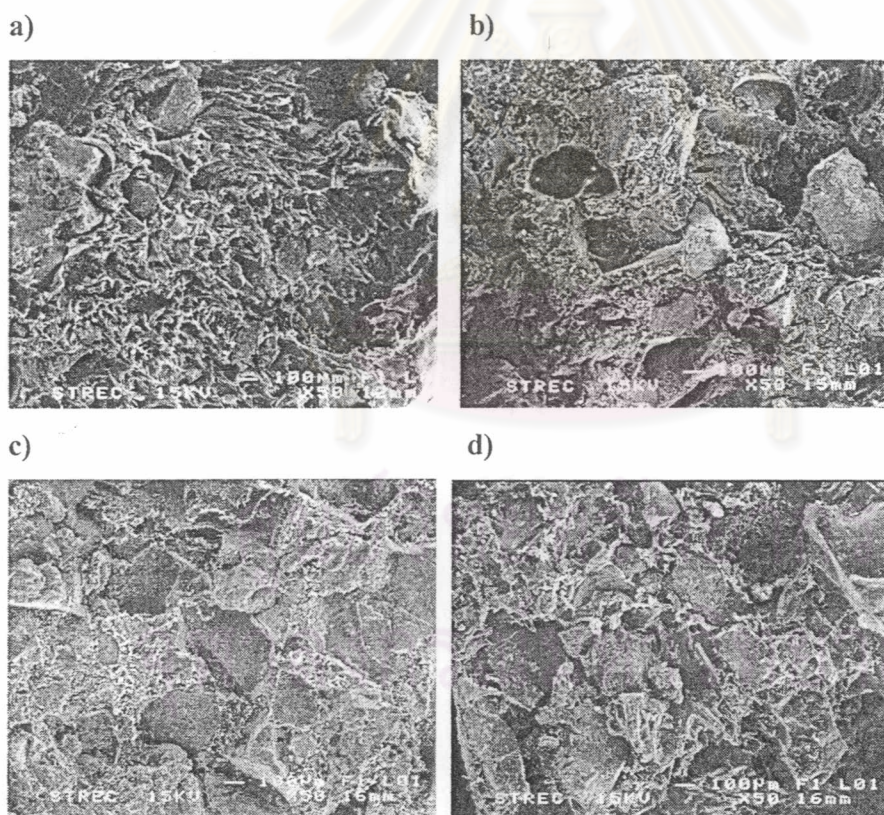


Figure 4.2.4 Scanning electron micrographs of RTR/LDPE blend with mixed vulcanizing agent; a)30/70, b)50/50, c) 70/30, d) 50/50 without vulcanizing agent.

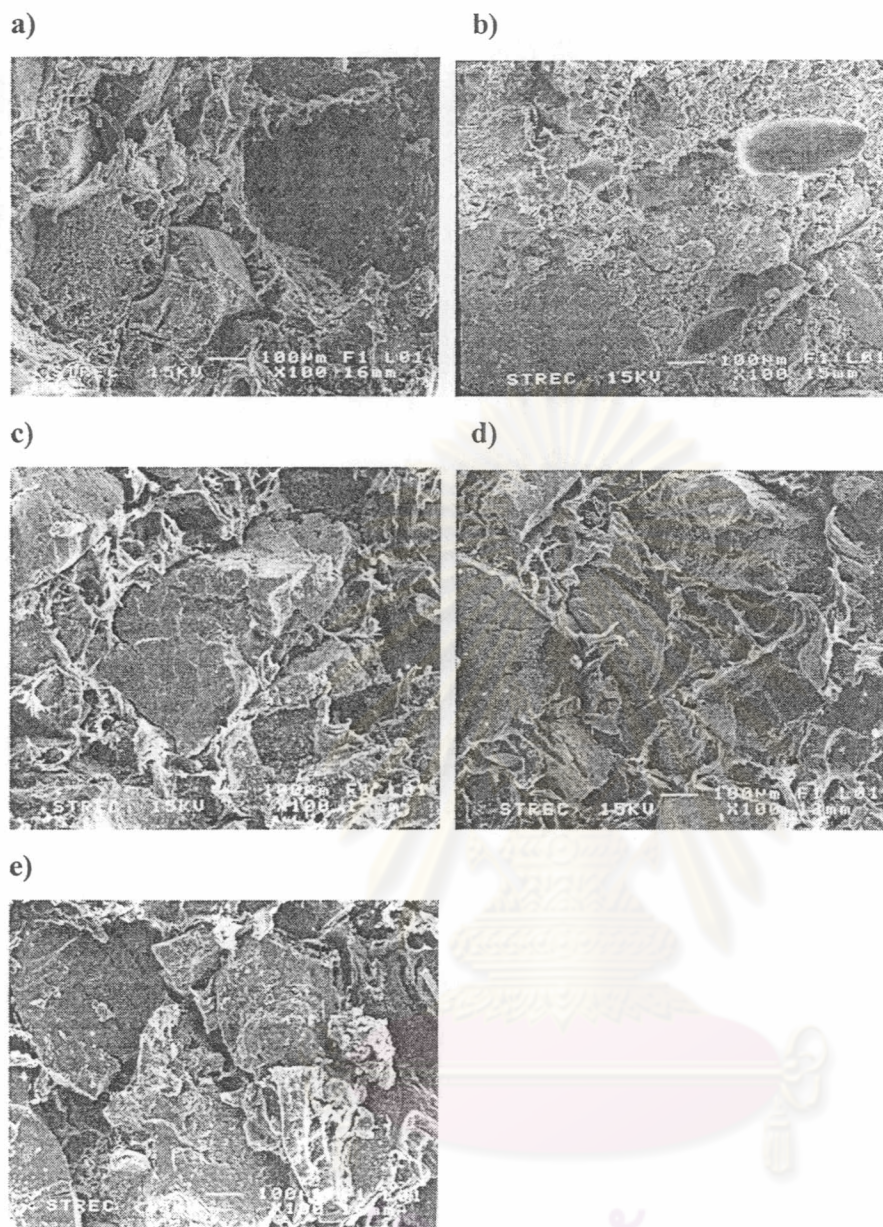


Figure 4.2.5 Scanning electron micrographs of 50/50 RTR/LDPE blends with different vulcanizing agents; a) sulphur system, b) mixed system, c) compatibilizer system, d) peroxide system, e) without vulcanizing agent.

4.2.7 Rheological Behavior

Figure 4.2.6 shows melt viscosities of RTR/LDPE blends with compatibilizer and different vulcanizing agents at different angular frequency. Rheological behavior

indicates that the viscosity decreases with increasing angular frequency which indicates pseudoplastic behavior. Viscosity of RTR/LDPE blends with mixed system show the highest viscosity. This indicates that the high viscosity might be due to the influence of the vulcanization system that results in high degree of crosslink. The lower deformation rate in the case of the cured samples could be due to the dispersed rubber particles into the LDPE matrix as a result of dynamic vulcanization [40].

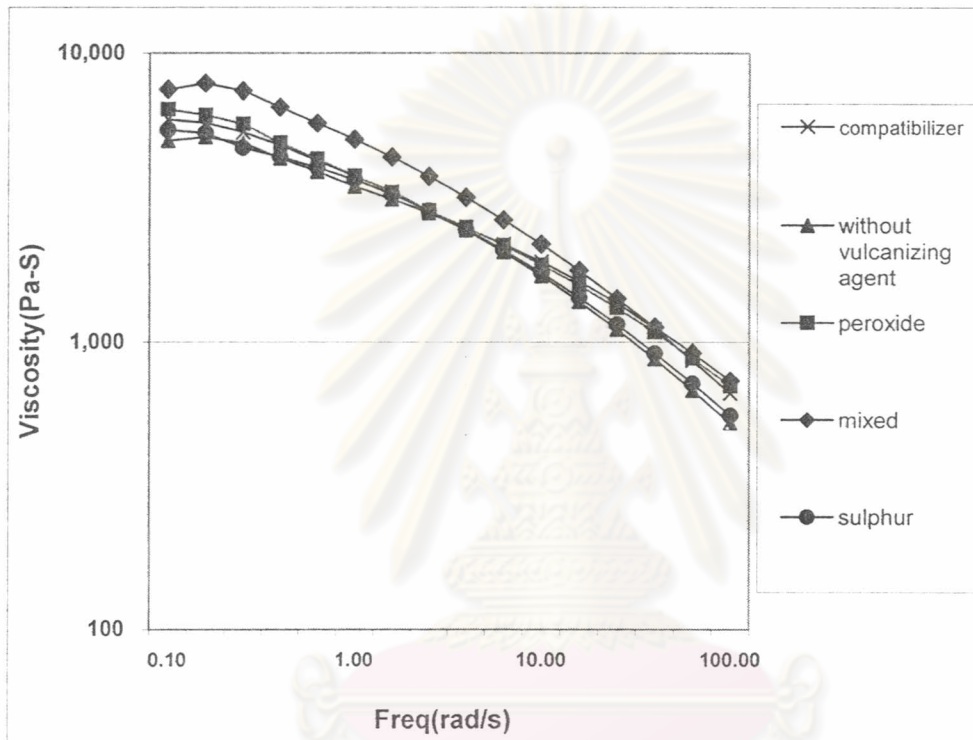


Figure 4.2.6 The effect of angular frequency on the apparent melt viscosity of 50/50 RTR/LDPE blends.

