CHAPTER IV

RESULTS AND DISCUSSION

4.1 Composition of Recycled Tire-Rubber

Wasted tires are composed of composite materials topped with rubber. For examples, the carcass of a tire is made of chemical cord e.g. polyester, rayon or aramid and the breakers from tires are made of plated steel cords. Other components are made of rubber compounds such as natural rubber (NR), styrene—butadiene rubber (SBR) or butadiene rubber (BR) which are all reinforced with carbon black. In this study, most of the carcass, belt, breakers and bead had been separated from rubber tires. Therefore, the material from rubber tires used in all these experiments was composed of hydrocarbons from the tread, shoulder and side wall, together with carbon black and other additives which already presented in the rubber tires.

The recycled tire-rubber can be obtained and classified into two types. The first one is known as ground rubber tire or GRT which was prepared by direct shredding of the rubber tire. The other is called reclaimed tire-rubber or RTR. The difference of RTR from GRT is that RTR is devulcanized during shredding. By thermogravimetric analysis (TGA), heating from 50°C to 850°C at a scanning rate of 20°C/min under oxygen atmosphere, it clearly exhibited that GRT composed of 5 different parts while only two parts existed in RTR as shown in Figures 4.1, 4.2 and Table 4.1.

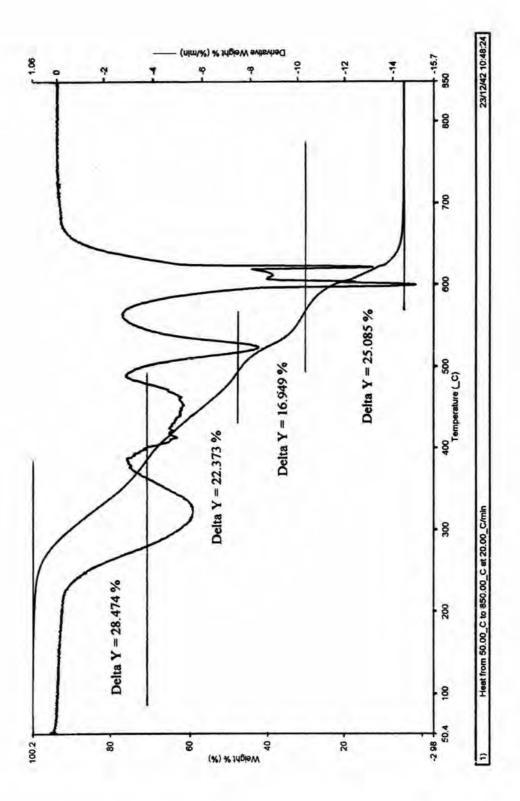


Figure 4.1 TGA thermogram of ground rubber tire (GRT)

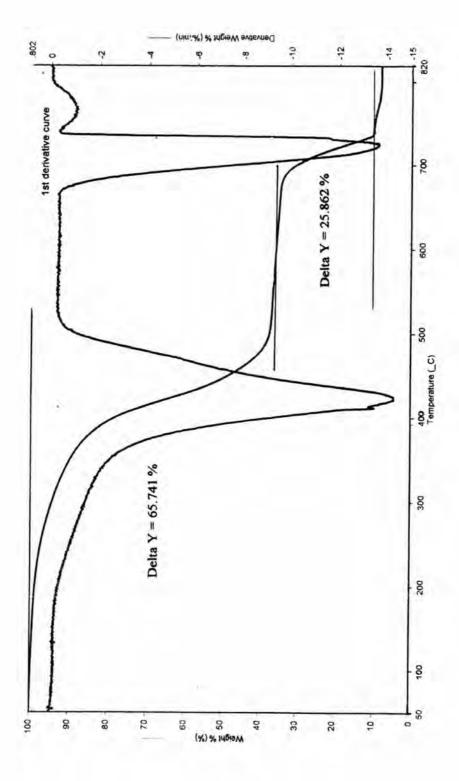


Figure 4.2 TGA thermogram of reclaimed tire-rubber (RTR)

Table 4.1 The components of recycled tire-rubber

	Recycled Tire-Rubber			
Component	GRT (%)	RTR (%)		
SBR	28.47]		
NR	22.37	65.74		
BR	16.95	J		
Carbon Black	25,08	25.86		
Residue	7.12	8.40		

It can be indicated that the last peak in Figure 4.1 belongs to carbon black due to its degradation at 600°C which is in the range of thermal degradation of carbon black, 400-1,600°C[12]. The amount of carbon black in GRT is 25.08% and there is the residue of 7.12% indicated by a peak at 850°C. In general, the amount of carbon black and the level of crosslinking will affect the temperature of mass loss [12]. However, the first three peaks were arbitrarily assigned for SBR, NR and BR since the elastomers usually degrade between 300-500°C in thermogravimetry [71]. In this study, the tread, mostly made of SBR, was used for recycling more than sidewall(NR) and shoulder (SBR/BR), the first peak at 325°C probably belongs to SBR 28.47%, while the second and third peaks can be assigned for NR 22.37% and BR 16.95%, respectively.

The TGA thermogram of RTR in Figure 4.2 shows that RTR consists of three components. The carbon black is amounted to 25.86% indicated by the peak at 720°C , and 65.74% of elastomers existed as a broad and intense peak at 420°C . The rest of 8.40% at 780°C is residue. In this case, the thermogram clearly revealed that all types of elastomers in recycled tire-rubber are miscible. This can be the results of devulcanization during shredding the tire-rubber. The sulfur crosslinking was removed which was shown by the analysis of sulfur content in RTR after devulcanization, less than 1% by weight of RTR reported by the manufacturer. This indicated that it was devulcanized almost completely. The miscibility was further confirmed by the glass-transition temperature (T_g) of RTR which was analyzed by differential scanning calorimeter (DSC), heated from -100°C to 50°C with a scanning rate of 20°C/min under helium atmosphere, shows in Figure 4.3. It was found that RTR had only one T_g at -73°C which is equal or close to the T_g of natural rubber [8].

