

CHAPTER IV

RESULTS AND DISCUSSION

This chapter was divided into three sections: material characterization, physical properties of PVC blended with rubber, and influence of the compatibilizers on the physical properties of blended PVC.

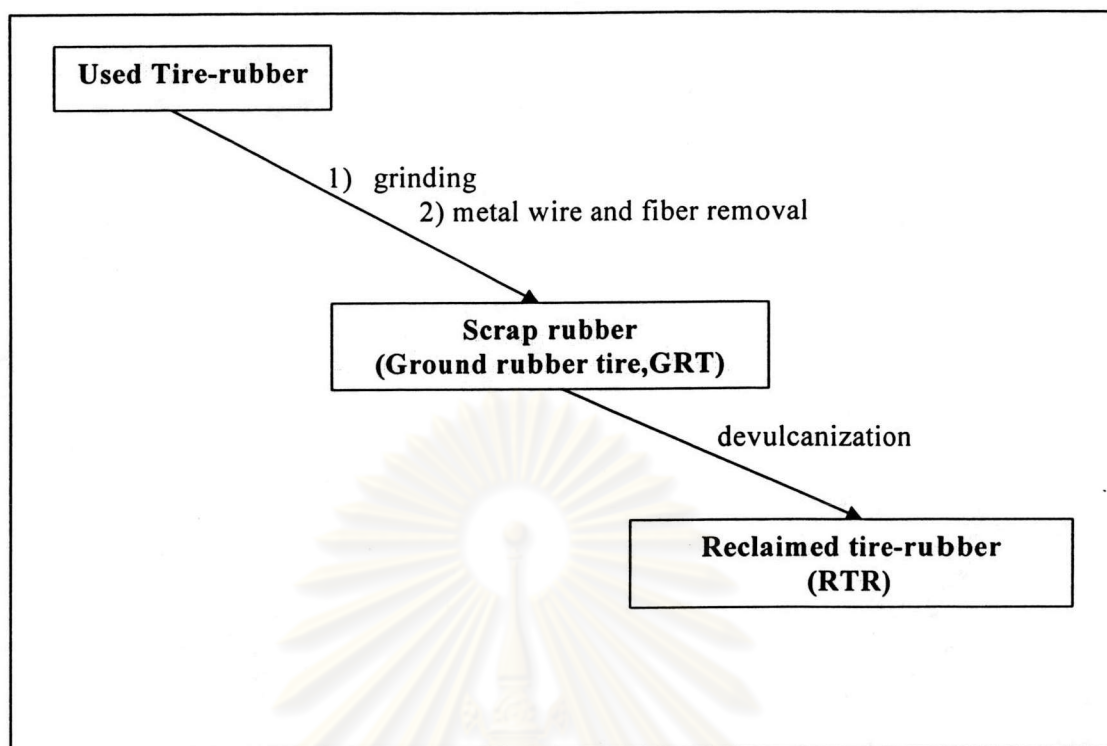
4.1 Material Characterization

PVCs (rigid and soft), tire-rubber wastes (GRT and RTR), and compatibilizers (CSPE and NBR) were used in this study. The physical properties of PVCs and compatibilizers are listed in **Table 4.1**.

Table 4.1 Physical properties of PVCs and compatibilizers.

Physical Properties	PVC		Compatibilizer	
	Rigid PVC	Soft PVC	CSPE	NBR
Impact Strength (J/cm)	2.3	-	-	-
Tensile Strength (MPa)	59	5	28	17.7
Elongation (%)	13	57	520	400
Hardness (Shore A)	-	-	53	70
Hardness (Shore D)	75.9	27	-	-

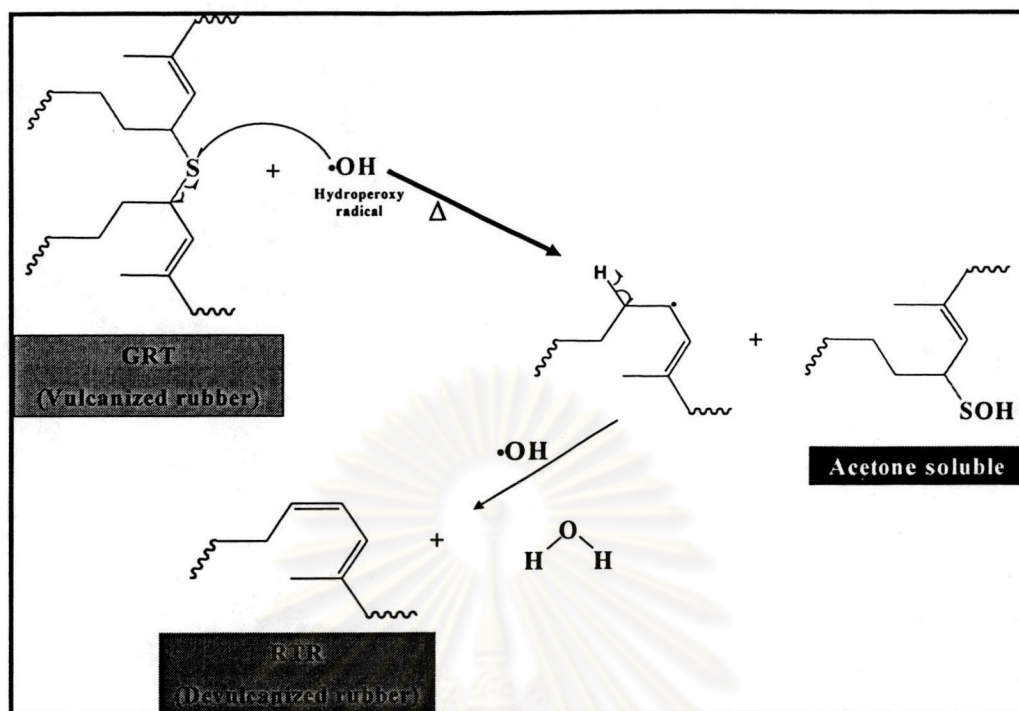
For tire-rubber wastes, the RTR was produced as shown in **Scheme 4.1**.



Scheme 4.1 Diagram of the reclaimed rubber process.

Commonly, the tire-rubber wastes are ground. Then the metal wire and fiber are removed from the scraped tire rubbers. The production of this step is called ground rubber tire (GRT). To produce RTR the devulcanization process of GRT is required. Hydroperoxide is used to chop the S-linkage (**Scheme 4.2**).

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Scheme 4.2 Diagram of devulcanization reaction of GRT

A sulfur derivative residue is generated in this step. To remove the sulfur derivative residue, the crude was extracted by soxhlet extraction with acetone. Then the acetone soluble fraction was identified by using $^1\text{H-NMR}$ technique and XRF technique.

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From XRF spectrum in **Figure 4.1**, it is found that the elements present in the acetone soluble fraction were S, Cl, and P.

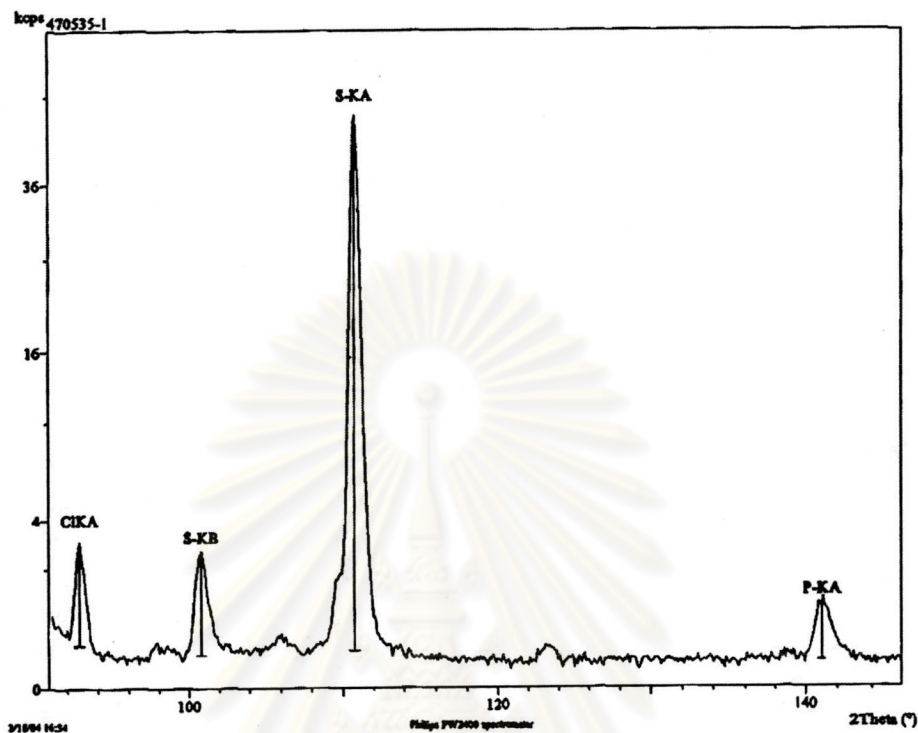


Figure 4.1 The XRF spectrum of acetone soluble fraction of tire-rubber wastes RTR.

In addition $^1\text{H-NMR}$ spectrum (**Figure 4.2**) shows chemical shifts at 1.6 ppm and 5.1 ppm, representing the H of $\beta\text{-C}$ atom and $\alpha\text{-C}$ atom, respectively. The peak at 2.0 ppm was assigned as the H of hydroxyl group connecting to S-atom. It is obviously that the result obtained from XRF spectrum corresponded to the information from $^1\text{H-NMR}$ spectrum. It can be concluded that the residue from devulcanization process of RTR was removed by using the acetone extraction method

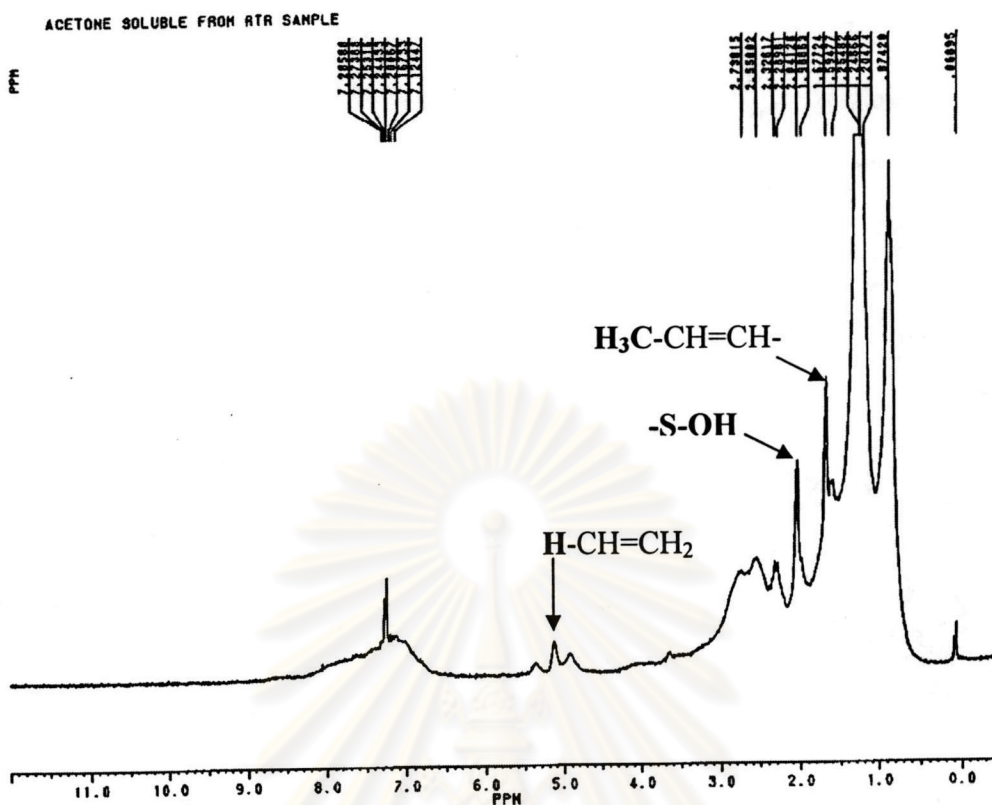


Figure 4.2 The ^1H -NMR spectrum of the acetone soluble fraction of RTR and GRT.

Weights of the acetone soluble fraction of GRT and RTR are shown in **Table 4.2**.