Figure 4.2.7 show the frequency dependency of storage modulus (G') of the blends. At high frequencies, G' value of the blends with mixed system are the highest. It can be attributed to entanglement of the LDPE chain segment with RTR. It may also indicate positive interaction between the two polymers and a higher elasticity can be observed. [41].

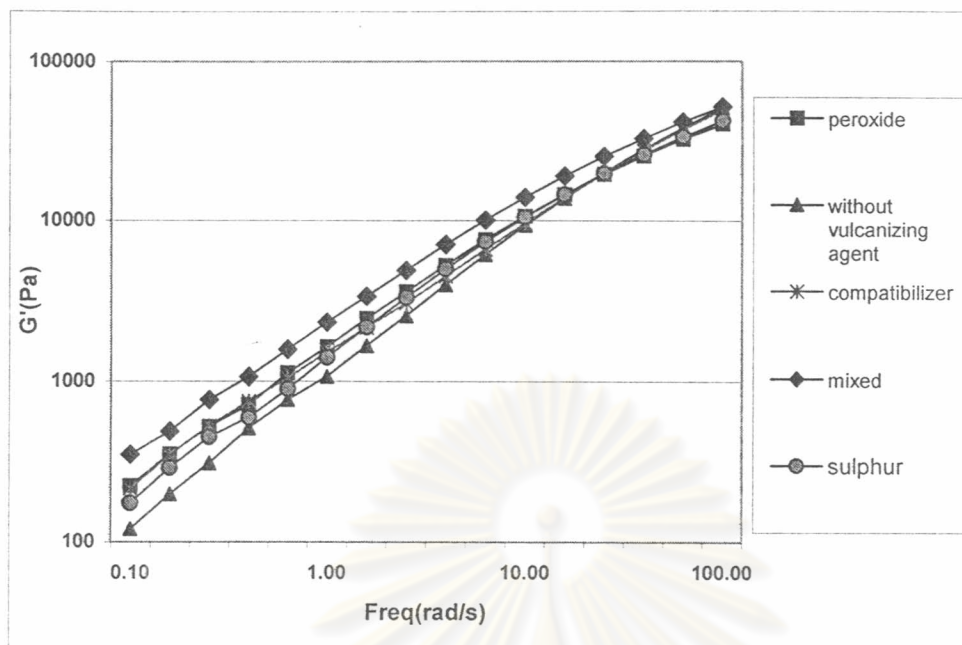


Figure 4.2.7 The effect of angular frequency on the storage modulus (G') of 50/50 RTR/LDPE blends.

4.3 RTR and LLDPE Blends.

4.3.1 Impact Testing

It is observed that impact strength of all blends increases with increasing RTR loading up to 50 pbw due to impact energy absorption of RTR. When the RTR was higher than 50 pbw, the impact strength of the blend dropped. This is probably attributable to the amount of carbon black that was already present in RTR that was critical point for the improvement. Thus at the critical carbon black concentration, the RTR/LLDPE blend can have a split in the layer structure providing a shorter path for fracture propagation, thereby causing the sudden decrease in impact strength [23, 36, 38].

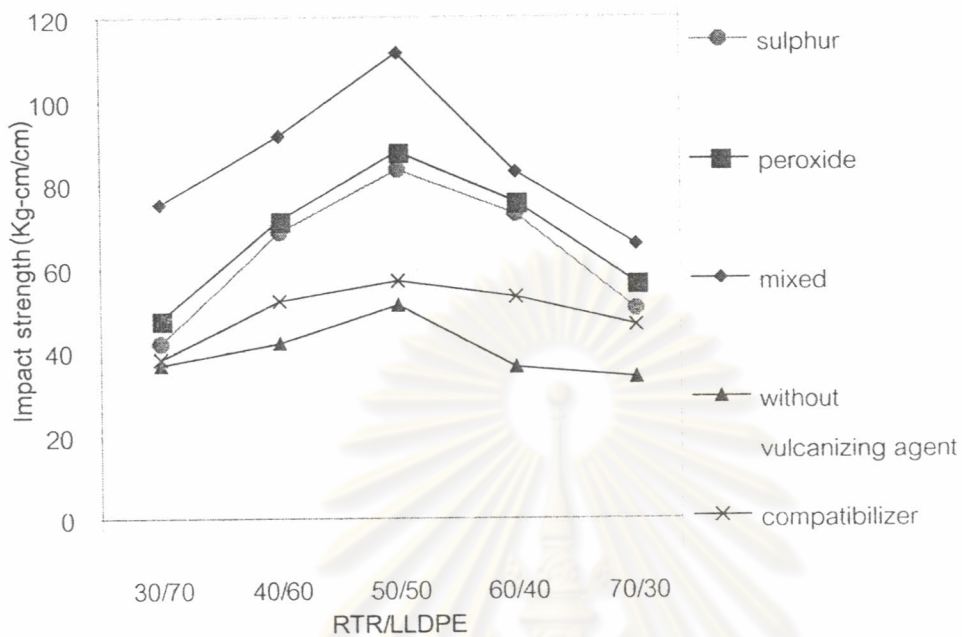


Figure 4.3.1 Impact strength of vulcanized RTR/LLDPE blends.

RTR/LLDPE blend without vulcanizing agent showed lower impact strength than the blends with compatibilizer, sulphur system, peroxide system, mixed system. Three types of crosslinking systems were compared. From the result in the Figure 4.3.1 also showed that the blend obtained from mixed vulcanization was found to exhibit highest impact strength whereas from the compatibilizer and without vulcanizing agent showed the lowest. That obtained from the peroxide and sulphur system showed an intermediate behavior.

4.3.2 Tensile Testing

Figure 4.3.2 shows that without vulcanizing agent blend exhibits lowest tensile strength at all blend ratios whereas RTR/LLDPE blends with compatibilizer, sulphur, peroxide and mixed system show higher tensile strength, respectively. It evidenced that a compatibilizer and dynamic vulcanization significantly improved the mechanical behavior of the blend. It is also observed that tensile strength decreases with higher RTR loading. This is probably attributable to the amount of carbon black that was already present in RTR which may inhibit the molecular orientations and mobility of the rubber. The similar observation was reported by Sombatsompop et al. [35]. RTR/LLDPE blends with mixed system showed the highest tensile strength at every ratio. This is due to the interfacial crosslinking via the formation of sulfur bridges in RTR particles and compatibilizing action of MA/DCP induced by the dipolar interaction between the MA graft LLDPE and NR, SBR components in RTR.

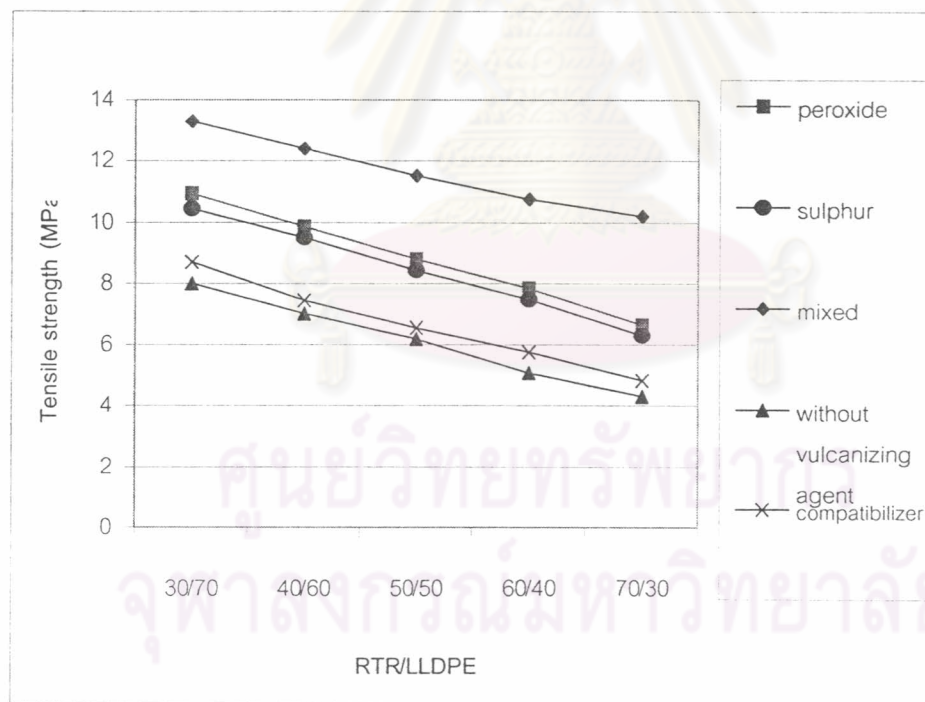


Figure 4.3.2 Tensile strength of vulcanized RTR/LLDPE blends.