Accordingly, GRT is the mixture of vulcanized NR, SBR and BR while RTR can be referred to miscible blend of NR, SBR and BR.

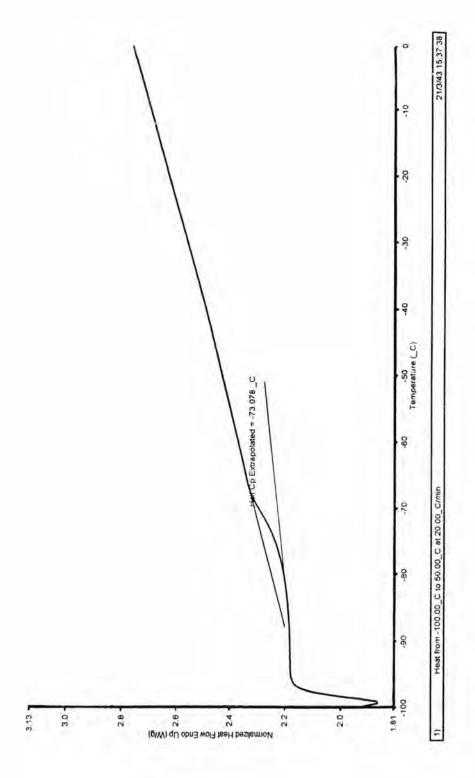


Figure 4.3 DSC plot showing glass-transition temperature of reclaimed tire-rubber (RTR)

4.2 Preparation of PP/Recycled Tire-Rubber Blends

In this study, recycled tire-rubber and polypropylene (PP) were melted firstly by using a two-roll mill and then counter-rotating twin screw extruder before subjecting to injection molding. In the two-roll mill, the blend of PP/recycled tire-rubber was normally cut diagonally from time to time and folded over several times during milling to ensure good mixing. The other ingredients were usually added to the blend of PP/recycled tire-rubber just above the nip between front roll and black roll. The mixing was then repeated as mentioned above before taking off the roller. The two-roll mill generally generates good mixing in the machine direction but poor mixing across the roll faces, thus being good at dispersion, but poor at distribution. To ensure the blend homogeneity, the second melt blend by counter-rotating twin screw extruder was applied. The blends were mixed by the afore mentioned method before molding to obtain the dumbbell-shaped tensile specimens for mechanical property testing. Each blend was prepared for at least two sets.

The notch-Izod impact strength and melt flow index (MFI) measurements were performed in accordance with ASTM D 256 and ASTM D 1238, respectively, for each blend. The measurement was made with six specimens for impact strength and three specimens for MFI. Their surface morphology was observed from freeze fractured surfaces of untested specimens which were immersed in liquid nitrogen and staining with osmium tetroxide (OsO₄) in order to give a good image contrast.

4.3 Effect of Blending Processes on Physical and Mechanical Properties of PP.

As mentioned in section 4.2, blending RTR with PP was carried out by two different processes, using a two-roll mill and a counter-rotating twin screw extruder, successively. Both processes, however, had to be operated at high temperature, 165-170°C and 190-205°C, respectively. Thus, the degradation of the PP matrix during mixing may be arised although antioxidant was added in these blends. The melt flow index (MFI) of PP before and after passing through two mixing processes was primarily considered. In addition, it would be noteworthy to observe the effect of blending processes on impact strength and crystallinity of PP as well.

Table 4.2 Effect of blending processes on impact strength, MFI and percentage crystallinity of PP.

PP before and after passing blending	MFI	Notch-Izod Impact Strength	Crystallinity
processes.	(g/10 min)	(kJ/m ²)	(%)
Before	3.11	3.12	44.95
After	3.15	3.07	45.01

Table 4.2 obviously indicates that no significant influence of the mixing processes on the physical and mechanical properties of PP. However, the physical and mechanical properties of PP/RTR blends were compared with PP after, rather than before, passing through the blending processes throughout this research work.

4.4 PP/GRT Blends using Sulfur Crosslinking Agent

Eventhough much attention has been paid to blending elastomer with thermoplastics, very few work on PP/GRT blend is reported [36,37,41]. In addition, it has already been known that vulcanization would improve the mechanical property of the blend [36] and the most common vulcanizing agent is sulfur. Thus, PP/GRT blend with sulfur crosslinking agents was prepared in this study. Furthermore, the effect of particle size of GRT, i.e., 8 mesh (2.38 mm.), 16 mesh (1.19mm.) and 40 mesh (0.42 mm.), on impact strength and MFI of the blends were investigated too. All samples were obtained from the same lot of recycled tire-rubber in order to ensure the same composition of elastomer. Table 4.3 exhibits the notch-Izod impact strength and MFI of 70/30 PP/GRT blends, and the plots of GRT particle size versus notch-Izod impact strength and MFI are shown in Figure 4.4 and 4.5, respectively.

Table 4.3 The notch-Izod impact strength and MFI of non-vulcanized and vulcanized 70/30 PP/GRT blends.