Table 4.2 Acetone soluble content of GRT and RTR samples (average of 10 samples).

Sample	% Acetone soluble fraction	SD	RSD
RTR	15.3±0.9	0.38	1.97
GRT	9.1±0.6	0.23	1.76

Note: When RSD is less than 10%, it means that the distribution of data is acceptable [41].

It indicated that not only RTR but also GRT contained the acetone soluble part but the acetone soluble value of RTR was higher than GRT because RTR was a devulcanized GRT. Due to GRT is vulcanized with sulfur to form a crosslinked tire

rubber and contacted with heat in that process. Some parts may degrade and remain in GRT matrix. When GRT was extracted with acetone, this residue was thus removed. Moreover, the bad smell of original tire-rubber wastes was also eliminated.

4.1.1 The Composition of tire-rubber wastes (GRT and RTR)

To identify the composition of rubber part, the both GRT and RTR were heated from 50°C to 300°C at a heating rate of 10°C/min under nitrogen atmosphere, 300°C to 500°C at a heating rate of 2°C/min under nitrogen atmosphere, and 550°C to 850°C at a heating rate of 10°C/min in nitrogen atmosphere. Because RTR used for this study was specially prepared from GRT which is the same lot number 4530012042, only RTR was analyzed as a representative for GRT. Its thermogram is shown in **Figure 4.3**.

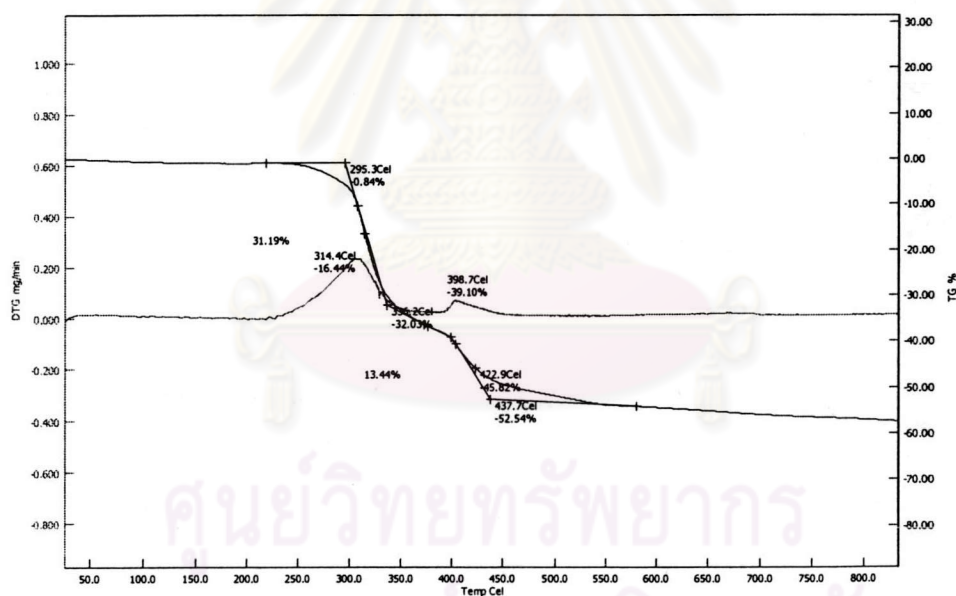
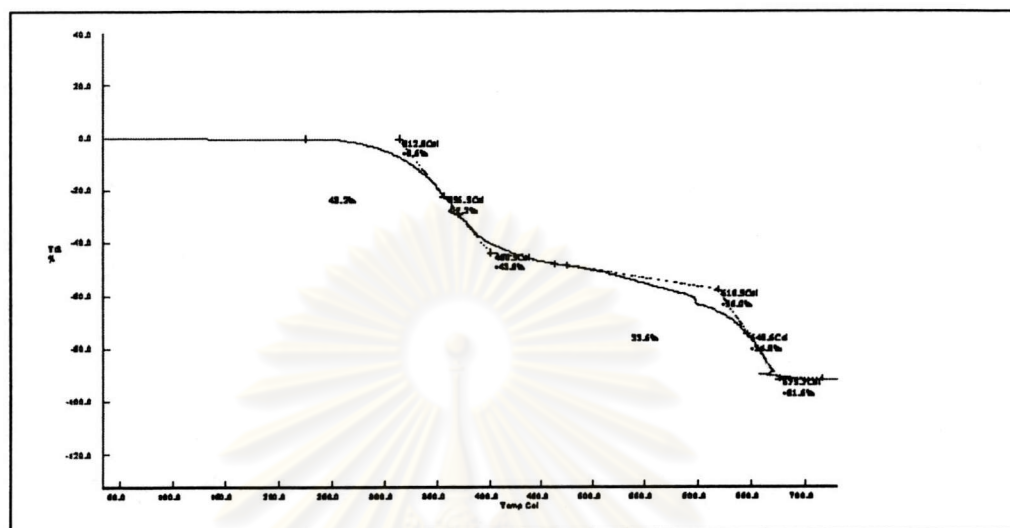


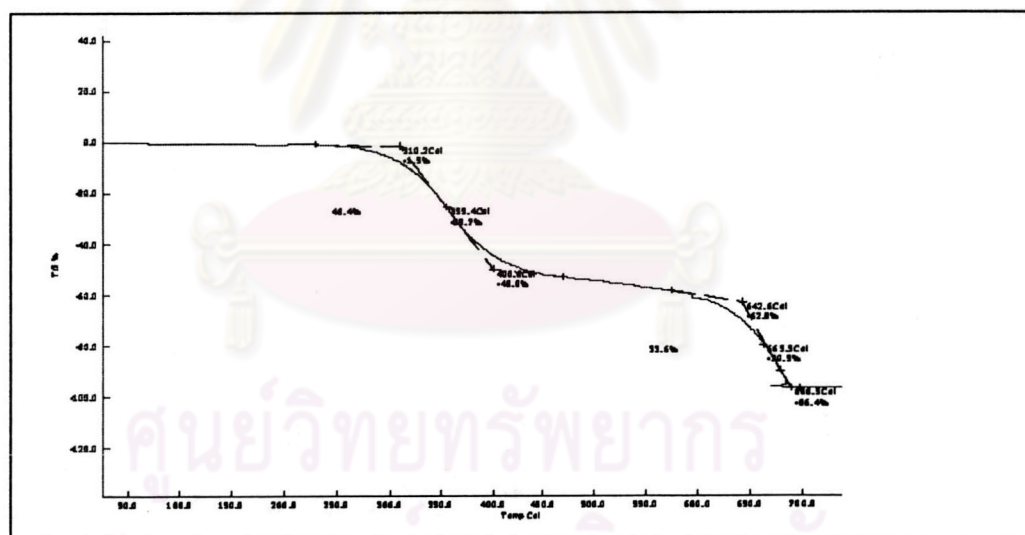
Figure 4.3 TGA Thermogram of Reclaimed Tire Rubber

The TGA thermogram and DTG curve of acetone extracted RTR showed two peaks (314°C and 399°C) in the rubber decomposition zone (350°C and 530°C). This indicated the presence of a rubber blend. So as to determine the composition of tire rubber waste quantitatively, the tire-rubber wastes were treated with the same procedure as the previous condition. But the nitrogen atmosphere was changed to oxygen

atmosphere at 550°C for the determination of carbon black content. Their thermograms are shown **Figure 4.4**.



(a)



(b)

Figure 4.4 TGA thermogram of the acetone extracted tire rubber wastes
(a) RTR (b) GRT

From the thermogram above, no weight loss was observed when heating from room temperature to 300 °C. When the chamber atmosphere was N₂, weight loss

started at a temperature higher than 300°C. At 550°C the chamber atmosphere was changed to oxygen. Carbon black started burning in an oxygen atmosphere to produce CO₂ at ~625°C. Weight loss occurred until all carbon black was oxidized. At this stage only inorganic residues were left. For this study, it indicated that these samples did not contain the carbonate compound because there was no weight loss in their thermogram even the chamber was heated further to 850°C.

The amount of rubber, carbon black, and inorganic residue which represented the inorganic removed additive in the tire-rubber wastes sample were shown in **Table 4.3**.

Table 4.3 The composition of GRT and RTR samples obtained from TGA.

Compositions	RTR	GRT
Rubber Phase (%)	43	48
Carbon Black (%)	34	34
Residue (%)	23	18

4.1.2 The difference of crosslink degree between GRT and RTR

As mentioned above, since RTR is a devulcanized tire rubber waste which it was prepared from the devulcanization process of GRT. To compare the density of crosslink between GRT and RTR, they were evaluated by comparing the swelling weights of GRT and RTR in toluene. It is noted that both GRT and RTR have to be extracted with acetone before use. Results are shown in **Table 4.4**.

Table 4.4 The swelling weight of RTR and GRT (average from 10 samples)

Sample	% weight swelling	SD	RSD
RTR	428.0±3.0	1.22	0.29
GRT	123.0±2.2	0.91	0.74

Remark: The range of interval values were referred at 95% confident level.

It is found that the swelling value of RTR was larger than GRT, indicating that the crosslink density of GRT was higher than that of RTR. Since the GRT is a highly crosslinked polymer, toluene molecule cannot be adsorbed and held in the void between rubber chains. From data above, it was implied that RTR contained double bonds more than GRT.

4.2 Blends of PVC and tire rubber wastes

The influence of tire-rubber wastes on the physical properties of soft PVC (S-PVC) and rigid PVC (R-PVC) is studied. This section is divided into 2 parts: The effect of non-chlorinated and chlorinated RTR and GRT on the physical properties of S-PVC and R-PVC blends. The results of these experiment are discussed in details as follows:

4.2.1 The effect of RTR and GRT on the physical properties of the blended PVC blends.

In this study, tire-rubber wastes and both PVCs were melted and mixed by using a two-roll mill. Then the blends were molded to obtain dumbbell shaped tensile specimens and impact strength specimens. Each blend was prepared into at least three sample sets.

Physical properties

The physical properties of all blends are shown in **Table 4.5**.

Table 4.5 The comparison of physical properties of composited PVCs filled with tire rubber wastes, RTR and GRT.

PVC	sample	Wt of PVC	Wt of used rubber		Physical properties			
			RTR	GRT	Tensile strength (MPa)	Elongation (%)	Hardness (ShoreD)	Impact strength (J/cm ²)
Plasticized PVC	S1	100	-	-	5.4±0.4	57.8±2.8	27.9±2.0	N/A
	I1	100	10	-	3.5±0.3	32.4±3.4	24.7±2.1	N/A
	I2	100	20	-	2.7±0.5	26.2±1.8	24.3±1.4	N/A
	I3	100	30	-	1.6±0.2	15.0±3.0	23.2±1.8	N/A
	I4	100	40	-	No Sheet			
	J1	100	-	10	6.0±0.3	61.7±3.6	26.1±1.6	N/A
	J2	100	-	20	8.4±0.2	52.1±2.7	25.7±1.8	N/A
	J3	100	-	30	4.6±0.4	37.0±5.1	24.5±1.6	N/A
	J4	100	-	40	2.8±0.6	12.6±4.1	23.4±1.6	N/A
	J5	100	-	50	No Sheet			
Rigid PVC	R1	100	-	-	58.6±1.8	13.3±2.9	78.1±2.1	2.3±0.2
	E1	100	10	-	42.7±3.5	11.6±2.2	74.5±1.4	2.4±0.2
	E2	100	20	-	33.0±2.5	10.9±1.3	69.6±2.2	2.6±0.2
	E3	100	30	-	21.7±2.0	9.1±0.5	63.4±2.8	3.0±0.2
	E4	100	40	-	19.2±7.1	4.7±0.7	58.5±2.6	3.0±0.4
	E5	100	50	-	No Sheet			
	F1	100	-	10	37.7±4.2	12.3±4.6	78.3±1.7	2.6±0.6
	F2	100	-	20	31.8±3.7	11.7±1.6	75.5±1.5	2.8±0.6
	F3	100	-	30	20.2±5.6	11.0±2.2	72.8±1.4	3.2±0.2
	F4	100	-	40	15.4±2.1	10.8±0.9	65.5±1.4	3.3±0.3
	F5	100	-	50	14.2±2.3	7.0±1.4	58.5±2.6	3.3±0.3
	F6	100	-	60	No Sheet			

Remark; -N/A = cannot be measured under this testing condition.

-No sheet = this composition could not form a sheet.