4.3.3 Solvent Swelling

Swell ratio of RTR/LLDPE blended with mixed system is the lowest whereas without vulcanizing agent is the highest. This indicates higher degree of crosslinking density and the filler-matrix interaction makes the physical bonds at the interface to withstand the shear force caused by swelling of polymer.

Table 4.3.1 Swell ratios of 50/50 RTR/LLDPE blends

Addition system	Swell ratio
Sulphur system	1.39
Mixed system	1.31
Peroxide system	1.35
Compatibilizer system	1.47
Without vulcanizing agent	1.53

4.3.4 Thermogravimetric Analysis (TGA)

In the TGA run, with the increase in temperature, the thermal degradation of filled polymer systems takes place through various steps. We studied the TGA scans of RTR/LLDPE blends at very low heating rate of 2 °C/min (Figure 4.3.3). The TGA scan shows sharp drop at 400 and 500 °C. It was found that degradation at 400 °C increased and 500 °C decreased with increasing RTR content in RTR/LLDPE blend.

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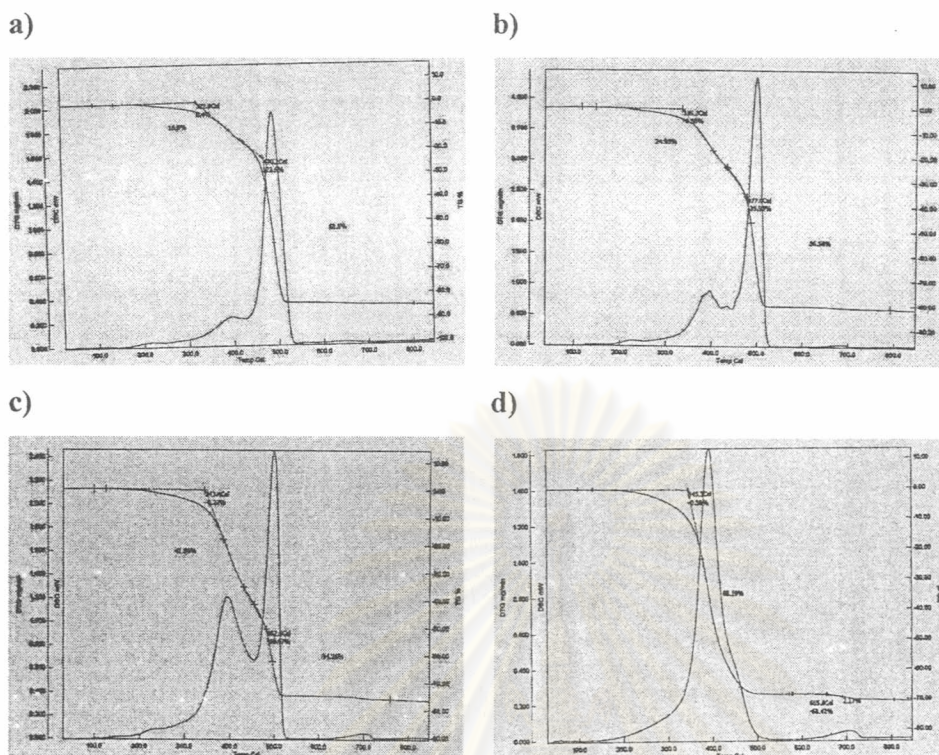


Figure 4.3.3 TGA thermograms of RTR/LLDPE blends using sulphur vulcanizing agent; a) 30/70, b) 50/50, c) 70/30, d) 100/0 .

4.3.5 Differential Scanning Calorimetry Analysis (DSC)

Glass transition temperature (T_g), melting temperature (T_m) and degree of crystallinity of RTR/LLDPE blends, as measured by DSC, are shown in Table 4.3.2.

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Table 4.3.2 Thermal analysis of RTR/LLDPE blends

Blend (RTR/LLDPE)	T _g (°C)	T _m (°C)	ΔH _f (J/g)	Crystallinity(%)
30/70 mixed system	-41.02	116.68	54.46	18.55
50/50 mixed system	-45.81	115.70	45.32	15.44
70/30 mixed system	-50.30	115.28	27.54	9.38
50/50 sulphur system	-55.17	115.72	40.87	13.92
50/50 peroxide system	-59.72	112.55	43.15	14.70
50/50 compatibilizer system	-59.87	116.90	40.38	13.75
50/50 without vulcanizing agent	-60.00	116.19	40.29	13.72

It found that the addition of RTR affected the T_g by shifting it towards lower temperatures with higher RTR loading. At 50/50 ratio, RTR/LLDPE blends using mixed system has the highest T_g. This indicates an effective crosslinking using mixed system for interfacial adhesion of RTR and LLDPE blends [42]. The low T_g obtained in the presence of RTR and peroxide, sulphur, compatibilizer, without vulcanizing agent indicated an increased segmental mobility of the rubber chains [32]. For the melting of RTR/LLDPE blends using mixed system, the T_m decreased with decreasing in concentration of the plastic phase (30/70 to 70/30 RTR/LLDPE). This is due to the fact that RTR has less ordered structure than the LLDPE. Also, the inclusion of the more flexible phase of RTR could disturb the packing of LLDPE chains. [36].

4.3.6 Phase Morphology of Blends

The phase morphology of unvulcanized and vulcanized RTR/LLDPE blends were studied (Figures 4.3.4-4.3.5). RTR/LLDPE blend without dynamic curing system (Figure 4.3.4d) appears to have larger RTR aggregates particle size than the blend with mixed system (Figure 4.3.4b). This result can be explained that better dispersion apparently occurs from the effective role of crosslink in resisting rubber

reagglomeration. Among mixed system, RTR/LLDPE blend (30/70-70/30), show RTR aggregates increase when the RTR content in the blends increases (Figures 4.3.4 a-c). This probably due to the limitation of the amount of carbon black in the blend since carbon black can partially immobilize the chain segment of rubber. This observation is consistent with the sudden drop of impact and tensile strength of RTR/LLDPE blend at 70/30. The morphology of 50/50 RTR/LLDPE blends with compatibilization and different dynamic curing systems are shown in Figure 4.3.5. This explains that RTR particles can better disperse in LLDPE matrix of the blend with mixed system than added with peroxide, sulphur, compatibilizer, and without vulcanizing agent. It is seen that the distribution of rubber is fine and, hence, the crosslinking is the most effective in these system causing improvement in physical properties [20, 36, 39].

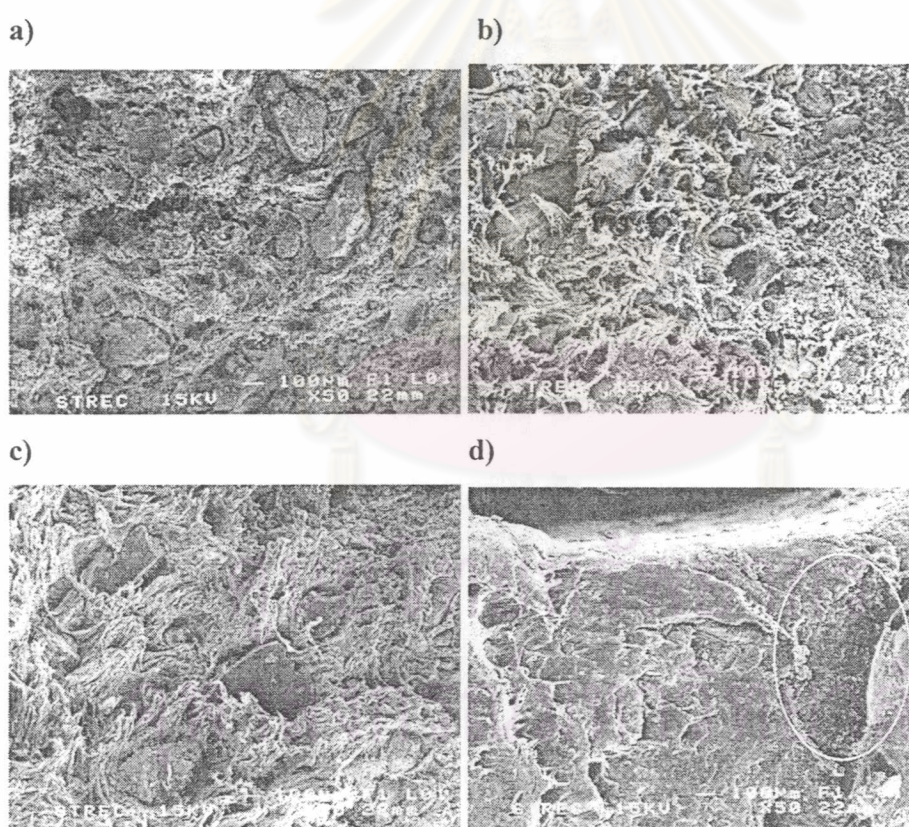


Figure 4.3.4 Scanning electron micrographs of RTR/LLDPE blends with mixed vulcanizing agent; a)30/70, b)50/50, c) 70/30, d) 50/50 without vulcanizing agent.