Composite No.	Notch-Izod Impact Strength (kJ/m²)			Melt Flow Index : MFI (g / 10 min.)		
	Average	SD	% Variation	Average	SD	% Variation
PP	3.07	0.10	3.26	3.15	0.01	0.32
Non-Vulcanized						
PP/GRT: S16 (40, 0.42 mm.)	3.30	0.09	2.73	2.97	0.01	0.34
S18 (16, 1.19 mm.)	3.27	0.10	3.06	3.10	0.00	0.00
S20 (8, 2.38 mm.)	3.22	0.08	2.48	3.12	0.02	0.64
Vulcanized PP/GRT:						
S17 (40, 0.42 mm.)	3.75	0.10	2.67	2.78	0.01	0.36
S19 (16, 1.19 mm.)	3.28	0.12	3.66	2.85	0.01	0.35
S21 (8, 2.38 mm.)	3.25	0.08	2.46	2.89	0.01	0.35

Note: The value in the parenthesis is referred to mesh size and particle size of GRT.

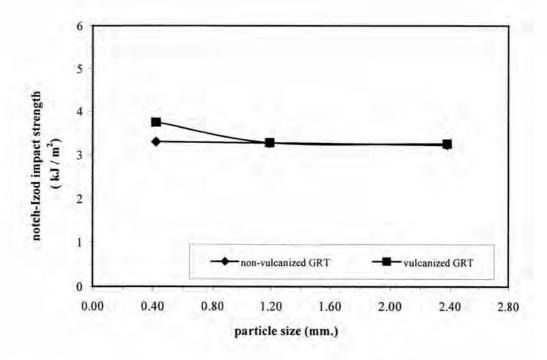


Figure 4.4 The plot of GRT particle size versus notch-Izod impact strength of 70/30 PP/GRT blends.

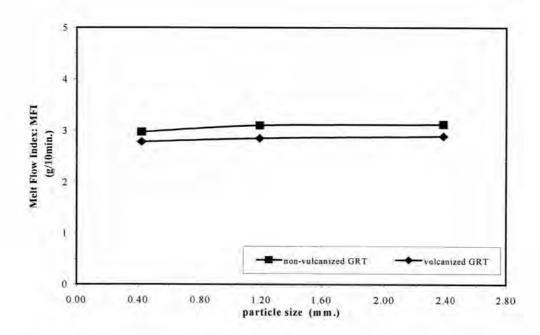


Figure 4.5 The plot of GRT particle size versus MFI of 70/30 PP/GRT blends.

It can be seen that all PP/GRT blends with and without vulcanization have higher impact strength than PP. This result is due to the impact energy absorption of GRT, which is a softer material than PP. In case of vulcanized PP/GRT blend, their impact strength is slightly higher than non-vulcanized PP/GRT blend at the same ratio. This indicates that crosslinking by sulfur may partially occurred. The adhesion between GRT and PP was scarcely possible because of the difference in polarity between GRT, which consisted of NR, BR and SBR, and PP. When tensile specimens of both vulcanized and non-vulcanized PP/GRT blends were tested for the elongation at break, the sudden break of all tensile specimens was resulted. This showed that all PP/GRT blends had only strength and no appreciate toughness.

In other research work [56], however, it was reported that 70/30 PP/GRT blend, at 40 mesh GRT particle size, had lower impact strength than PP. Eventhough this could be due to the lack of vulcanization, there must be other factor influenced the impact strength. Since the same blend without sulfur crosslinking agent (S16) was prepared in this study, but it showed the impact strength 6% higher than PP. Consequently, the difference between both results may arise from the mixing processes, characteristics of PP and technique for blending.

Figures 4.6(a) and (b) show the dispersion and distribution of GRT (white) into PP matrix phase (black). It can be observed that vulcanized PP/GRT blend had better dispersion and distribution of GRT into PP matrix than non-vulcanized one. This can be said that sulfur is combined in the vulcanization network preventing the coalescence of rubber. Therefore, PP/GRT blend has higher impact strength than non-vulcanized one. In addition, it is also observed that GRT particle size insignificantly influences the impact strength of both vulcanized and non-vulcanized PP/GRT blends. However, it can be observed that the S16 blend has 20% higher impact strength than PP, whereas other blends show only 6% improvement. This can be explained that GRT with smaller particle size could be vulcanized more easily. Thus the impact strength of the blends was greater enhanced. Normally, GRT particle becomes smaller during both shear processes, two-roll mill and

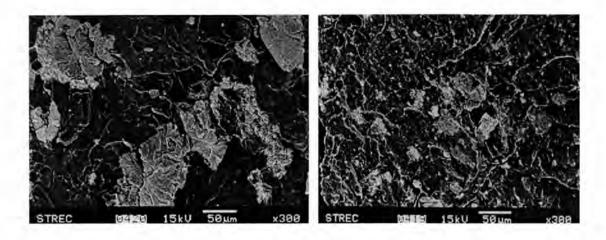


Figure 4.6 SEM micrographs of: (a) non-vulcanized PP/GRT40 (70/30) blend (b) vulcanized PP/GRT40 (70/30) blend.

extrusion, which lead to easily disperse into PP matrix, and more crosslinking can occur. This consequently creates larger vulcanization network and better blend is obtained. Similar result, by Rajalingam and coworkers [42], LLDPE/GRT blend using ethylene glycidyl methacrylate copolymer as the compatibilizer, concluded that smaller GRT particle size results in a small increase in impact strength of the composites.

The MFI of each PP/GRT blends were not significantly differed from PP. This indicated that GRT had at least influence in processability of the blends.

In summary, the addition of GRT into PP increases the impact energy and decrease the MFI of the composites. It is noted that the changes in the impact energy and MFI, as a function of rubber size, are similar for both composites blended with and without sulfur crosslinking agent. It appears that the rubber size has only a minor effect on impact energy and viscosity.