In the case of S-PVC blended with the tire-rubber wastes, all tested physical properties were not improved. Especially the impact strength could not be tested because the resulting blend was too soft. It seems that S-PVC is not suitable for this study. Therefore, only R-PVC is continued to be investigated in this study.

For R-PVC, it is found that impact strength slightly increases when the loading of tire-rubber wastes is increased. On the contrary, the tensile strength, elongation and hardness decreased, due to the presence of rubber particles that were

not quite form good interface with PVC. Differences between the impact strength of composites containing with RTR and GRT are not significant enough to draw a conclusion.

At RTR loading higher than 40 phr and GRT loading higher than 50 phr, the blend could not form sheets, because both RTR and GRT contain high amount of carbon black (34 %wt). It could be resulted from the formation of layer-like structure of carbon black in the blend. This phenomenon corresponds to the study done by J.R. Michel [20].

Morphology

SEM photomicrographs of the cryo-fractured surface where from rubber particles had been etched out by boiling in nitric acid were shown in **Figure 4.5**. Pits and holes shown in the pictures are areas where the rubber particles used to be.

From SEM micrographs of the blended PVCs loaded with 50 phr of GRT and 40 phr of RTR, respectively. It was found that a big hold representing the agglomeration of rubber particles was taken place when the loading of tire-rubber wastes was high.

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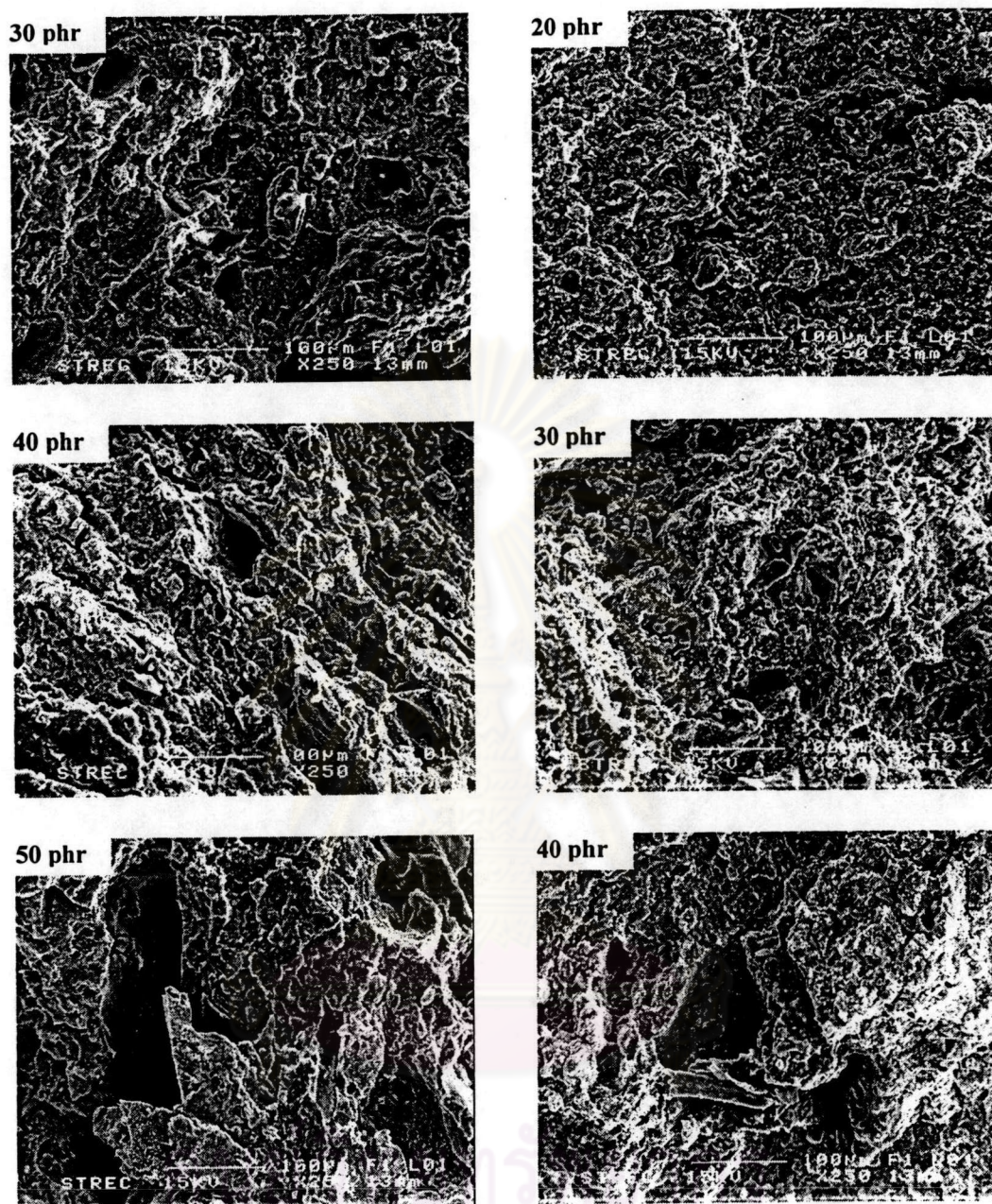


Figure 4.5 SEM photomicrographs of R-PVC/GRT compositions where from GRT phase has been etched out (left) and R-PVC/ RTR compositions (right)

From this study, it could be summarized that rigid PVC was more suitable for further study than plasticized PVC because the quantity of rubber loading both GRT and RTR for rigid PVC was higher than plasticized one. Moreover, it is clear that tire-rubber wastes could improve the impact strength and toughness of rigid PVC. The proper amount of rubber was 30 phr for RTR and 40 phr for GRT, respectively.

4.2.2 The influence of modified tire rubber on the physical properties of rigid PVC.

To reach the aim of this study the used tire-rubber wastes were modified at their surface by chlorinating with trichloroisocyanuric acid (TCICA) [14,16,40]. Then, chlorinated RTR and GRT were blended with R-PVC.

4.2.2.1 Chlorination of tire-rubber wastes, GRT and RTR.

After GRT and RTR were purified by acetone extraction and dried, they were immersed in a freshly prepared TCICA solution in methanol, for 20 min at 25°C. Three concentrations were investigated: 1, 3 and 5% w/v. Then these particles were filtered, washed thoroughly under tap water and dried at 50°C in the oven. The chloride content in the rubber particles was analyzed by means of X-ray fluorescence (XRF). Analysis results of Cl-RTR were exhibited in **Figure 4.6** and **Table 4.6**.

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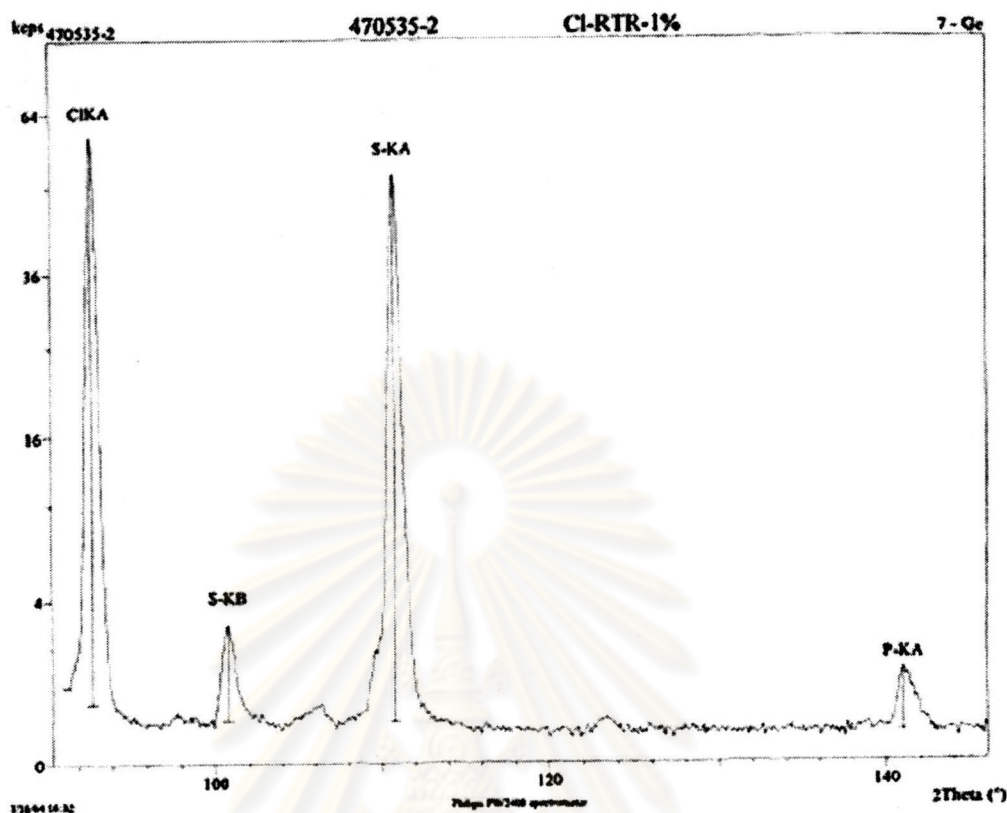


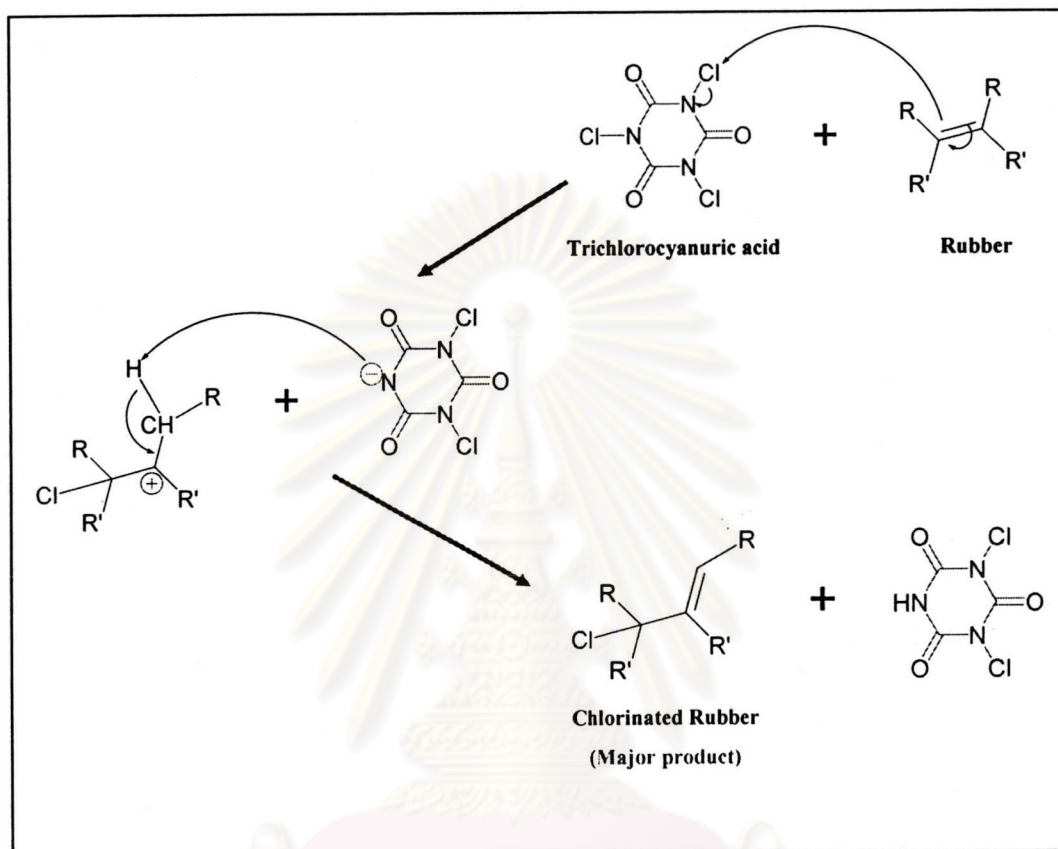
Figure 4.6 : The XRF spectrum of CI-RTR 1%

Table 4.6 The comparison of chloride content in RTR with different concentration of TCICA.