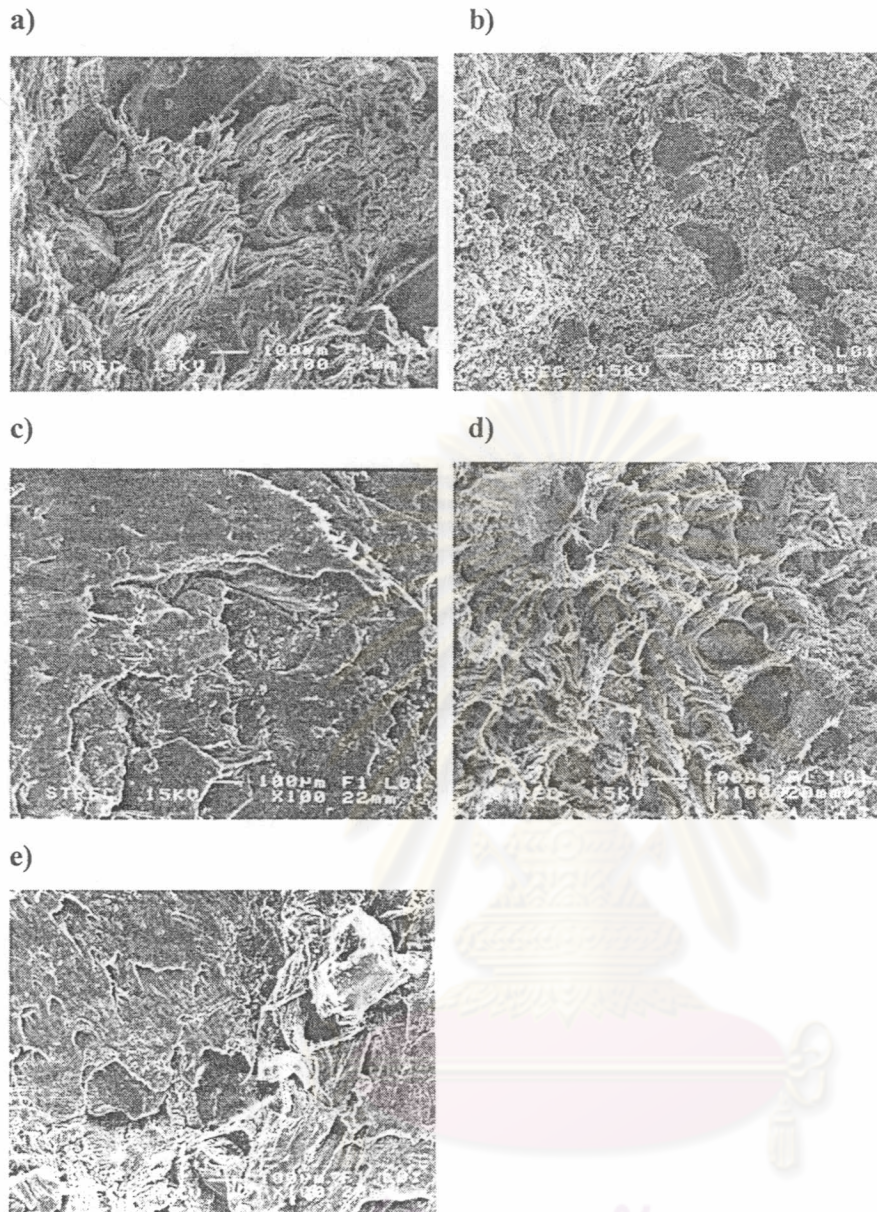


Figure 4.3.5 Scanning electron micrographs of 50/50 RTR/LLDPE blends with different vulcanizing agents; a) sulphur system, b) mixed system, c) compatibilizer system, d) peroxide system, e) without vulcanizing agent.

4.3.7 Rheological Behavior

Figure 4.3.6 showed melt viscosities of RTR/LLDPE blends with compatibilizer and different vulcanizing agent at different angular frequency.

Rheological behavior indicated that the viscosity decreases with increasing angular frequency which indicated pseudoplastic behavior. Viscosity of RTR/LLDPE blends with mixed system showed the highest viscosity whereas the blends with compatibilization and without dynamic curing showed the lowest. The peroxide and sulphur system showed an intermediate behavior. This indicates that the high viscosity might be due to the influence of the vulcanization system which results in high degree of crosslink. The lower deformation rate in the case of the cured samples could be due to the dispersed rubber particles into the LLDPE matrix as a result of dynamic vulcanization [40].

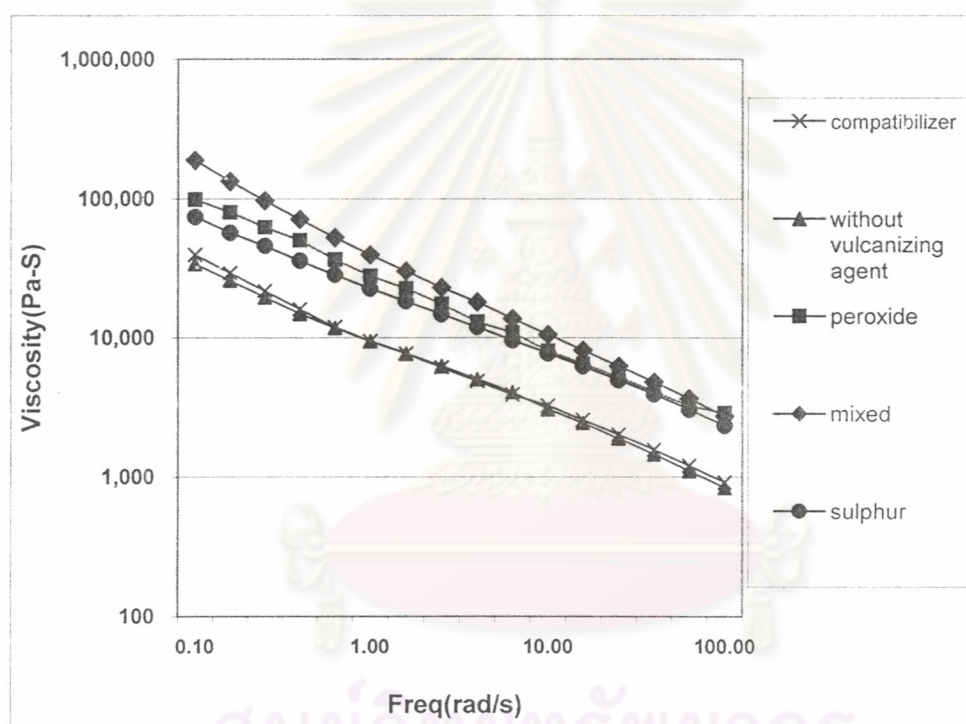


Figure 4.3.6 The effect of angular frequency on the apparent melt viscosity of 50/50 RTR/LLDPE blends.

Figure 4.3.7 also show the frequency dependency of storage modulus (G') of the blends. G' value of the blends with mixed system are the highest. It can be attributed to entanglement of the LLDPE chain segment with RTR. It may also indicate positive interaction between the two polymers [41]. It also showed that RTR/LLDPE blend with peroxide and sulphur system showed an intermediate

behavior whereas with compatibilizer and without vulcanizing agent showed the lowest storage modulus.