4.5 PP/RTR Blends using Sulfur Crosslinking Agent

As revealed in section 4.1, RTR is the miscible elastomers consisted of NR, SBR and BR, it is thus interesting to blend RTR with PP and investigate the properties of the blends. It is also well-known that crosslinking among to polymer chains would enhance the strength of the material. Therefore, blending of PP and RTR in the presence of sulfur crosslinking agent, the most economical one, was firstly performed.

It was reported that the properties of thermoplastic elastomer blends were largely depended on the ratio of the two components [17]. The effect of RTR loading on notch-Izod impact strength, melt flow index (MFI), morphology and thermal properties of composites were thus explored. The sulfur crosslinking agent used in this research work composes of elemental sulfur (S) acted as a crosslinker, tetramethyl thiuramdisulfide (TMTD) and 2-mercaptobenzothiazole (MBT) acted as the accelerators, and zinc oxide (ZnO) and steric acid acted as the activators.

4.5.1 Effect of RTR Loading

The loading of the rubber is the main factor that affected mechanical properties of the blends. Generally, for the GRT/thermoplastic blends, the change in properties depended on the nature and loading of GRT, polymer matrix types and adhesion between the GRT/polymer matrix [66-68]. For a particular polymer matrix, it was reported that the mechanical properties got worse with increasing amount and particle size of scrap rubber [67]. On the other hand, the low polarity and/or the low crystallinity of a polymer matrix appeared to favor better

compatibility with GRT [68]. Earlier work by R.D. Deanin [69] showed that GRT could be incorporated into linear low-density polyethylene (LLDPE) up to 50% by weight. This caused a drop in impact resistance by 50-70% depending upon the GRT type and average mesh size of GRT.

However, there is no report on blending RTR with thermoplastic yet. Thus, in this section, the various amount of RTR was blending with PP. To investigate the effect of RTR loading on the properties of the blend, impact strength, morphology, crystallinity and melt flow index (MFI) of each blend were explored.

4.5.1.1 Effect of RTR Loading on Impact Strength

The impact strength measurements were made to assess the contribution of the RTR phase to the performance of the blend. Table 4.4 and Figure 4.7 present the impact energy for the V-notched configuration for PP, non-vulcanized PP/RTR blends and vulcanized PP/RTR blends by sulfur crosslinking agent.

Table 4.4 The notch-Izod impact strength of PP/RTR blends at various RTR loading

Composite	Notch-Izod Impact Strength (kJ/m²)			
No.	Average	SD	%Variation	
PP	3.07	0.10	3.26	
Non-Vulcanization:				
S2 (20)	3.15	0.05	1.59	
S4 (25)	3.35	0.10	2.98	
S6 (30)	3.52	0.08	2.27	
S8 (35)	3.47	0.10	2.88	
S10 (40)	3.38	0.08	2.37	
Vulcanization:				
S3 (20)	4.82	0.12	3.14	
S5 (25)	5.50	0.09	2.00	
S7 (30)	6.38	0.08	1.49	
S9 (35)	6.13	0.05	0.97	
S11 (40)	5.82	0.12	2.49	

Note: The value in parenthesis is referred to RTR loading

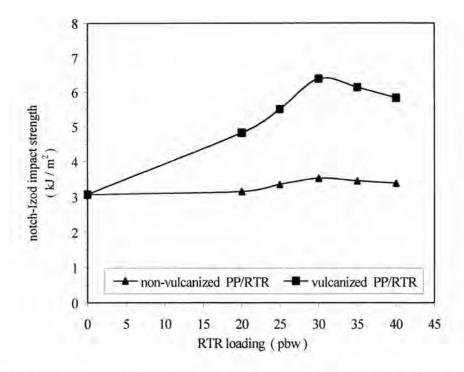


Figure 4.7 Effect of RTR loading on the notch-Izod impact strength of vulcanized and non-vulcanized PP/RTR blends.

It is obvious that all the blends, both with vulcanization and non-vulcanization, exhibit higher impact strength than PP. The explanation is that RTR can serve to absorb energy for polymers the same as natural rubber or other elastomer. The elastic energy stored in the RTR particles during stretching is dissipated irreversibly when the particle rupture. It shall be noted that vulcanized PP/RTR blends has much higher impact strength than all of non-vulcanized PP/RTR blends.

When RTR loading up to 30 pbw, the non-vulcanized PP/RTR blends showed the marginal increase in impact strength up to 15%, and the vulcanized PP/RTR blends showed continuously increase in impact strength up to 108% comparing to PP. At higher loading than 30 pbw, the impact strength of both types

of the blends were dropped. It can be expected that the loading of RTR into PP has a critical point for the improvement of the impact properties.

The marginal increase in impact strength of non-vulcanized PP/RTR blend at the RTR loading up to 30 pbw, is due to the impact energy absorption of RTR. RTR can absorb impact energy and allow its rubber particles to undergo deformation before the fracture of the blends since RTR is a softer material than PP and therefore, as expected, results in the increase impact strength of PP. In case of vulcanized PP/RTR blend the significant increase in impact strength comparing to non-vulcanized PP/RTR blend and PP is observed. The more RTR is present in the blend, the higher the impact strength exhibits. This can be resulted from not only the impact energy absorption of RTR but also the sulfur crosslinking between RTR particles. Crosslinking in the rubber phase will increase cohesive strength and allow the rubber particles to undergo greater deformation before cohesive failure.

In other work [78], ethylene vinyl acetate copolymer (EVA) were used as an impact modifier for PP, which was melt-mixed in a twin-screw extruder at 200°C, it was found that PP/EVA blend at 30 pbw EVA showed 99% increase in impact strength. Whereas, in this study, vulcanized PP/RTR blend at 30 pbw RTR showed 108% increase in impact strength, comparing to PP. Although the impact strength of PP/RTR blend is about the same as PP/EVA blend at the same loading of an elastomer but it still has the advantage in the lower cost of RTR than EVA. It has been reported that the impact toughening of PP varies with types and loading of elastomer.