Sample	%Cl (w/w)
Chlorination 1%TCICA	1.0
Chlorination 3% TCICA	1.7
Chlorination 5%TCICA	1.9

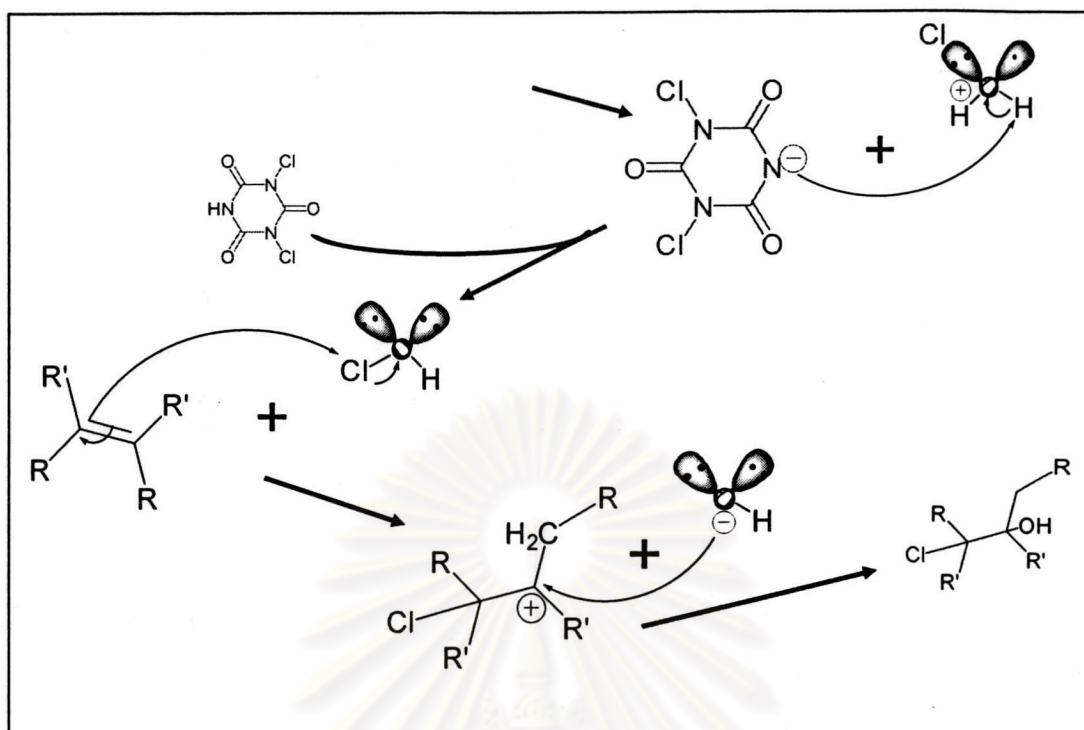
From XRF spectrum, it shows that CI-RTR contains not only chlorine atom but sulfur atom as well. This evidence confirmed that RTR was partially devulcanized and also contained some S-linkage in the crosslink. Sometimes RTR could be called as a natural rubber like (NR) or polydiene compound. In addition the chloride contents were not gone over than 2% w/w although the concentration of TCICA solution was 3 % and 5% w/v. This indicated that the quantity of chloride in RTR depended on the number of double bonds formed during devulcanization of RTR.

Naskar et al. (2001) and Lawson et al. (1996) proposed the chlorination mechanism of polydiene compound by using TCICA. Thus chlorination reaction of RTR with TCICA was proposed in **Scheme 4.3** as a predominant reaction.



Scheme 4.3 The chlorination reaction of RTR with TCICA

Moreover, the side reaction in **Scheme 4.4** might occur because water was used for leaching excess TCICA on the surface of RTR [16].



Scheme 4.4 The side reaction of RTR chlorination during water leaching.

From the above mentioned, the tire-rubber wastes could be modified by chlorinating with TCICA solution. This information is used for the further step of this study.

4.2.2.2 Optimum chloride loading in tire-rubber wastes.

Since the modification of rubber surface is a strategy to increase the interaction between rubber particles and PVC matrix. Increasing chloride content on rubber surface enhances the interaction of both phases. The chlorinated rubbers will be compatible with PVC [39]. Thus the tensile strength, % elongation, hardness, impact strength and also weight swelling would be affected by this phenomenon. In this section, the quantity of modified RTR (Cl-RTR) and modified GRT (Cl-GRT) were fixed at 30 phr and at 40 phr, respectively. These ratios were obtained from section 4.2.1. Physical properties, morphology, and thermal properties were taken into account for finding the optimum recipe of the PVC and modified rubber waste composite.

From **Table 4.7**, the hardness, and impact strength of the composite increased slightly when the concentration of TCICA used for modification of rubber surface was increased. At 5% w/v of TCICA, however, other physical properties except hardness of both Cl-RTR and Cl-GRT dropped to a lower value than the original R-PVC.

The percentage of weight swelling was decreased when the %TCICA was risen. It indicated that the dipole-dipole interaction between PVC and chlorinated rubber particles was strengthened. Thus solvent molecules cannot penetrate into the composite PVC matrix. From all data, the proper concentration of TCICA used to treat tire-rubber waste is 3 %w/v.

Table 4.7 Physical properties of PVC blended with Cl-RTR (30 phr) and GRT (40 phr).

Chlorinated rubber	Physical properties	Concentration of TCICA in methanol (w/v)			
		0%	1%	3%	5%
Cl-RTR	Tensile strength (MPa)	21.7±2.0	22.7±4.3	21.1±2.0	18.1±1.6
	Elongation (%)	9.1±0.5	8.4±0.7	9.7±0.5	9.0±0.6
	Hardness (Shore D)	63.4±2.8	67.7±1.9	68.5±1.4	70.7±1.8
	Impact strength (J/cm ²)	3.1±0.4	3.1±0.2	3.3±0.2	3.2±0.3
	Weight swelling (%)	34.3±2.5	33.4±2.3	30.2±1.7	28.6±4.6
Cl-GRT	Tensile strength (MPa)	15.4±2.1	15.9±1.6	17.7±1.1	14.4±3.4
	Elongation (%)	10.8±0.9	9.8±2.0	11.1±2.0	7.9±2.9
	Hardness (Shore D)	58.5±2.6	70.4±1.3	71.7±1.2	72.4±1.3
	Impact strength (J/cm ²)	3.4±0.4	3.5±0.6	3.6±0.4	3.2± 0.3
	Weight swelling (%)	38.1±2.2	35.4±3.9	26.2±5.8	25.2±2.2

Morphology

To observe the miscibility of the composite PVC with chlorinated tire rubber, SEM photomicrographs were investigated. Their results are exhibited in **Figure 4.7** for PVC/Cl-RTR and **Figure 4.8** for PVC/Cl-GRT.

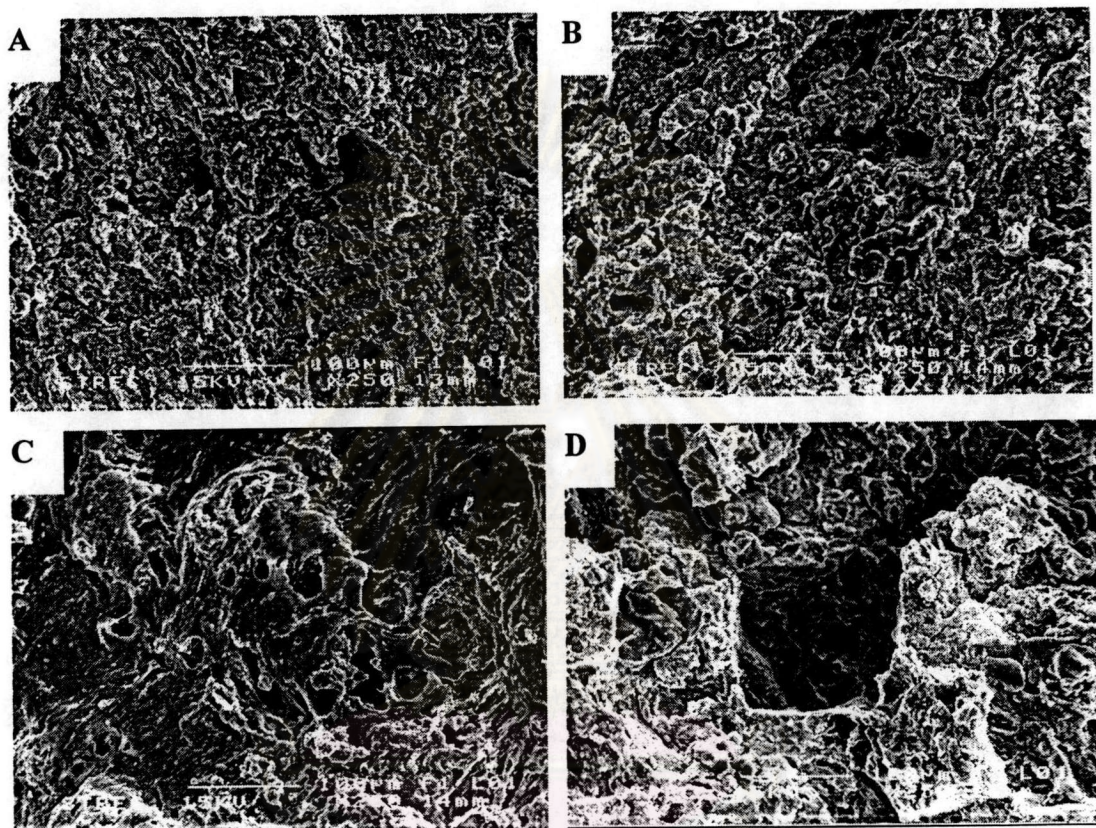


Figure 4.7 SEM micrographs of PVC/Cl-RTR (30 phr), where Cl-RTR phase has been etched out; (A) TCICA, 0%w/v (B) TCICA, 1%w/v (C) TCICA, 3%w/v (D) TCICA, 5%w/v.

In the case of PVC/Cl-RTR, the holes in picture (D) were the biggest when compared with the others. Besides the morphology of PVC/Cl-RTR, 3 %w/v in picture (C) was more smooth than the others. For PVC/Cl-GRT (Figure 4.8 (A)-(D)), all pictures show similar morphology to these of PVC/Cl-RTR. Therefore the TCICA concentration should be 3%w/v.