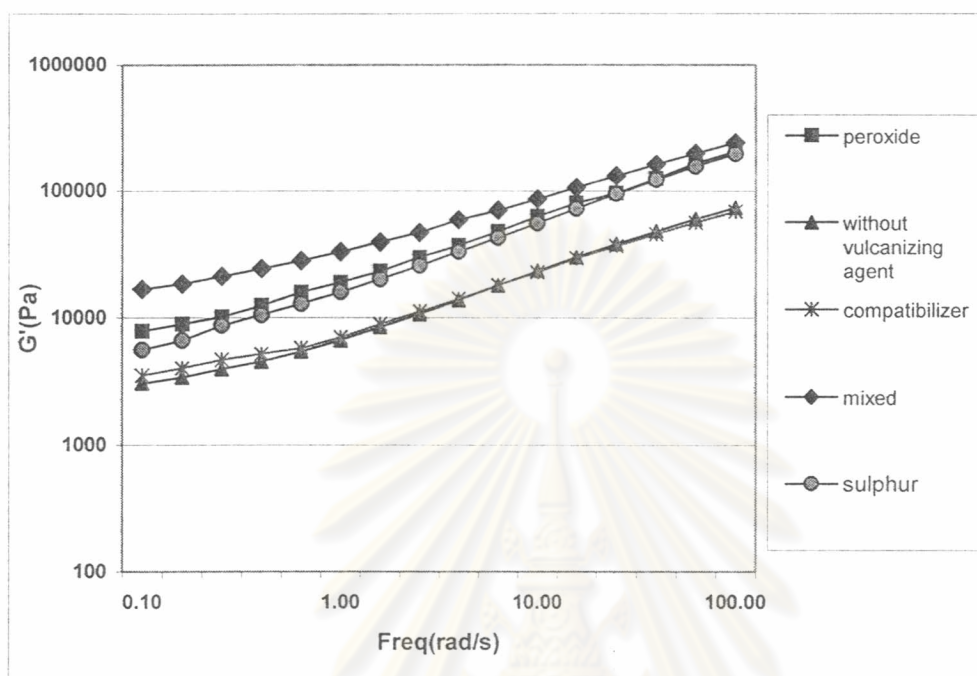


Figure 4.3.7 The effect of angular frequency on the storage modulus (G') of 50/50 RTR/LLDPE blend with compatibilizer and different vulcanizing agents.

4.4 RTR and PP blends.

4.4.1 Impact Testing

It is observed that the impact strength of all blends increases with increasing RTR loading up to 60 pbw due to impact energy absorption of RTR. At higher loading, the impact strength of each blend was dropped. Thus at the critical carbon black concentration, the RTR/PP blend can have a split in the layer structure providing a shorter path for fracture propagation, thereby causing the sudden decrease in impact strength [23, 36, 38]. RTR/PP blend without vulcanizing agent showed lower impact strength than the blends with sulphur system, mixed system compatibilizer, peroxide system. In vulcanization system, three types of crosslinking systems have been used.

From the result in the Figure 4.4.1 also showed that dynamic vulcanization by peroxide system was found to exhibit highest impact strength, without vulcanizing agent showed the lowest. The sulphur, mixed and compatibilizer system showed an intermediate behavior.

Figure 4.4.1 also shows that RTR/PP blend with a compatibilizer exhibits high impact strength, This can be explained that MZ203D (maleic anhydride modified polypropylene) is a suitable compatibilizer for this blend. MZ203D helps reduce the interfacial energy of both phases. This results improved interfacial adhesion and leads to the immiscible blend.

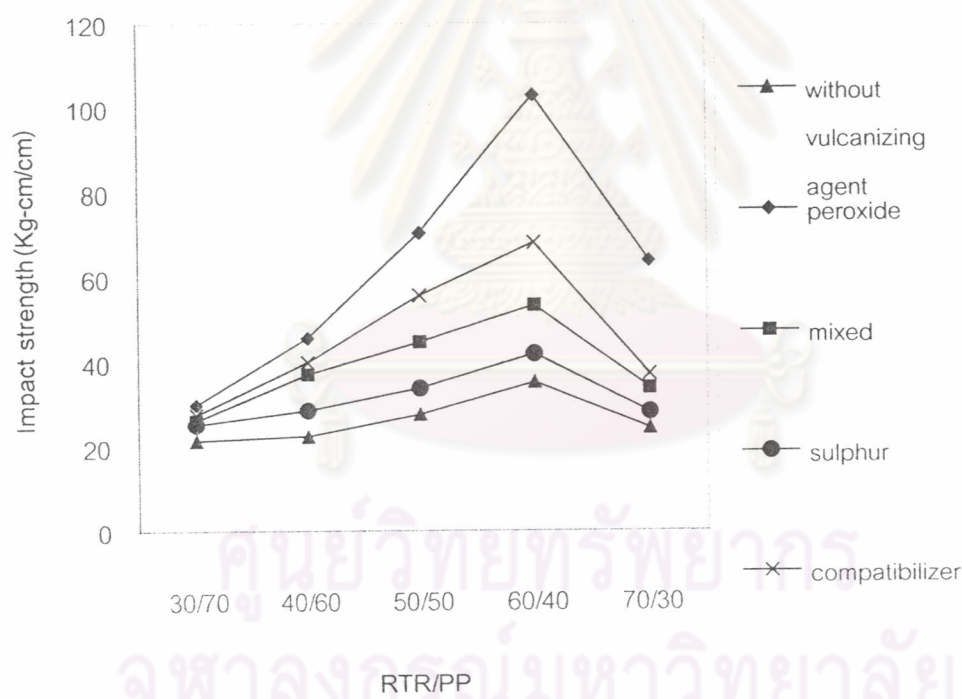


Figure 4.4.1 Impact strength of vulcanized RTR/PP blends.

4.4.2 Tensile Testing

Figure 4.4.2 shows that without vulcanization blend exhibits the lowest tensile strength at all blend ratios whereas RTR/PP blends with sulphur, mixed, compatibilizer and peroxide system show higher tensile strength, respectively. It evidenced that a compatibilizer and dynamic vulcanization significantly improved the mechanical behavior of the blend. It is also observed that tensile strength decreases with higher RTR loading. This is probably attributable to the amount of carbon black that was already present in RTR which may inhibit the molecular orientations and mobility of the rubber. The similar observation was reported by N. Sombatsompop et al. [35]. RTR/PP blends with peroxide system showed the highest tensile strength at every ratio. This is due to the higher opportunity to form crosslink between PP and rubber phase in RTR/PP blend. DCP can initiate free radical and then abstract hydrogen from PP to form PP radical, which reacts with MA and then MA groups are grafted onto PP chain backbone. The compatibilizing action of MA/DCP is induced by the dipolar interaction between the MA grafted PP and recycled NR, BP or SBR, the components in RTR. This causes an increase in interfacial adhesion, which increases the impact and tensile strength of the composite.

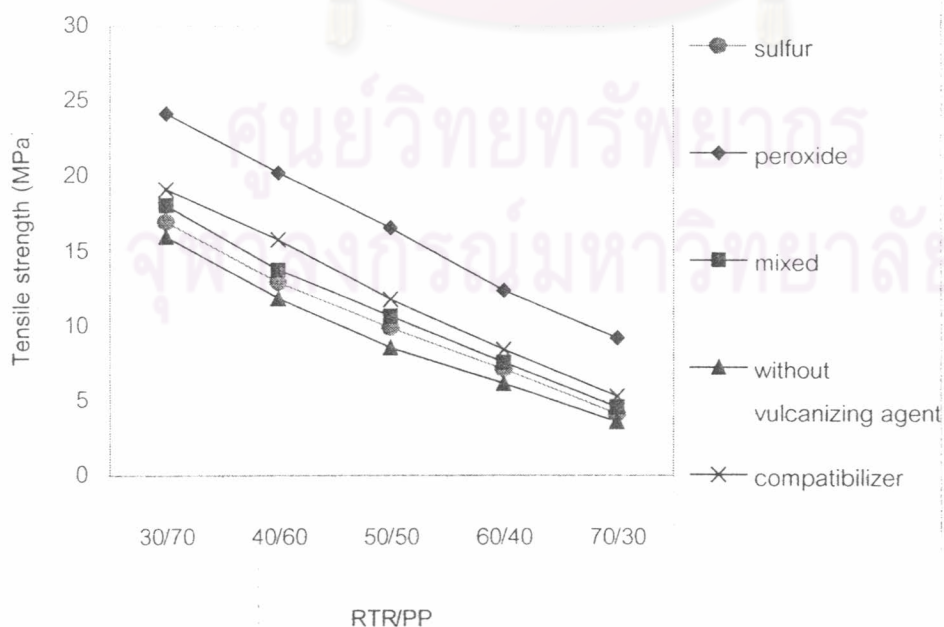


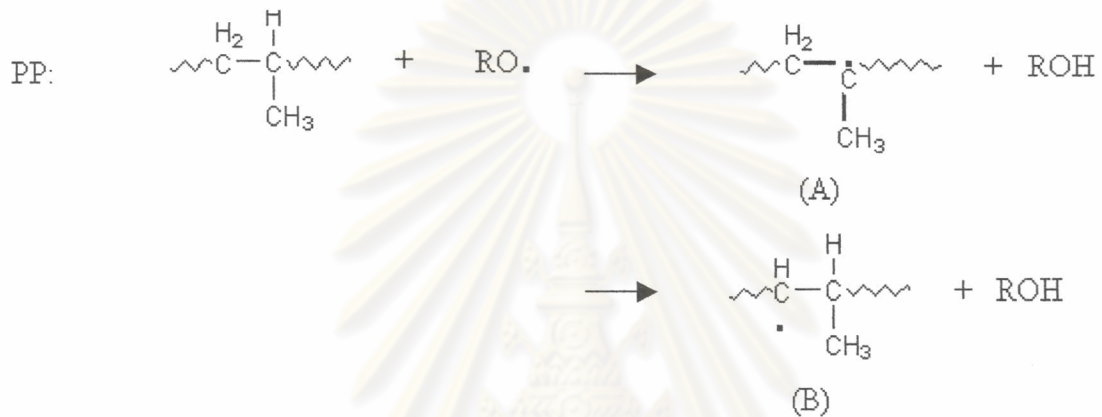
Figure 4.4.2 Tensile strength of vulcanized RTR/PP blends.