At RTR loading higher than 30 pbw, the decrease in impact strength of PP/RTR blends both vulcanization and non-vulcanization is observed. This probably due to the amount of carbon black which was already presented in RTR. It can be rationalized that incorporation of higher brittle and rigid material, like carbon black in PP matrix, can form a layer-like structure depending on the amount of carbon black in the blend. Thus at the critical carbon black concentration, the impact

strength of PP/RTR blend can have a split in the layer structure provides a shorter path for fracture propagation, thereby reducing the impact strength.

The rationalization mentioned above can be supported by many other research works. When virgin elastomer was blended with thermoplastic, the notch-Izod impact strength of these blends continued to rise with higher elastomer loading, for instances, PP/EVA [78], PP/EPDM [78,81] and PP/NR [80]. In case of used-tire rubber, such as GRT, it contains carbon black, 20-30% by weight of rubber, which can influence the impact strength of the blends. For example, J.R., Michel and coworkers [41] found that the rise in the impact strength of LLDPE/GRT blends is observed, at 10-40 % by weight GRT. After this region the impact strength of the blend dropped suddenly. A.A., Phadke and S.K., De [40] blended 100 pbw PP, 20 pbw NR and various GRT loading at 20-60 pbw. They reported that the impact strength continued to rise until GRT loading up to 40 pbw. A higher GRT loading a fall in impact strength was observed. The sudden fall in impact strength of these blends at a certain level of GRT loading must be resulted from the formation of layer-like structure of carbon black in the blend. Such phenomenon is similar to the result of this study, eventhough RTR was used instead of GRT.

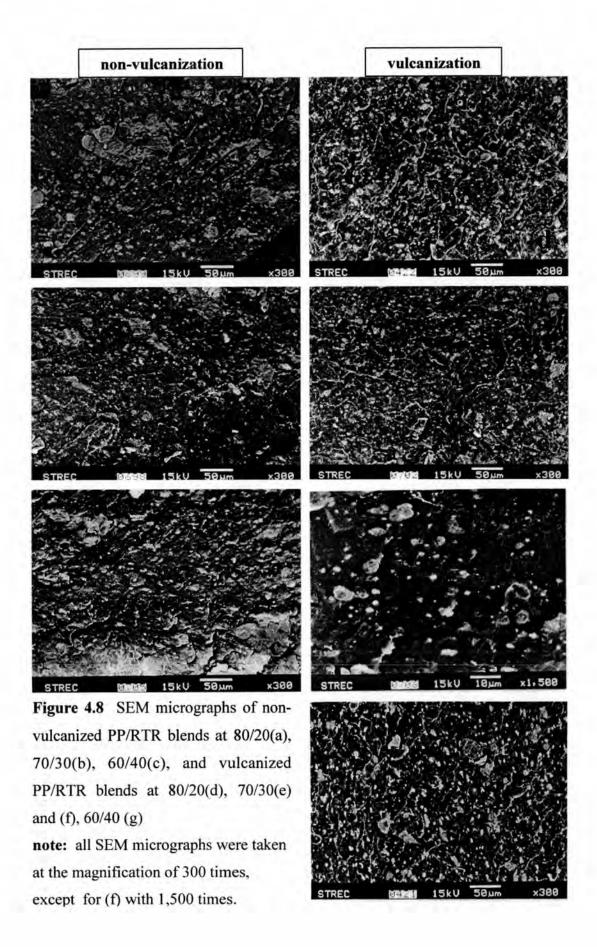
4.5.1.2 Effect of RTR Loading on Morphology

One aspect of blend characteristics is to investigated rubber-phase dispersion. In this study, the dispersion of various RTR loading into PP matrix was studied. The molded samples were placed in liquid nitrogen at the end of which the samples were fractured and the surfaces was examined by Scanning Electron Microscope (SEM) which detected the electron with a backscattered electron emission detector. Because of the similar structure of the main component, hydrocarbon polymer, PP and RTR, staining the rubber phase with osmium

tetroxide (OsO₄) and sputter coating with gold were needed in order to produce image contrast. Figure 4.8 presents SEM micrographs of the frozen fractured surfaces of PP/RTR blends. Those micrographs showed the rubber phase in white and the PP matrix phase in black.

All non-vulcanized blends, (Figure 4.8 (a), (b) and (c)), appear to have larger RTR aggregates particle size than all vulcanized blends (Figure 4.8 (d), (e), (f) and (g)), indicating worse distribution RTR into PP matrix. This result can be explained that better dispersion apparently occurs from the effective role of crosslink in resisting rubber reagglomeration. This phenomenon has also been observed by K.C. Dao [82], who investigated the effect of degree of crosslinking on the dispersion of EPDM in PP and he concluded that high crosslink concentration resulted in the finest dispersion.

Among vulcanized PP/RTR blends, the scanning electron micrographs of PP/RTR blends at 80/20 and 70/30 clearly show that RTR phase can distribute into PP matrix evenly while some larger RTR aggregates can be observed in case of PP/RTR blend at 60/40. 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 rationalization is consistent with the sudden drop of impact strength of PP/RTR blend at 60/40.