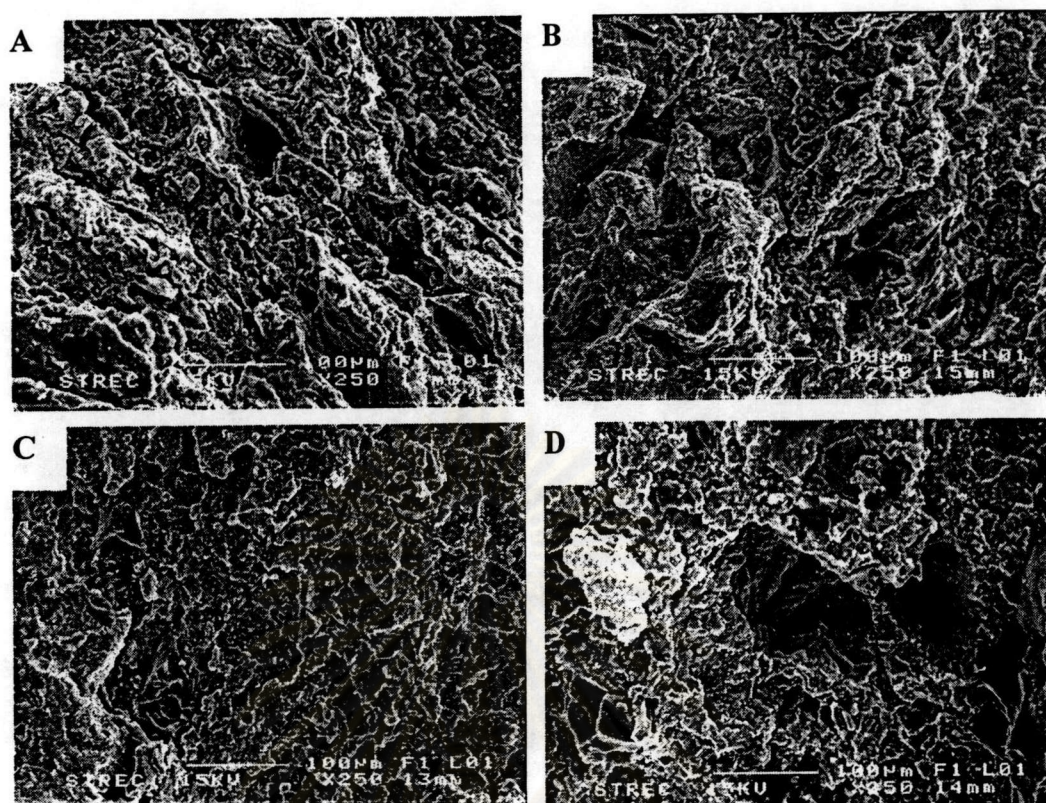
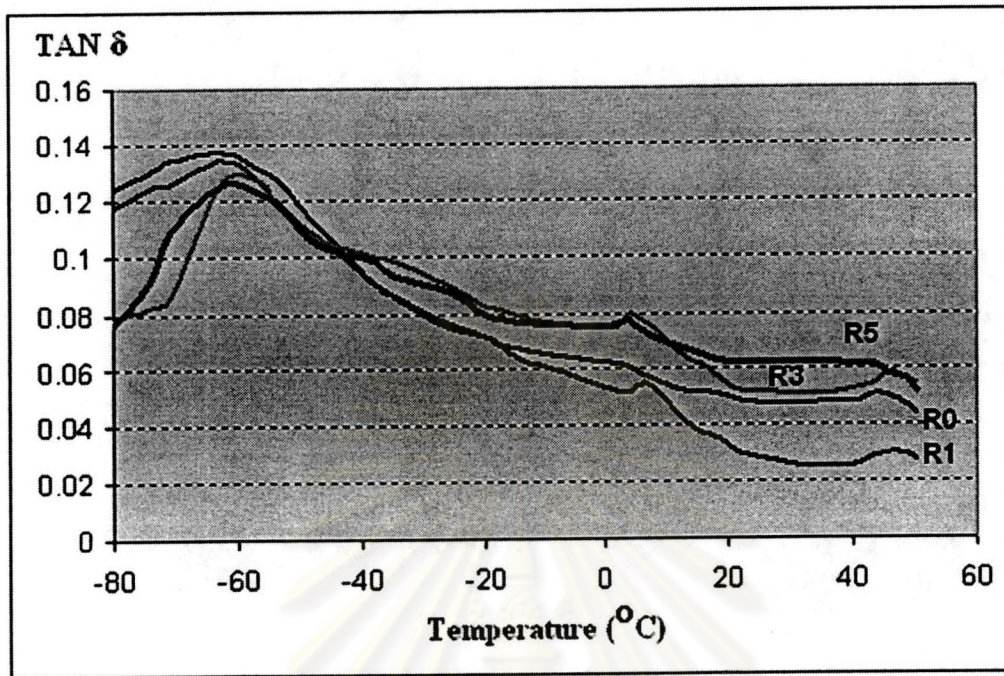


Figure 4.8 SEM micrographs of PVC/Cl-GRT composition 40 phr, where from Cl-GRT phase has been etched out (A) TCICA, 0%w/v (B) TCICA, 1%w/v (C) TCICA, 3%w/v (D) TCICA, 5%w/v.

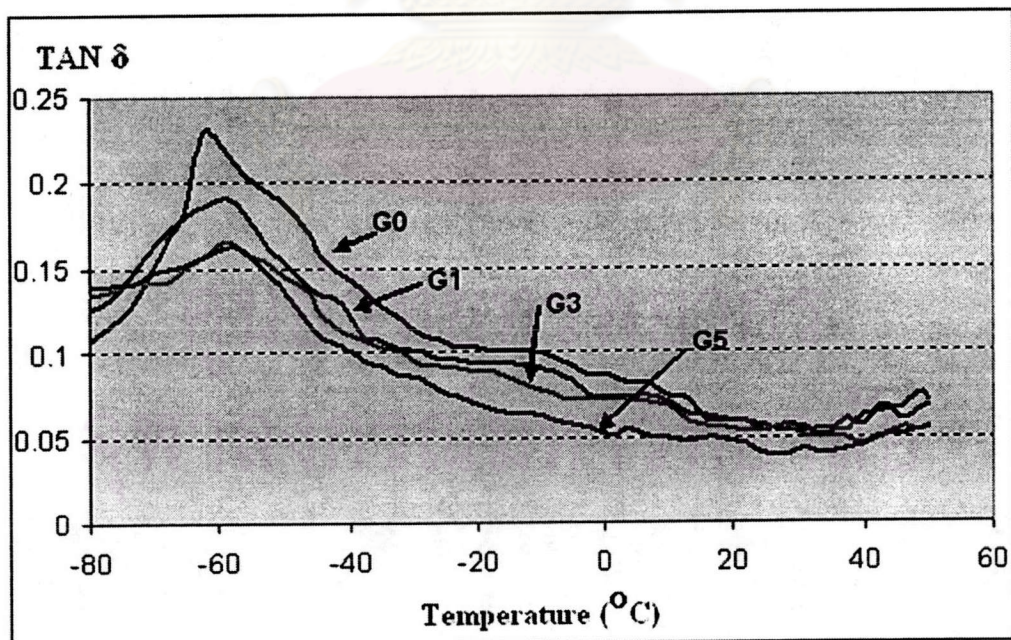
Dynamic Mechanical Thermal Analysis.

Loss tangent spectra of the different PVC and tire-rubber waste composite are shown in **Figure 4.9**. PVC/Cl-RTR showed a maximum at -62°C , a peak belongs to the T_g of the rubber phase. PVC/Cl-GRT, on the other hand, has a peak at -58°C which was 4 degree higher than that of R-PVC without the rubber. With increase in chlorine content from R0 to R5 for RTR and G0 to G5 for RTR, T_g did not shift in case of RTR but, T_g of GRT samples shifted slightly to a higher temperature. In addition, $(\tan \delta)_{\max}$ value decreased after chlorination of the rubber phase an indicative of enhances compatibility between rubber and PVC phase.

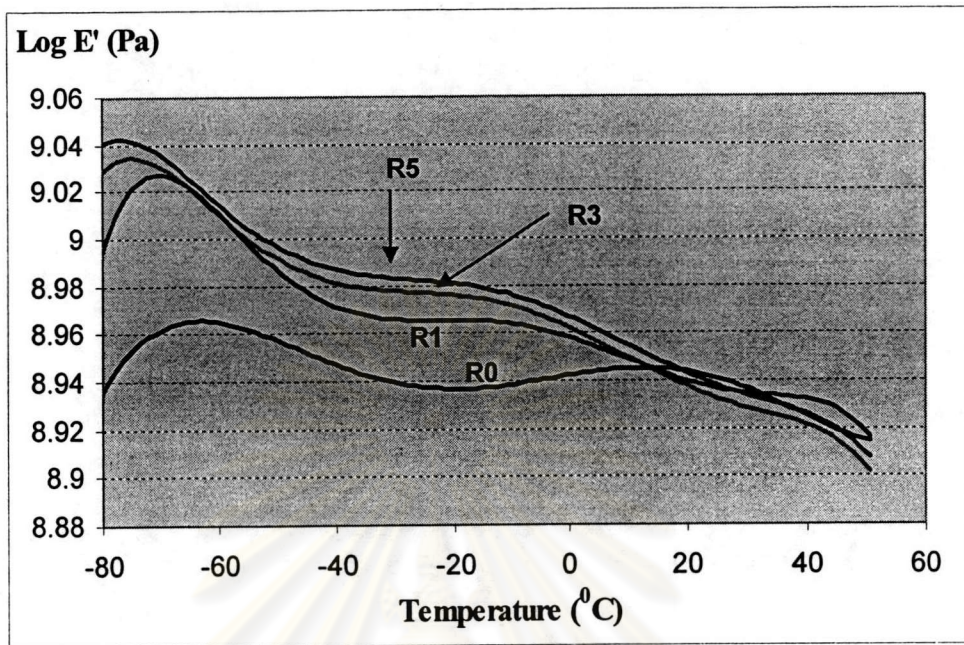
(a) RTR series



(b) GRT series

**Figure 4.9** Loss tangent vs temperature of molded (a) RTR and (b) GRT samples.

(a) RTR series



(b) GRT series

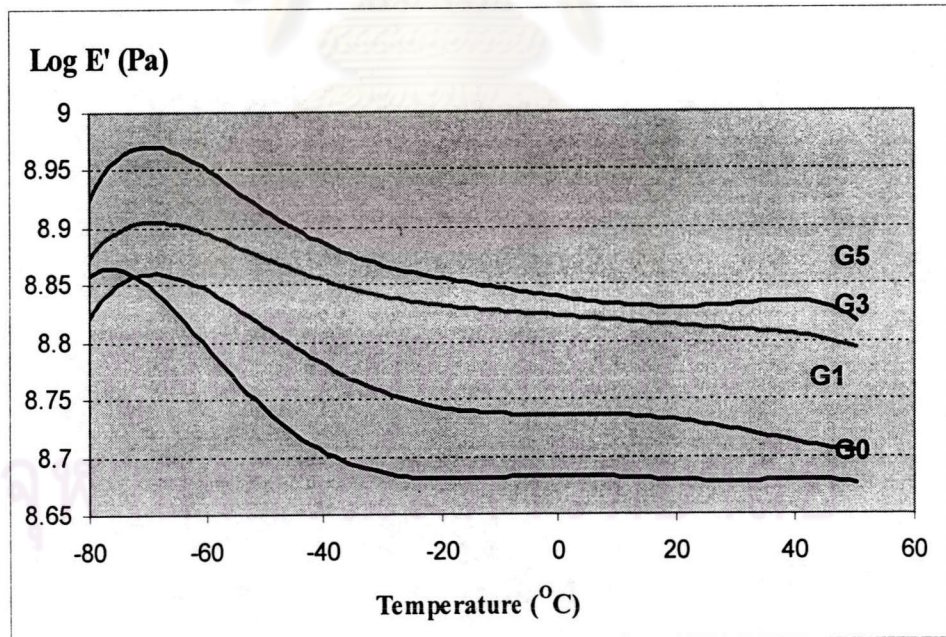


Figure 4.10 Storage modulus vs temperature of molded (a) RTR and (b) GRT samples.

For RTR samples, apart from the Tg of the rubbery phase, the chlorinated samples show another peak at about 10°C. This peak is due to the relaxation of the hard phase (PVC) formed by C-Cl dipole-dipole interaction. This peak is not observed for the unmodified RTR (R0). Such a peak, however, was not present in the GRT samples in this analysis condition.

The storage modulus (E') spectra for RTR, as shown in **Figure 4.10**, increased when the chlorine content increased possibly due to dipole-dipole interaction. For GRT samples, the tendency of crosslink density was also the same as that of the RTR.

It could be concluded that the Cl-atom applied on the surface of rubber particles could increase the interaction between PVC phase and rubber phase. The compatibility between blended PVC with modified tire rubber waste is improved. Therefore, the proper concentration of TCICA solution was about 3% w/v to reach an optimum physical properties of blended PVC. In the next section, the effect of tire-rubber waste loading on physical properties was studied.

4.2.3 Effect of the quantity of modified tire-rubber wastes on the physical properties.

For this section, effects of the quantity of RTR and GRT with and without chlorination on physical properties and swelling weight were investigated. The results were discussed as follows.

Physical properties.

Physical properties of the composites are summarized in **Table 4.8**. It can be seen that rubber loading is the main factor affecting the mechanical properties of the blends. Generally, the change in properties depends on the nature and loading of rubber. The tensile strength and hardness decreased with increasing the weight ratio of all types of rubber wastes. It is also found that the tire-rubber wastes loading is over 40 phr for RTR, 50 phr for Cl-RTR and GRT, and 60 phr for Cl-GRT, the blends could not be shaped into sheets. The decrease of the tensile strength and hardness is possibly caused by incompatibility between the R-PVC and rubber phase, even for the

chlorinated rubber. It could be that %chlorination is too low to increase interaction between the polar PVC and non-polar rubber. Nevertheless, the impact strength was increased when not only the polarity of rubber but also its loading ratio. To find more evidences, SEM micrographs were investigated as the following.



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Table 4.8 Physical properties of the composite PVC blended with RTR (modified and unmodified) and GRT(modified and unmodified).