The crosslink between PP and rubber by the corporation reaction of MA and DCP as follows;

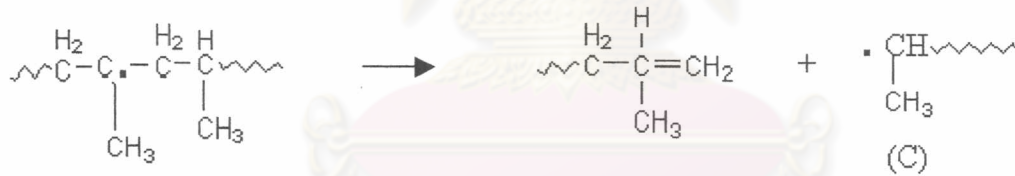
Initial Decomposition of DCP



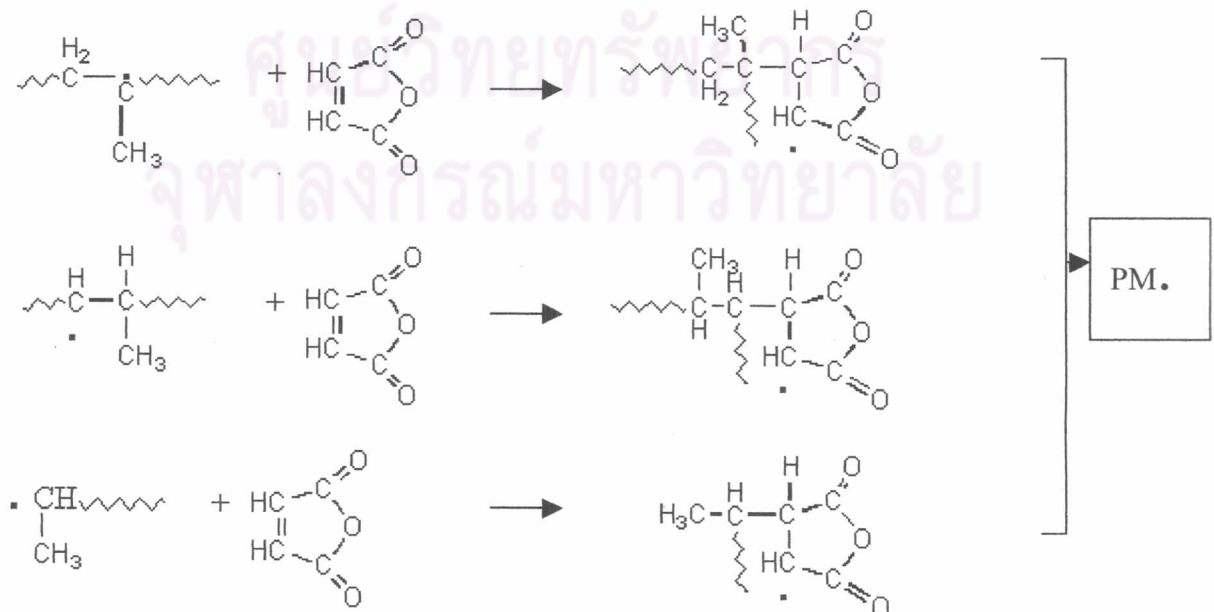
H-abstraction



Beta-scission of PP



Anhydride grafting



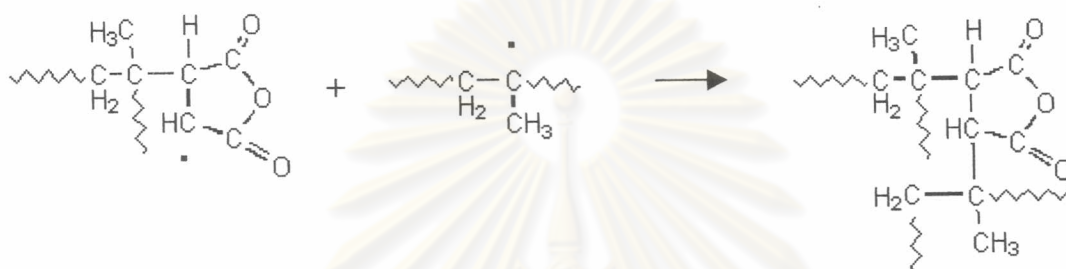
PM.

Chain transfer



Termination

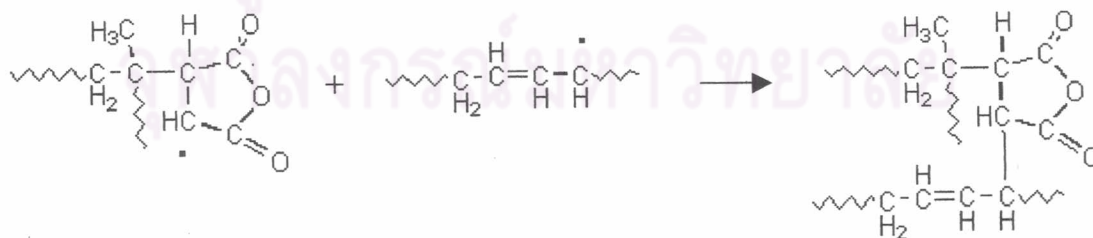
- Termination via combination of PP-PP

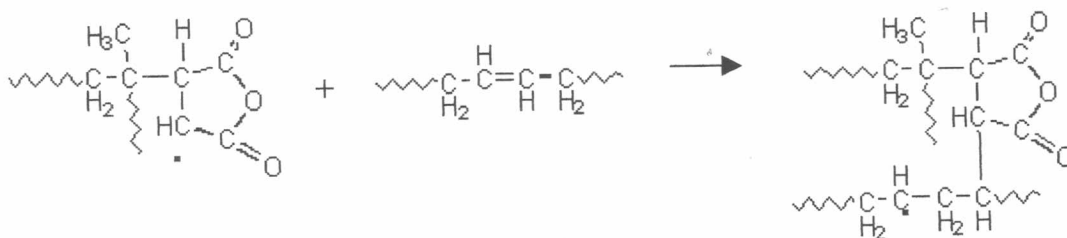


- Termination via disproportionation of PP-PP



- Termination via disproportionation of PP-Rubber





4.4.3 Solvent Swelling

Results of equilibrium swelling studies of the blends in toluene provide information about the filler-matrix interaction. Swell ratio of RTR/PP blended with peroxide is lower than the ones with compatibilizer, mixed, sulphur and without vulcanizing agent. This indicates higher degree of the filler-matrix interaction makes the physical bonds at the interface to withstand the shear force caused by swelling of polymer [31].

Table 4.4.1 Swell ratios of 60/40 RTR/PP blends

Addition system	Swell ratio
Sulphur system	1.47
Mixed system	1.42
Peroxide system	1.38
Compatibilizer system	1.40
Without vulcanizing agent	1.52

4.4.4 Thermogravimetric Analysis (TGA)

Generally, all commercial elastomers degrade between 300 and 550 °C in a usual TGA because of their hydrocarbon nature and each degradation step can be attributed to the characteristic feature of the individual polymer and its specific architecture. In the TGA run, with the increase in temperature, the thermal degradation of filled polymer systems takes place through various steps. We studied the TGA scans of RTR/PP blends at very low heating rate of 2 °C/min (Figure 4.4.3).

The TGA scan shows sharp drop at 400 and 500°C. It was found that degradation at 400°C increased but at 500°C decreased with increasing RTR content in the RTR/PP blend. The TGA scan of RTR/PP blends with different vulcanizing agents shows no different result of degradation [34].