4.5.1.3 Effect of RTR Loading on Thermal Properties

Thermal analysis techniques by Differential Scanning Calorimeter (DSC) is the most widely used for measuring the heat flow directly into (endothermic reaction) or away (exothermic reaction) from a substance as it undergoes a transition. In this study, the focus was on melting temperature and the percentage crystallinity. Table 4.5 exhibits thermal properties data of PP/RTR blends and Figure 4.9 and 4.10 present the DSC thermograms of non-vulcanized and vulcanized PP/RTR blends prepared at various loading of RTR, respectively.

Table 4.5 Thermal analysis of vulcanized and non-vulcanized PP/RTR blends at various RTR loading.

Composite No.	T _{onset}	T _m	ΔH_f (J/g _{composite})	ΔH_f (J/g _{PP})	Crystallinity (%)
PP	147.13	161.33	85.52	85.52	45.01
Non-Vulcanization:					
S2 (20)	148.60	162.67	68.18	85.23	44.86
S4 (25)	148.64	163.00	63.55	84.74	44.60
S6 (30)	147.80	162.34	57.29	81.85	43.08
S8 (35)	151.90	162.67	49.50	82.52	43.42
S10 (40)	151.76	164.67	55.38	85.20	44.84
Vulcanization:					
S3 (20)	148,80	161.00	63.24	79.05	41.60
S5 (25)	152.20	163.33	55.91	74.55	39.24
S7 (30)	147.73	162.00	49.60	70.86	37.29
S9 (35)	153.82	164.67	47.22	72.65	38.24
S11 (40)	152.71	164.00	44.14	73.56	38.72

Note: The value in parenthesis is referred to RTR loading (pbw).

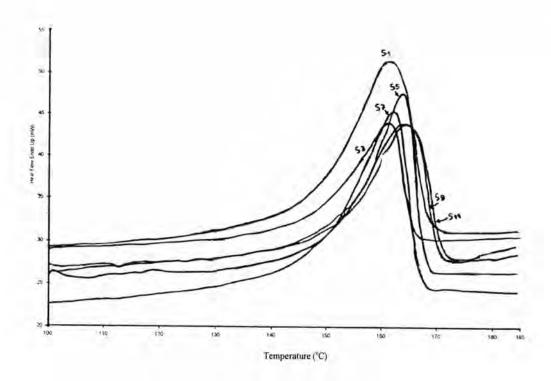


Figure 4.9 DSC thermograms of the non-vulcanized PP/RTR blends at various RTR loading.

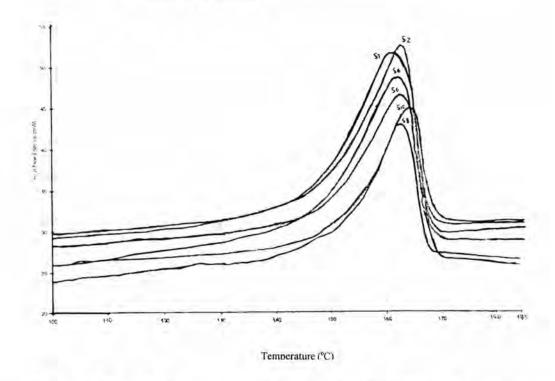


Figure 4.10 DSC thermograms of the vulcanized PP/RTR blends at various RTR loading.

It was found that both melting temperature (T_m) and onset temperature (T_{onset}) of all composites from moulded specimens were not significantly differed from PP. The percentage crystallinity of PP decreased when RTR was presented in both vulcanized and non-vulcanized composites. The decrease in percentage crystallinity was due to the inclusion of the more flexible RTR, which could disturb the packing of polypropylene chains. When more RTR was thus loaded, the lower percentage crystallinity was obtained. However, at RTR loading higher than 30 pbw, the percentage crystallinity increased. This probably caused by the high amount of carbon black enough to form the layer-like structure which could restrict the penetration of RTR. Accordingly, at 30 pbw RTR loading, for both vulcanized and non-vulcanized blends, the inclusion of more RTR would increase rubber-rich amorphous regions which exhibited the lowest percentage crystallinity. This is consistent with the observed highest impact strength.

At 30 pbw RTR loading, vulcanized PP/RTR blend had lower percentage crystallinity than non-vulcanized one comparing to PP. This can be explained by the sulfur crosslinking of RTR which acted as local defects, not allowing close packing of the polymer chains, leading to the higher decrease in percentage crystallinity of PP.

In the meantime, it is noted that the melt temperature is not significantly affected by the incorporation of RTR, whereas, the percentage of crystallinity of PP is significantly affected by RTR.

4.5.1.4 Effect of RTR Loading on MFI

The measurements of the melt flow index (MFI) were primarily considered as a measure of stability for PP/RTR blends. Generally, the rubber characteristics, such as high molecular weight and reversible elongation at relatively low stresses,

reduced the melt flow rate of the composites. The MFI can be related to melt viscosity. The lower MFI would indicate the higher viscosity. In addition, MFI may give a relative indication of processability eventhough the measurements are conducted at one very low shear rate and one temperature set by ASTM standard. The results of MFI measurement are shown in Table 4.6. Figure 4.11 shows the MFI of vulcanized and non-vulcanized PP/RTR blends as a function of composition.

Table 4.6 The MFI of vulcanized and non-vulcanized PP/RTR blends at various RTR loading.