Sample	PVC loading (phr)	Waste Tire Rubber (phr)		Physical properties					
		Non-modified	Modified	Tensile strength(MPa)	Elongation (%)	Hardness (Shore D)	Impact strength (J/cm ²)	Weight Swelling(%)	
R-PVC	100	-	-	58.6±1.8	13.3±2.9	78.1±2.1	3.3±0.2	-	
	100	10	-	42.7±3.5	11.6±2.2	74.5±1.4	2.3±0.2	17.1±1.3	
	100	20	-	33.0±2.5	10.9±1.3	69.6±2.2	2.6±0.2	20.0±3.0	
	100	30	-	21.7±2.0	9.1±0.5	63.4±2.8	3.0±0.2	34.3±2.5	
RTR	100	40	-	19.2±7.1	4.7±0.7	58.5±2.6	3.0±0.2	42.4±2.3	
	100	50	-	No Sheet					
	100	-	10	41.8±3.3	12.2±2.3	75.8±1.7	2.5±0.4	15.0±2.3	
	100	-	20	31.2±3.0	11.3±1.7	72.3±1.2	2.8±0.5	18.4±1.5	
	100	-	30	21.1±2.0	9.7±0.5	68.5±1.4	3.4±0.4	30.2±1.7	
	100	-	40	18.5±2.1	8.5±0.6	65.3±1.6	3.7±0.7	32.3±1.5	
	100	-	50	9.1±2.0	6.2±0.5	62.6±1.9	3.0±0.6	34.1±1.7	
	100	-	60	No Sheet					
	GRT	100	10	-	37.7±4.2	12.3±4.6	78.3±1.7	2.6±0.6	16.1±1.4
		100	20	-	31.8±3.7	11.7±1.6	75.5±1.5	2.8±0.6	19.2±4.5
		100	30	-	20.2±5.6	11.0±2.2	72.8±1.4	3.2±0.2	33.1±2.4
100		40	-	15.4±2.1	10.8±0.9	58.5±2.6	3.4±0.3	38.1±2.2	
100		50	-	14.2±2.7	7.0±1.4	62.5±1.4	3.3±0.3	48.1±2.2	
100		60	-	No Sheet					
100		-	10	32.6±2.5	12.2±1.8	77.3±1.6	2.7±0.4	14.4±1.9	
100		-	20	30.0±2.8	11.5±1.3	75.6±1.9	3.0±0.4	16.4±2.1	
100		-	30	18.9±1.1	11.4±2.5	73.3±1.5	3.3±0.5	20.2±2.1	
100		-	40	17.7±1.1	11.1±2.0	71.8±1.4	3.6±0.3	26.2±5.8	
100		-	50	15.0±0.8	8.8±0.4	69.3±1.8	3.8±0.4	31.4±2.4	
100	-	60	9.1±1.8	5.9±1.4	67.5±1.9	3.4±0.3	33.3±1.3		
100	-	70	No Sheet						

Morphology

From the SEM photomicrographs (X250) in **Figure 4.11**, it was exhibited that the dispersion of RTR and Cl-RTR particles was homogenous. Except for the PVC/RTR (40 phr) and PVC/Cl-RTR (50 phr), their SEM micrographs displayed ununiformed morphology. A huge pit represents the rubber particles. This suggests that the rubber particles start to agglomerate. This phenomenon became more obvious when the rubber loading was higher.

In order to observe their morphology clearly, the higher magnification (X4000) was used. It was shown in **Figure 4.12**. It shows clearly that for PVC/RTR at 40 phr, rubber particles agglomerate.



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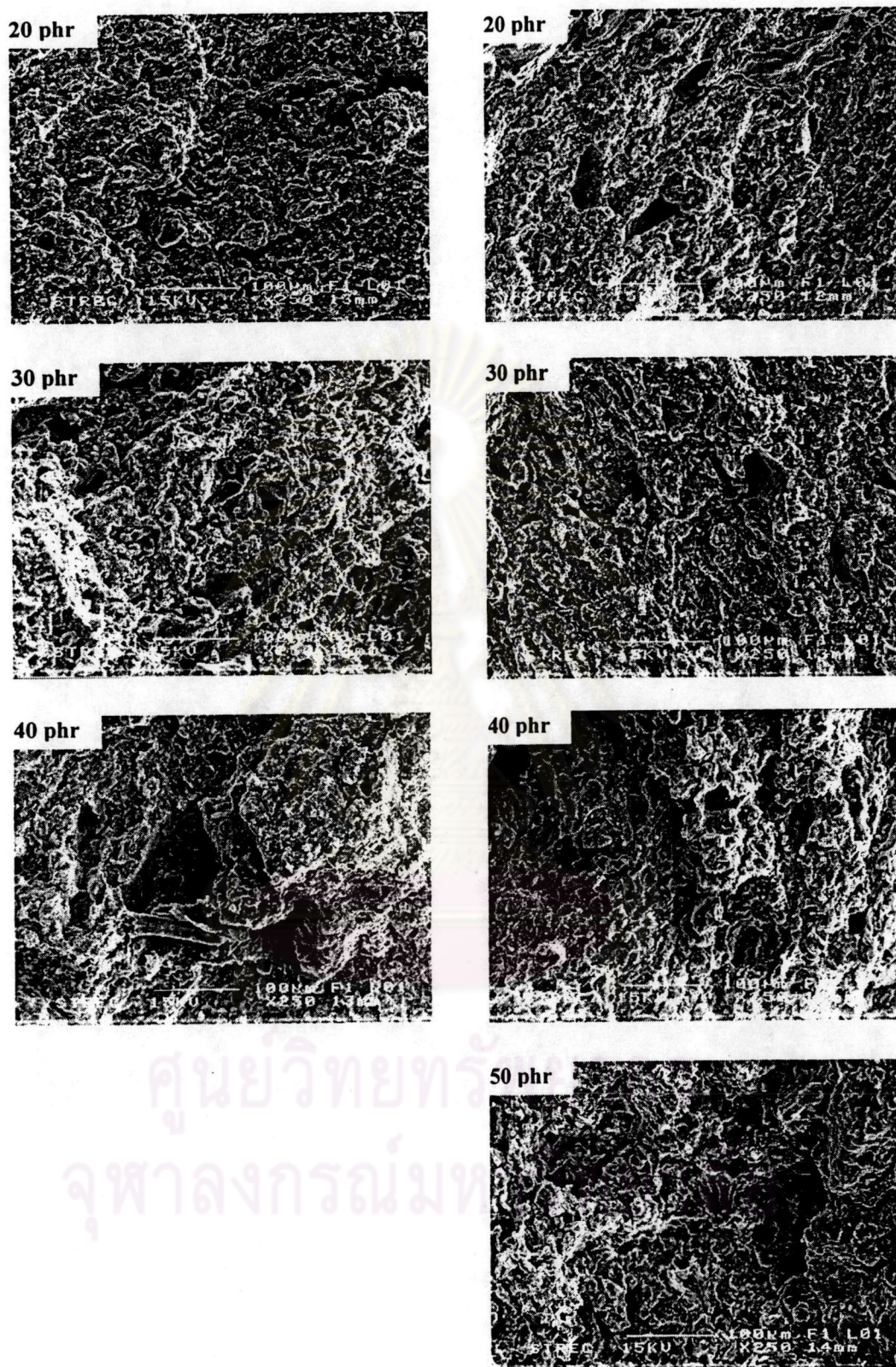


Figure 4.11 SEM micrographs (X250) of PVC/RTR (left) and PVC/CI-RTR (right)

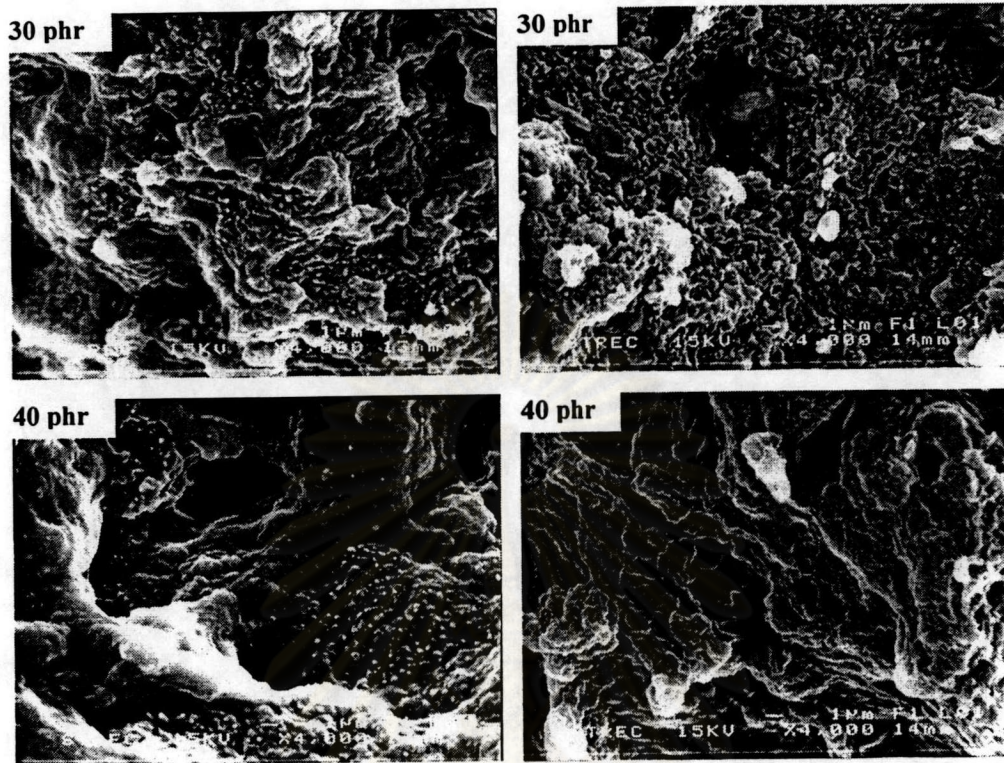


Figure 4.12 SEM micrographs (X4000) of PVC/RTR (left) and PVC/CI-RTR (right)

In case of GRTs, their SEM micrographs are shown in **Figure 4.13**.

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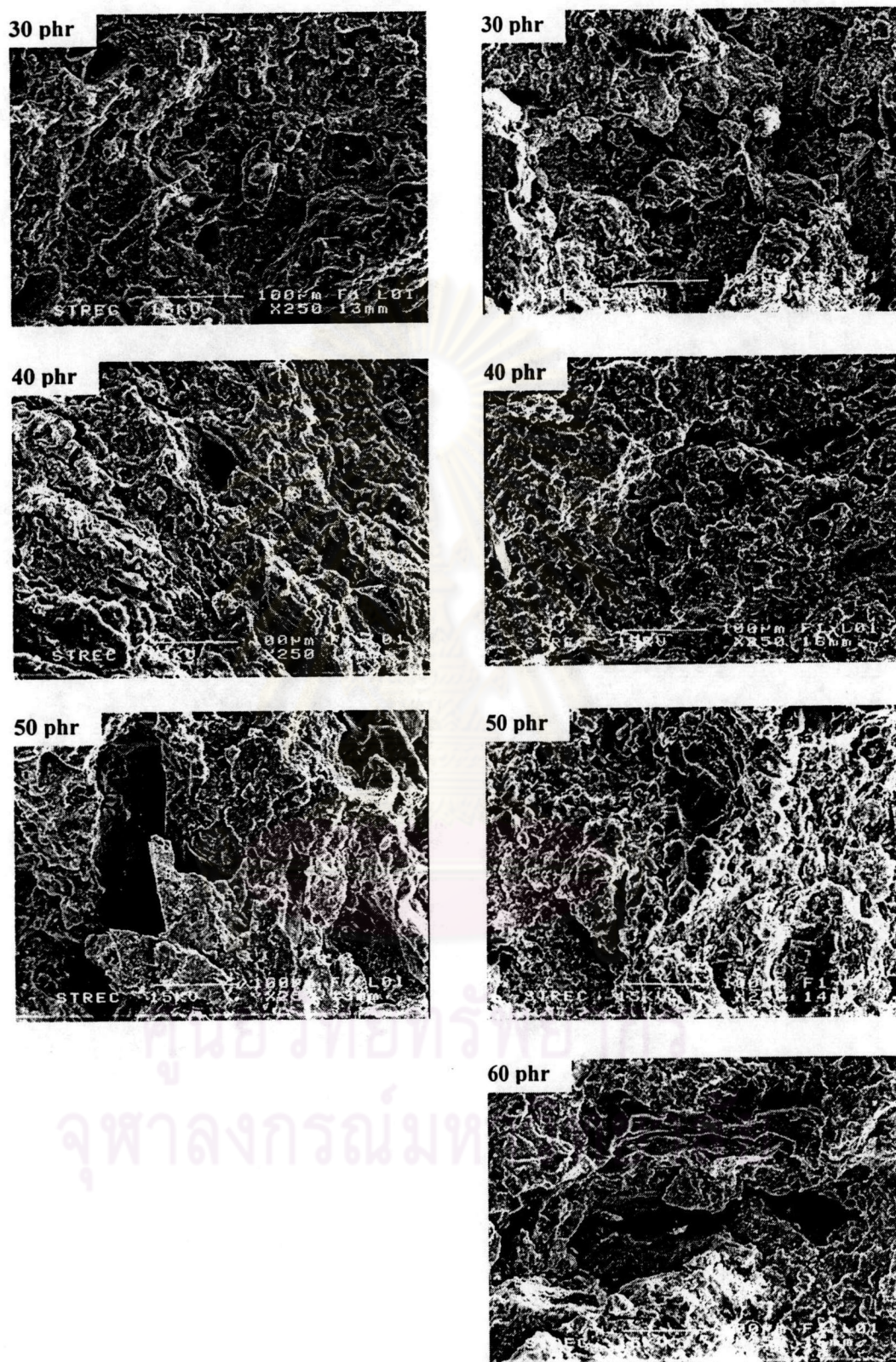


Figure 4.13 SEM micrographs (X250) of PVC/GRT (left) and PVC/Cl-GRT (right)

It is found that the morphology of blended PVC with GRT is the same as a blended PVC with CI-GRT. However, the quantity of rubber loading was different. Especially, the rubber loading should be more than 50 phr for non-modified rubber and 60 phr for modified rubber. The higher magnification was applied for observation in more details. It was shown in **Figure 4.14**.