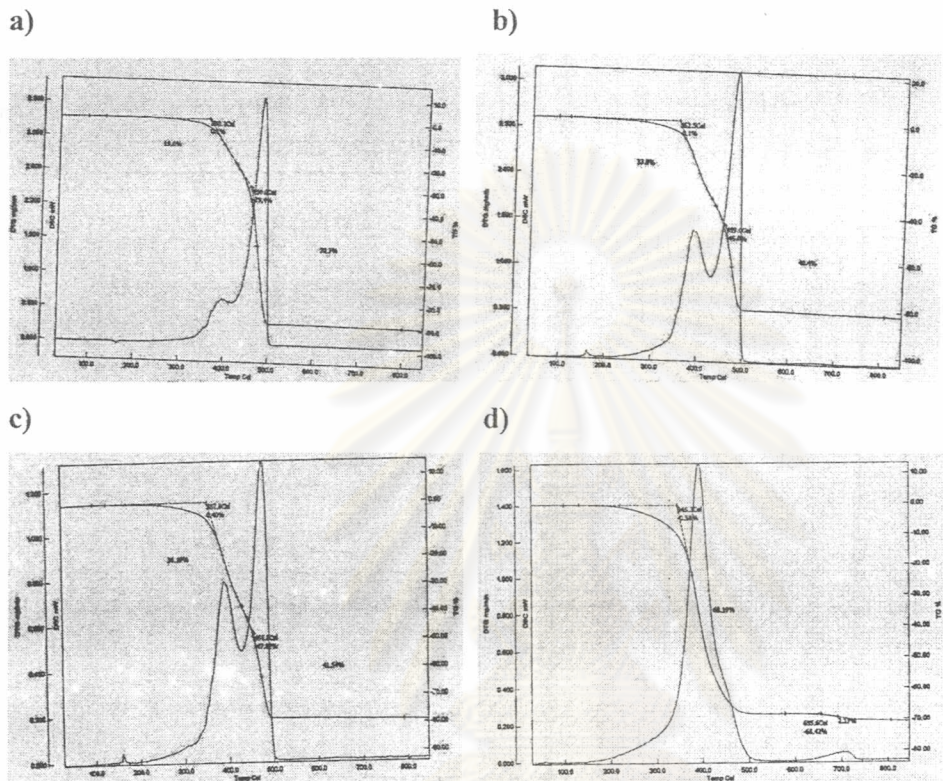


Figure 4.4.3 TGA thermograms of RTR/PP blends using peroxide vulcanizing agents; a) 30/70, b) 50/50, c) 70/30, d) 100/0.

4.4.5 Differential Scanning Calorimetry Analysis (DSC)

Glass transition temperature (T_g), melting temperature (T_m) and degree of crystallinity of RTR/PP blends, as measured by DSC, are shown in Table 4.4.2.

Table 4.4.2 Thermal analysis of RTR/PP blends

Blend (RTR/PP)	T _g (°C)	T _m (°C)	ΔH _f (J/g)	Crystallinity(%)
30/70 peroxide system	-56.46	167.76	73.22	35.36
60/40 peroxide system	-57.22	164.07	41.15	19.87
70/30 peroxide system	-58.38	163.44	37.06	17.89
60/40 mixed system	-58.61	162.56	27.09	13.08
60/40 sulphur system	-58.76	162.49	23.86	11.52
60/40 compatibilizer	-57.44	164.28	41.64	20.11
60/40 without vulcanizing agent	-60.56	163.28	41.62	20.10

It found that the addition of RTR affected T_g by shifting it towards lower temperatures with higher RTR loading. At 60/40 ratio, RTR/PP blends using peroxide system has the highest T_g. This indicates an effective crosslinking using peroxide system for interfacial adhesion of RTR and PP blends [42]. The low T_g obtained in the presence of RTR and without vulcanizing agent, sulphur, mixed, compatibilizer indicate an increased segmental mobility of the rubber chains [32]. For T_m of RTR/PP blends using peroxide system, it is found to decrease with a decrease in concentration of the plastic phase (30/70 to 70/30 RTR/PP). This caused by the lower percentage crystallinity of PP due to more RTR present in the blends. The inclusion of the more flexible phase of RTR could disturb the packing of PP chains. [36].

4.4.6 Phase Morphology of Blends

The phase morphology of without vulcanized and vulcanized RTR/PP blends were studied (Figures 4.4.4-4.4.5). RTR/PP blend without dynamic curing system (Figure 4.4.4d) appears to have larger RTR aggregates particle size than the blend with peroxide system (Figure 4.4.4b). This result can be explained that better dispersion apparently occurs from the effective role of crosslink in resisting rubber reagglomeration. Among peroxide system, RTR/PP blend (30/70-70/30), show RTR aggregates increase when more RTR content of blends (Figures 4.4.4 a-c). This

probably due to the limitation of the amount of carbon black in the blend since carbon black can produce a partial immobilization of the chain segment of rubber. This observation is consistent with the sudden drop of impact and tensile strength of RTR/PP blend at 70/30. The morphology of 60/40 RTR/PP blends with compatibilizer and different vulcanizing agents are shown in Figure 4.4.5. This explains that RTR particles can better disperse and finer distribution in PP matrix of the blend with peroxide system than compatibilizer, mixed, sulphur and without vulcanizing agent. It is seen that the distribution is fine and, hence, the crosslinking is the most effective in these system causing improvement in physical properties [20, 36, 39].

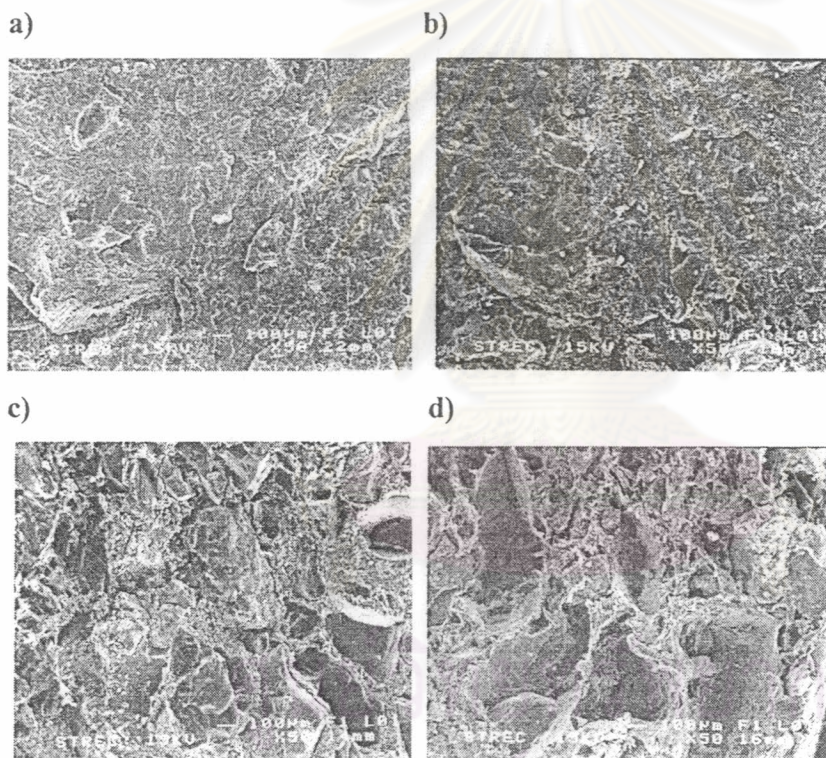


Figure 4.4.4 Scanning electron micrographs of RTR/LDPE blend with peroxide vulcanizing agent; a)30/70, b)60/40, c) 70/30, d) 60/40 without vulcanizing agent.