Composite	Melt Flow Index : MFI (g / 10min.)			
No.	Average	SD	%Variation	
PP	3.15	0.01	0.32	
Non-vulcanization:				
S2 (20)	3.08	0.01	0.32	
S4 (25)	2.90	0.01	0.34	
S6 (30)	2.81	0.00	0.00	
S8 (35)	2.77	0.01	0.36	
S10 (40)	2.74	0.01	0.36	
Vulcanization:				
S3 (20)	2.61	0.02	0.77	
S5 (25)	1.96	0.01	0.51	
S7 (30)	1.80	0.01	0.56	
S9 (35)	1.75	0.01	0.57	
S11 (40)	1.70	0.01	0.59	

Note: The value in parenthesis referred to RTR loading (pbw)

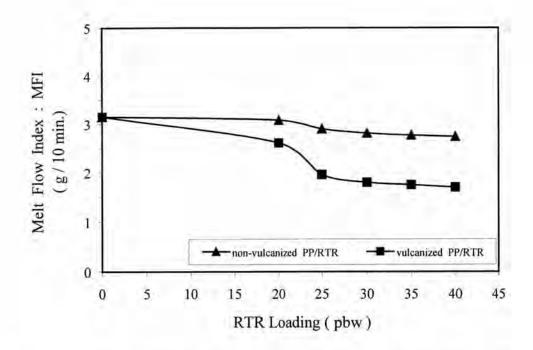


Figure 4.11 Effect of RTR loading on MFI of vulcanized and non-vulcanized PP/RTR blends.

It was firstly noted that all PP/RTR blends had less MFI than PP. When RTR increased, a continuously drop in the MFI was occurred. This behavior is expected as lower MFI corresponds to the higher viscosity and that in turn must have been imparted by the dispersed phase.

The vulcanized PP/RTR blends exhibited the relatively larger drop in MFI than non-vulcanized PP/RTR blends, at the same ratio. For example, 42% decrease in MFI of vulcanized blend, whereas, 11% decrease in MFI of non-vulcanized blend, at 30 pbw RTR loading and comparing with PP. This result may be explained that the cured RTR phase contributed to a higher viscosity.

PP/RTR blend at the ratio of 70/30 was the best composition that gave the highest notch-Izod impact strength and lowest percentage crystallinity and MFI. It had a good dispersion and distribution of RTR into PP.

4.6 Comparison of PP/RTR with PP/GRT Blends

In this section, the impact strength and morphology of PP/RTR blends were compared with PP/GRT blends, Table 4.7 and Figure 4.12, respectively.

Table 4.7 The notch-Izod impact strength of 70/30 PP/RTR and PP/GRT blends.

Composite	notch-Izod impact strength (kJ/m²)	% improvement*
PP	3.07	5
Non-vulcanization:		
PP/GRT	3.30 (S16)	7.49
PP/RTR	3.52 (S6)	12.78
Vulcanization:		
PP/GRT	3.75 (S17)	22.15
PP/RTR	6.38 (S7)	107.82

Note: The number in the parenthesis is referred to the composite number.

It is clearly observed that PP/RTR blends have better impact strength than PP/GRT blends both with and without vulcanization. This probably due to the different nature of RTR and GRT, which are the mixture of devulcanized and vulcanized NR, SBR and BR, respectively. The crosslink density of GRT makes it

[%] improvement of impact strength compare with PP.

difficult for any interpenetration of GRT and PP phases at the interface. In contrary, no crosslink in RTR allows the capable dispersion of rubber chains in RTR into PP matrix higher than GRT, which leads to the better adhesion and higher impact strength. Therefore, non-vulcanized PP/RTR blend exhibited 12.78% increase in impact strength whereas lower improvement of 7.49% was obtained for non-vulcanized PP/GRT blend. Furthermore, the significant increase in impact strength of 107.82% for vulcanized PP/RTR comparing to the improvement of only 22.15% for vulcanized PP/GRT was astonishing. The explanation for this observation had already been elaborated in section 4.5.1.1.

Figure 4.12 shows the SEM micrographs of PP/GRT blends and PP/RTR blends at the same blend ratio, 70/30, for comparison.

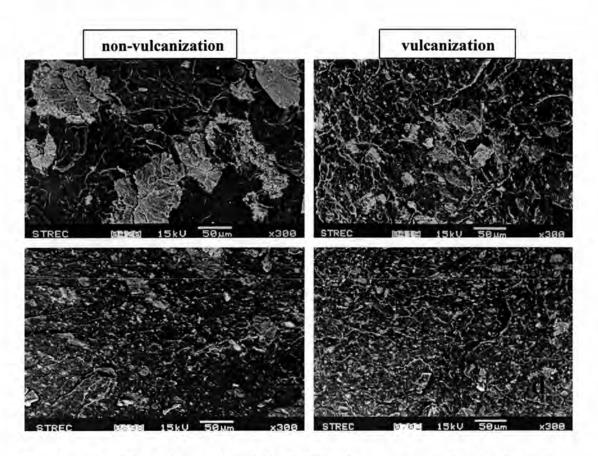


Figure 4.12 SEM micrographs of PP/GRT blends (a,b; non-vulcanization and vulcanization) and PP/RTR blends (c,d; non-vulcanization and vulcanization), at 70/30 blend ratio.

The micrographs cleary revealed that the best dispersion and distribution of the rubber phase into matrix (Figure 4.12d) could be achieved by firstly devulcanization of recycled tire-rubber and then revulcanization of the rubber phase during melt-mixing with PP.

4.7 PP/RTR Blends using MA/DCP

Generally, the toughening improvement of thermoplastic depends on the type of toughening agent and thermoplastic matrix. Eventhough sulfur crosslinking agent is the common one, several others are also been used. P.K. Pramanik and coworkers [35] attempted to use dicumyl peroxide (DCP) and maleic anhydride (MA) in toughening low density polyethylene (LLDPE). Recently N.R. Choudhury and coworkers proposed reactive blending between low – density polyethylene (LDPE) and GRT using chlorinated polyethylene (CPE) as a compatibilizer.