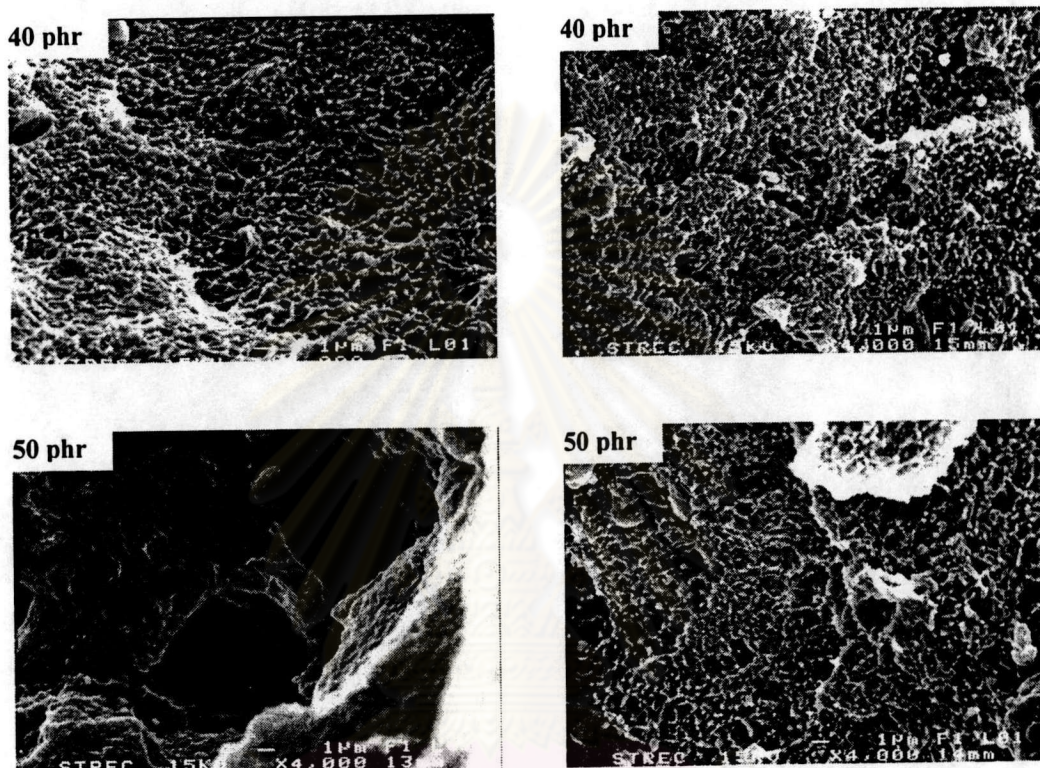


Figure 4.14 SEM micrographs (X4000) of PVC/GRT (left) and PVC/CI-GRT (right)

It is obvious that the rubber particles of composite PVC/GRT were bigger than those of PVC/CI-GRT, PVC/RTR and PVC/CI-RTR. This result agrees well with the fact that the polarity of GRT is less than RTR. Thus the compatibility of RTR filled in PVC would be better than that of GRT. From this reason the GRT particles tend to agglomerate more easily to do when they were mixed into PVC matrix. Therefore, RTR and CI-RTR distributed in PVC matrix more homogeneously than GRT and CI-GRT aid. To observe more information, the thermal properties were studied as the following.

Thermal properties

The thermal properties of blended PVCs with both modified tire-rubber wastes, (Cl-RTR and Cl-GRT) and unmodified tire-rubber wastes (RTR and GRT) were analyzed by DSC. Only samples from optimum mixing recipes were analyzed, 30 phr for RTR, 40 phr for Cl-RTR, 40 phr for GRT, and 50 phr for Cl-GRT. Their results are shown in **Table 4.9**.

Table 4.9 The glass-transition temperature of blended PVC with modified and unmodified tire-rubber wastes.

Sample		Glass transition temperature (°C)	
		Rubber phase	Plastic phase
R-PVC	-	-	78
PVC/RTR	RTR (30 phr)	-62	79
	Cl-RTR (40 phr)	-63	75
PVC/GRT	GRT (40 phr)	-63	79
	Cl-GRT (50 phr)	-62	77

Two glass-transitions were found for all blends. The T_g of the rubber phase was not changed for all PVC rubber blends. Whereas, the T_g of PVC phase was shifted to a significantly lower value only for the blend with Cl-RTR. It means that there is an interaction between PVC and rubber phase in the case of R-PVC/Cl-RTR. This finding agrees well with the results from SEM analysis in the previous section, that this blend has a smoother matrix than the others do. These results suggest that the chlorinated RTR is more compatible with R-PVC than the other rubber wastes.

Moreover, the T_g of rubber phase appears to be stable even when it is blended with R-PVC. This means that the rubber particle does not dissolve into the PVC matrix. As confirmed by the SEM micrographs, the remaining pits caused by the rubber aggregates could be seen.

From the study in this section, it can be concluded that surface modification of rubber particles via chlorination with 3% TCICA solution in methanol could improve the compatibility between R-PVC and tire-rubber wastes. In addition, the optimum loading of modified tire-rubber waste filled in composited PVC was 40 phr for Cl-RTR and 50 phr for Cl-GRT.

4.3 The effect of compatibilizers on the physical properties of blended PVC with tire-rubber waste.

In this section, the influences of the compatibilizers on the physical properties of blended PVC containing the modified tire-rubber wastes are investigated. It has been known the compatibilizer can improve the solubility of a minor phase in a major a phase and the surface tension of a matrix phase. So, the homogeneity and dispersity of a minor component in the composited polymer is better. It results in the improvement of physical properties of blended polymer.

The effects of both chlorosulfonated polyethylene (CSPE) and nitrile butyl rubber (NBR) as the compatibilizers on the physical properties of PVC mixed with Cl-RTR and Cl-GRT were investigated. The results were shown as follows.

Physical properties

The physical properties of the blended PVC/modified rubber containing the compatibilizers CSPE and NBR are shown in **Table 4.10**. The PVCs without a compatibilizer (G_1 and H_1) were also presented for comparison with the data of the blended PVCs.

Table 4.10 The physical properties of blended PVC with Cl-RTR and Cl-GRT compatibilized with CSPE and NBR.

Sample	Wt of PVC	Modified tire-rubber			Terpolymer		Physical properties				
		Cl-RTR	Cl-GRT	CSPE	NBR	Tensile Strength(MPa)	Elongation (%)	Hardness (shore D)	Impact Strength (J/cm)	Weight Swelling (%)	
PVC	100	-	-	-	-	58.6 ±1.8	13.3± 2.9	78.1± 2.1	2.3± 2.4	-	
G1	100	40	-	-	-	18.5±2.1	8.5 ±0.6	65.3 ±1.6	3.8± 0.4	32.3± 1.5	
G2	100	40	-	10	-	21.7±2.2	13.9 ±2.2	65.3 ±2.8	4.1± 0.4	33.3± 2.3	
G3	100	40	-	20	-	19.5±2.0	16.5± 1.3	63.3 ±2.3	4.9±0.6	34.3± 2.4	
G4	100	40	-	30	-	18.3±1.7	31.1± 1.3	61.6± 1.6	7.5 ±0.7	35.2± 2.1	
G5	100	40	-	-	10	20.6±3.6	15.0 ±1.9	69.1± 2.1	3.8± 0.6	34.1± 3.0	
G6	100	40	-	-	20	24.5±3.3	12.5 ±3.8	63.2± 2.1	4.1 ±0.5	35.3 ±1.9	
G7	100	40	-	-	30	25.7±1.8	11.3± 1.7	59.4± 1.8	5.0 ±0.7	36.1± 1.1	
H1	100	-	50	-	-	15.0 ± 0.8	8.8 ±0.4	69.3± 1.8	3.7± 0.7	31.4±2.4	
H2	100	-	50	10	-	25.2 ±3.8	16.0± 2.6	68.4 ±1.8	3.8 ±0.5	32.4 ±2.7	
H3	100	-	50	20	-	21.0 ±1.7	24.8 ±2.2	66.6 ±2.1	4.7 ±1.0	33.4± 2.0	
H4	100	-	50	30	-	17.8 ±2.4	30.0 ±2.9	65.0± 1.3	5.1 ±0.7	34.3 ±2.0	
H5	100	-	50	-	10	28.3 ±3.2	13.6± 3.4	67.4 ±1.6	3.9± 0.5	33.5 ±2.3	
H6	100	-	50	-	20	25.2 ±2.1	14.5± 1.9	64.9± 2.1	5.0± 0.8	34.3 ±1.9	
H7	100	-	50	-	30	17.9± 4.1	20.9 ±3.4	63.7 ±1.8	8.0± 0.5	35.4 ±1.0	

Remark Tire-rubber wastes, RTR and GRT, was modified with 3%w/v TCICA solution in methanol.

In case of R-PVC/CI-RTR (G series), it was found that the tensile and impact strengths of the blend was dramatically improved after the terpolymer was added to the composite. Furthermore, the physical properties of R-PVC/CI-RTR with NBR was higher than the R-PVC/CI-RTR containing CSPE.

In the case of R-PVC/CI-GRT (H series), both compatibilizers can improve the physical properties like tensile strength, and impact strength of the blends.

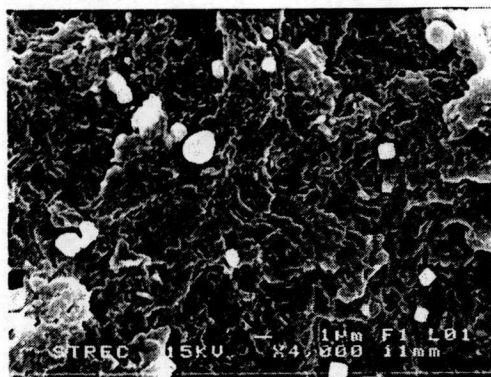
From the mentioned above, it clearly indicates that the toughness of blended PVC can be improved by adding the terpolymer. Without the terpolymer, their physical properties were not changed that much. To confirm this, the compatibility of blended PVCs containing the terpolymer was investigated by means of SEM. The results were discussed as the following.

Morphology

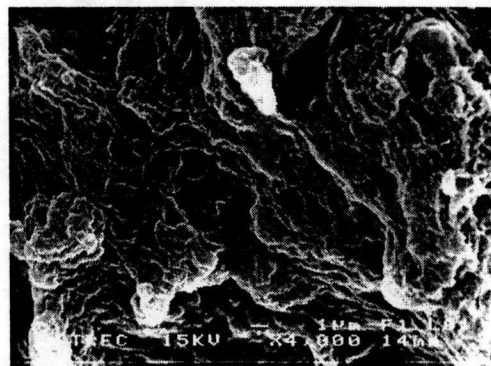
To investigate and compare the compatibility of blended PVC easily, the morphology of blended PVC with terpolymers were observed (**Figure 4.15**). It was found that the surface of PVC/CI-RTR/CSPE blend was more smooth than the others.