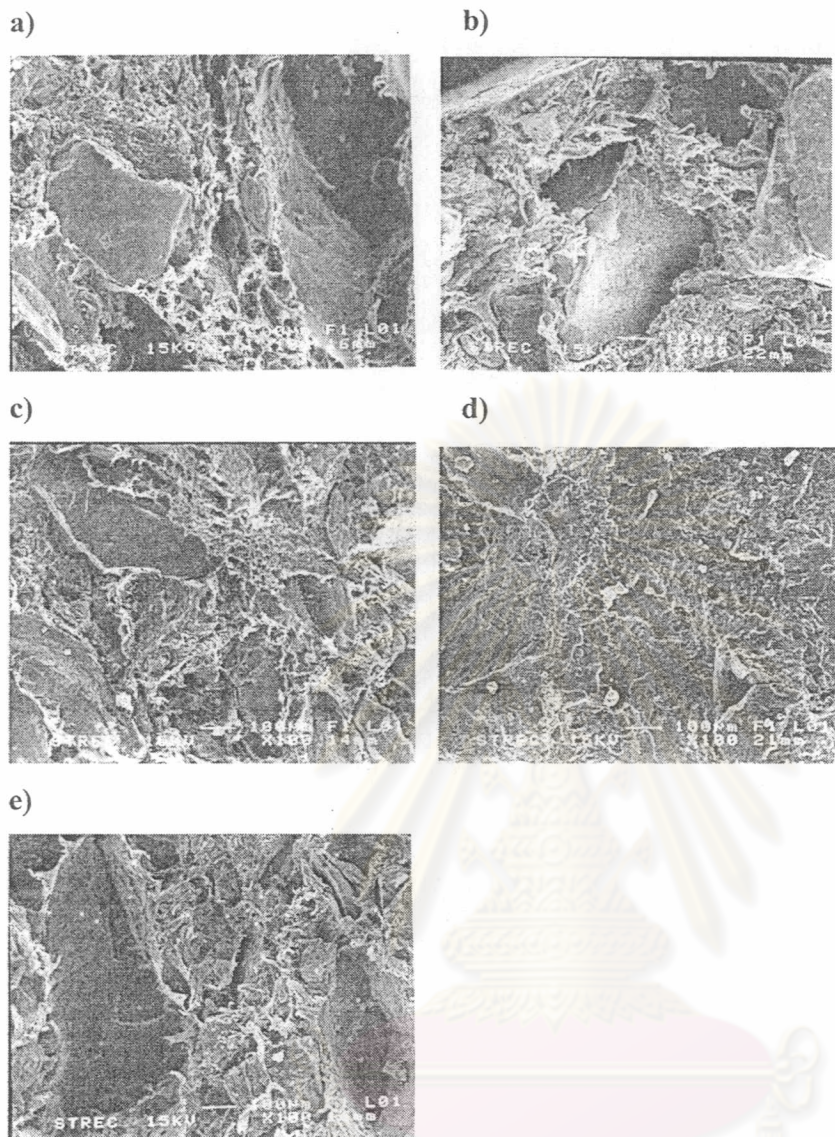


Figure 4.4.5 Scanning electron micrographs of 60/40 RTR/PP blends with different vulcanizing agents; a) sulphur system, b) mixed system, c) compatibilizer system, d) peroxide system, e) without vulcanizing agent.

4.4.6 Rheological Behavior

Figure 4.4.6 shows melt viscosities of RTR/PP blends with compatibilizer and different vulcanizing agent at different angular frequency. Rheological behavior indicates that the viscosity decreases with increasing angular frequency which indicates pseudoplastic behavior. Viscosity of RTR/PP blends with peroxide system

show the highest viscosity. This indicates that the high viscosity might be due to the influence of the vulcanization system which results in high degree of crosslink. The lower deformation rate in the case of the cured samples could be due to the dispersed rubber particles into the PP matrix as a result of dynamic vulcanization [40].

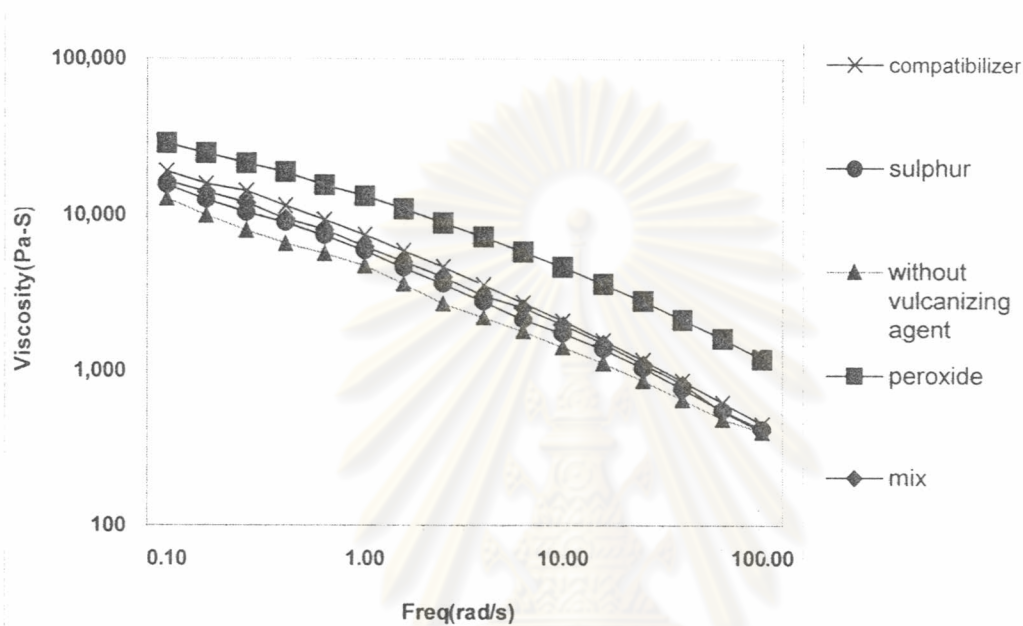


Figure 4.4.6 The effect of angular frequency on the apparent melt viscosity of 60/40 RTR/PP blends.

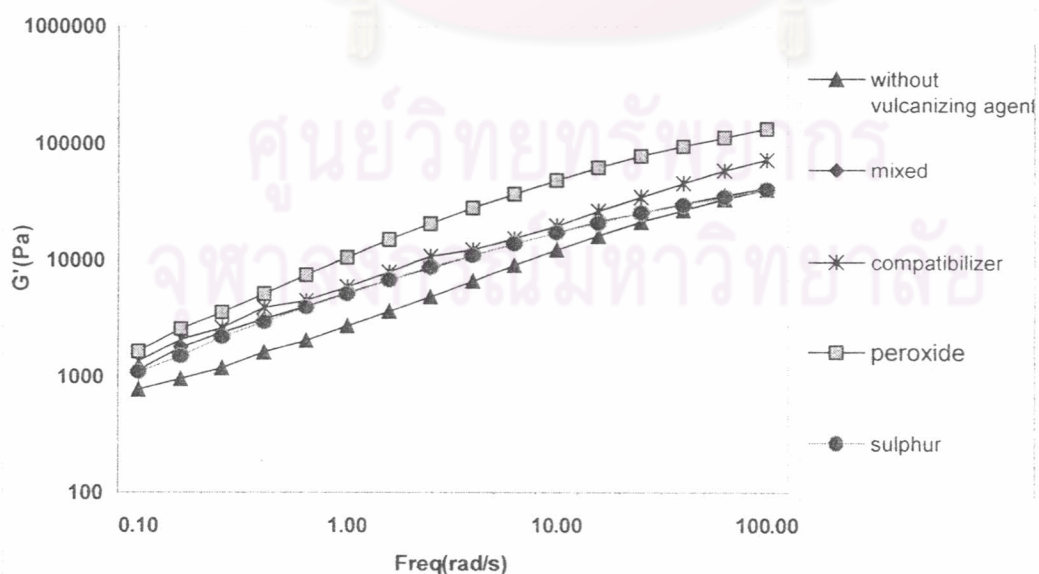


Figure 4.4.7 The effect of shear frequency on the storage modulus (G') of 60/40 RTR/PP blends.

Figure 4.4.7 show the frequency dependency of storage modulus (G') of the blends. At high frequencies, G' value of the blends with peroxide system are the highest. It can be attributed to entanglement of the PP chain segment with RTR. It may also indicate positive interaction between the two polymers and a higher elasticity can be observed. [41].

4.5 Comparison.

Table 4.5 shows RTR/polyolefin blends at ratio that display the best mechanical properties. This indicates that sulphur vulcanizing agent is suitable for RTR/HDPE blend due to sulphur crosslinking occur between RTR molecule and also depend on structure of HDPE is dense and not allow peroxide molecule react into intramolecular or intermolecular of HDPE. Mix vulcanizing agent is suitable for RTR/LDPE and RTR/LLDPE blend due to their branch structure allows peroxide molecule to react into molecular of LDPE or LLDPE and compatibilizing action of MA/DCP induced by the dipolar interaction between the MA graft PE and NR, SBR components in RTR. RTR/PP blends with peroxide system showed the highest tensile physical properties. This is due to the positive induction effect of the methyl group of PP facilitates a Beta-scission of the C-H bonds and initiate free radical by peroxide, which reacts with MA and then MA groups are grafted onto PP chain backbone. The compatibilizing action of MA/DCP is induced by the dipolar interaction between the MA grafted PP and recycled NR, BR or SBR, the components in the RTR [19,36]. From Table 4.5 show that RTR/LLDPE blend using mix vulcanizing agent showed the highest ultimate elongation and high impact strength and tensile strength. This blend has similar properties to thermoplastic elastomer which have mechanical properties as rubber and are processable as thermoplastic. However, they have to further investigation to obtain more data.

Table 4.5 Properties of RTR and polyolefin blends at the highest physical properties.

RTR/Polyolefin				
Properties	RTR/HDPE	RTR/LDPE	RTR/LLDPE	RTR/PP
RTR/Polyolefin ratio	50:50	50:50	50:50	60:40
Vulcanizing agent	sulphur	mix	mix	peroxide
Impact strength((Kg-cm)/cm)	111.48	57.59	111.22	102.84
Tensile strength (MPa)	9.99	5.14	11.53	12.33
Ultimate Elongation(%)	35.03	36.94	406.19	34.41



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