In the case of PVC/CI-GRT/CSPE and PVC/CI-GRT/NBR, their SEM micrographs are shown in **Figure 4.16**.

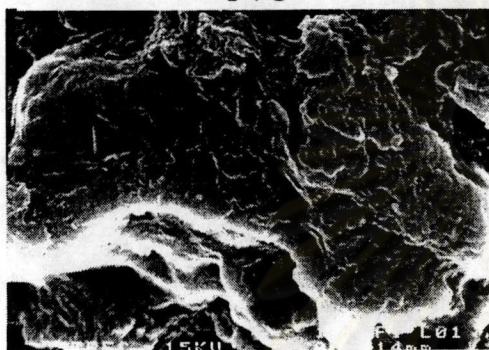
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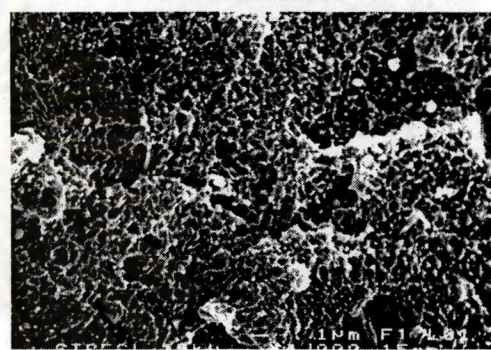
PVC



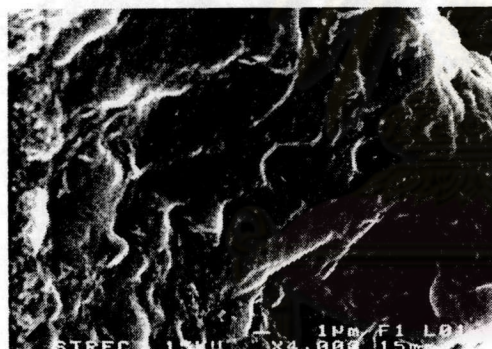
PVC/CI-RTR



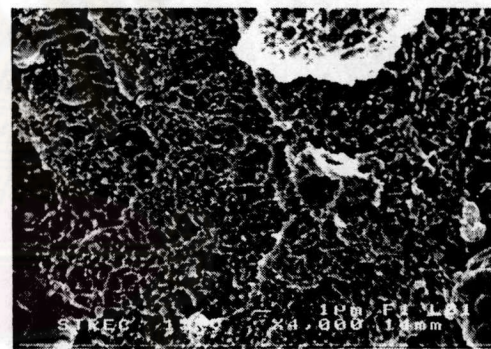
PVC/CI-RTR/CSPE (10 phr)



PVC/CI-RTR/NBR (10 phr)



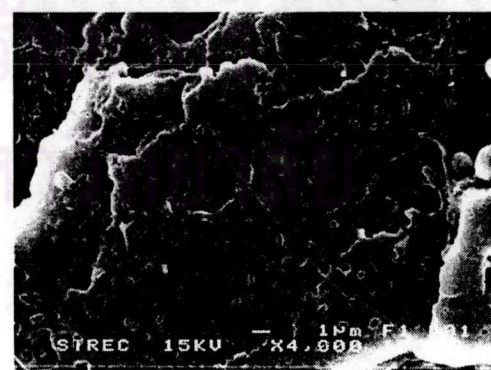
PVC/CI-RTR/CSPE (20 phr)



PVC/CI-RTR/NBR (20 phr)

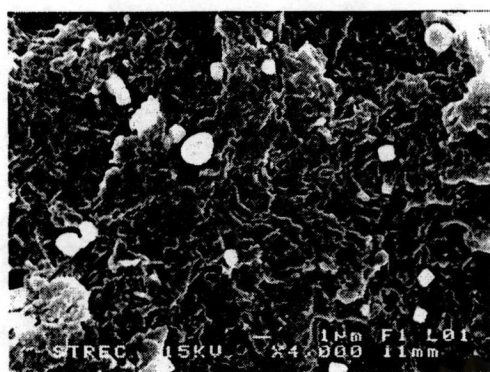


PVC/CI-RTR/CSPE (30 phr)

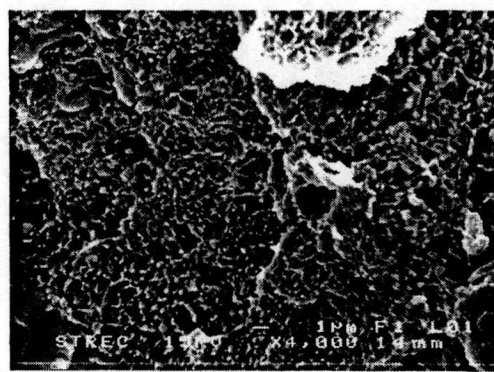


PVC/CI-RTR/NBR (30 phr)

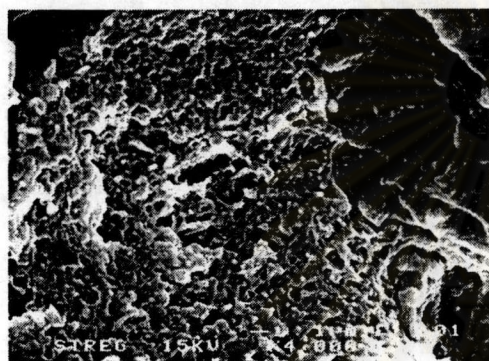
Figure 4.15 SEM photomicrographs (X4000) of PVC blends.



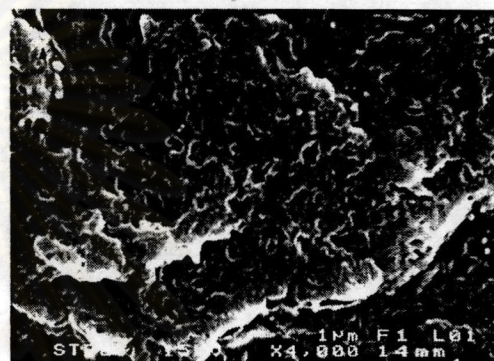
PVC



PVC/CI-GRT



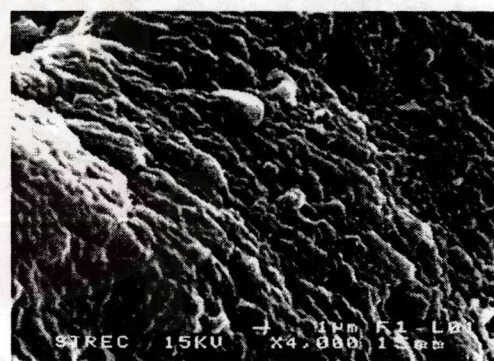
PVC/CI-GRT/CSPE (10 phr)



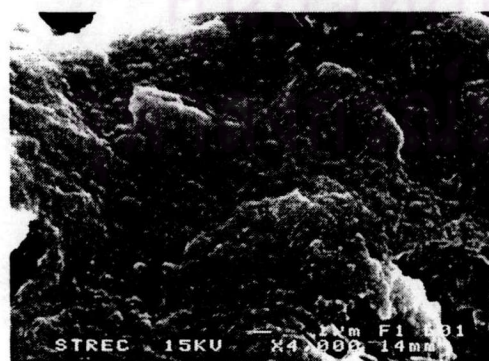
PVC/CI-GRT/NBR(10 phr)



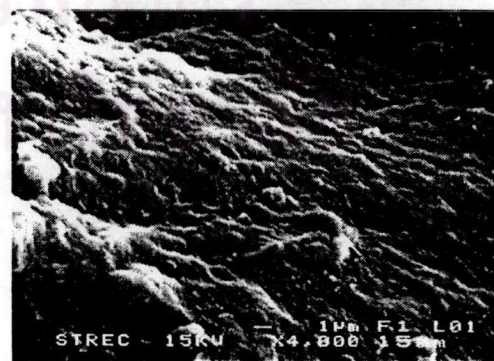
PVC/CI-GRT/CSPE (20 phr)



PVC/CI-GRT/NBR(20 phr)



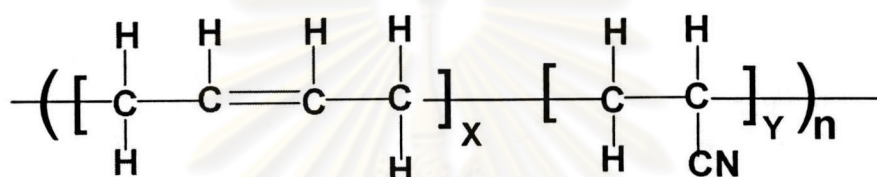
PVC/CI-GRT/CSPE (30 phr)



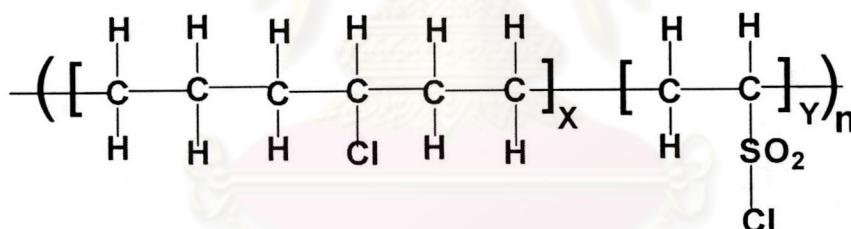
PVC/CI-GRT/NBR(30 phr)

Figure 4.16 SEM photomicrographs (X4000) of PVC blends.

From the mentioned above, the compatibility of blended PVCs was improved with compatibilizer. The reason why CSPE and NBR could improve the compatibility was explained as following. Since PVC is a polar matrix and rubber particles are non-polar for GRT as a vulcanized rubber, and slightly polar for RTR as a devulcanized rubber, there is no interaction or adhesion between matrix and rubber particles. Therefore, the ways to increase the interaction between two phases are by the chlorination with TCICA solution and by using terpolymer. For this study, CSPE and NBR were chosen as terpolymer for improving the compatibility of blended polymer compatibilizers.



Acrylonitrile-butadiene rubber or nitrile rubber (NBR).



Chlorosulfonated polyethylene rubber (CSPE).

CSPE contains hydrocarbon backbone (non-polar part), -Cl and -SO₂Cl group (polar part). Therefore CSPE acts like a bridge to increase the interaction between PVC matrix and rubber particles. The same concept is applied to NBR, which has a nitrile group as the polar group. From this point of view, both CSPE and NBR could increase the compatibility of the blended PVC as reported results earlier.

Thermal properties

For this section, to prove the compatibilizing effect of CSPE and NBR, DSC was used to analyze the Tg of all blends (Table 4.11).

Table 4.11 The glass-transition temperature (Tg) of PVC/Cl-RTR (G) and PVC/Cl-GRT (H) filled with CSPE or NBR as a compatibilizer.

Sample	Compatibilizers		Glass-transition temperature (°C)	
	CSPE	NBR	Rubber Phase	Plastic Phase
G1	-	-	-62	75
G2	10	-	-63	75
G3	20	-	-62	77.5
G4	30	-	-62	80
G5	-	10	-62	62
G6	-	20	-62	60
G7	-	30	-62	56
H1	-	-	-62	77
H2	10	-	-62	43
H3	20	-	-63	61
H4	30	-	-62	76
H5	-	10	-62	61
H6	-	20	-62.5	56
H7	-	30	-63	43

From the data above, the Tg of rubber phase does not change whereas the Tg of plastic phase shifts from that of the blend was a compatible. The changing of Tg resulted from the alteration of interaction between rubber phase, and plastic phase. It meant that the compatibility of these blended R-PVC was affected by the thermopolymer. The Tg of the blend with CSPE became higher, especially at high CSPE content. It resulted from the melting temperature of CSPE which is 108.52°C, higher than the Tg of PVC. On the other hand, when NBR was filled in the blended R-

PVC, the T_g of plastic phase decreased. This is because the T_g of NBR is blended -23.91°C much lower than PVC

It can be concluded that both CSPE and NBR can be used as a compatibilizer for PVC blended with Cl-RTR and Cl-GRT. The proper loading of each recipe was 100:40:30 R-PVC/Cl-RTR/CSPE and 100:50:30 for R-PVC/Cl-GRT/NBR.



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