Since Maleic anhydride (MA) is frequently used to compatibilize thermoplastic elastomer blends which requires the initiator. Organic peroxides such as dicumyl peroxide are known to be the initiators necessary for the vulcanization of saturated rubber. In this study, the combination of MA and DCP was utilized instead of sulfur crosslinking agent with the aim to increase the impact strength of PP/RTR blends. The same preparation of the blends, as mentioned in section 4.2, was carried out.

4.7.1 Impact strength of PP/RTR blends using MA/DCP

The notch-Izod impact strength of 70/30 PP/RTR blends in the presence of different compatibilizer and crosslinking agent comparing to PP exhibited in Table 4.8.

Table 4.8 The notch-Izod impact strength of 70/30 PP/RTR blends using MA/DCP.

Composite	Notch – Izod Impact Strength (kJ/m²)				
No.	Average	SD	%Variation		
PP	3.07	0.10	3.26		
S12 (PP/RTR)	3.52	0.10	2.84		
S13 (PP/RTR/MA)	5.70	0.00	0.00		
S14 (PP/RTR/DCP)	6.62	0.10	1.51		
S15 (PP/RTR/MA/DCP)	8.07	0.05	0.62		

4.7.1.1 Utilization of MA

From Table 4.8, it can be firstly observed that the impact strength of PP/RTR blend using only MA (S13) is higher than PP and PP/RTR blend without MA (S12). This clearly indicates the influence of MA in the blend.

MA can react with polymeric double bonds of recycled NR, BR and SBR, the components in RTR, via four different basic reactions as shown in Scheme 4.1. These reactions require only heat to occur. Among these four reactions the intermolecular addition to double bonds in different polymer chains (c) and the

intermolecular addition to α-methylenic carbon atoms in adjacent chains (d) creates the cohesive strength between the rubber chains that will enhance the impact strength of PP/RTR blend. However, the impact strength of PP/RTR blend using MA is still lower than PP/RTR blend using sulfur crosslinking agent (S7), as shown in Table 4.4. With sulfur crosslinking agent, the presence of TMTD and MBT, ZnO and steric acid, which are the accelerators and activators promoting sulfur crosslink between rubber particles, while MA generally can not react efficiently in the absence of organic peroxide. This crosslinking in S7 was possibly more than S14 which attributed to higher impact strength.

Scheme 4.1 The addition reaction of maleic anhydride onto natural rubber: (a) addition to α-methylenic carbon atom; (b) intramolecular addition to the double bond; (c) intermolecular addition to double bonds in different polymer chains; (d) intermolecular addition to α-methylenic carbon atoms in adjacent chains.

4.7.1.2 Utilization of DCP

From Table 4.8, the impact strength of PP/RTR blend using only DCP is higher than both PP/RTR blends using sulfur crosslinking agent and only MA. DCP can be decomposed to form radicals and initiated polymer chain to form polymer radical, and these chains can then combine to form three different crosslinks, between rubber-rubber, PP-PP and PP-rubber (Scheme 4.2). In case of MA and sulfur crosslinking agent, the crosslink between PP-rubber in RTR can not occur. The crosslink between PP-rubber in RTR causes the increase in interfacial adhesion, which leads to rise in compatibility and impact strength of the composites. Increasing interfacial adhesion allows the interface to withstand a greater stress before the particle debonds. When interfacial adhesion is low, the rubber particles caught in a craze may debond from the matrix generating a void within the craze, which can grow into a crack and precipitate failure. There is a possibility of degradation of the PP phase in the presence of DCP. However the crosslinking reaction usually predominates over degradation reaction, hence higher in impact strength.

Initial Decomposition of DCP

$$\bigcirc \begin{matrix} CH_3 & CH_3 \\ CH_3 & CH_3 \end{matrix} \xrightarrow{Heat} 2 \bigcirc \begin{matrix} CH_3 \\ CH_3 \end{matrix} = RO$$

H-abstraction

Beta-Scission of PP

$$CH_2$$
- C - CH_2 - CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3

Chain Transfer

Termination

Termination of PP-PP

- Termination via combination

- Termination via disproportionation

[Structure A+B, Structure A+C, Structure B+C, Structure C+C]

Termination of PP-Rubber in RTR

PP' + BR' :
$$CH_3$$
 CH_2
 CH_3
 CH_2
 CH_3
 CH_3
 CH_3
 CH_2
 CH_3
 CH_2
 CH_3
 CH_2
 CH_3
 CH_2
 CH_3
 CH_2
 CH_3
 CH_2
 CH_3
 CH_3
 CH_3
 CH_2
 CH_3
 CH_3

Scheme 4.2 The crosslink formation reaction by dicumyl peroxide.

4.7.1.3 Utilization of MA and DCP

Table 4.8 shows that the impact strength of PP/RTR blend using MA and DCP is higher than PP/RTR blend using only DCP or only MA or the sulfur crosslinking agent. This higher impact strength is attributed to the higher opportunity to form crosslink between PP and rubber phase in PP/RTR blend due to corporation reaction of MA and DCP (Scheme 4.3). 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, BR, or SBR, the components in RTR. This causes an increase in interfacial adhesion, which increases the impact strength of the composite.

H-abstraction

Beta-Scission of PP

$$\text{CH}_2$$
- $\dot{\text{C}}$ - $\text{CH}_{\frac{7}{2}}$ $\overset{\text{CH}}{\text{CH}_3}$ $\overset{\text{CH}}{\text{CH}_3}$ $\overset{\text{CH}_2}{\text{CH}_3}$ $\overset{\text{CH}_2}{\text{CH}_3}$ $\overset{\text{CH}_3}{\text{CH}_3}$ $\overset{\text{CH}_3}{\text{CH}_3}$ $\overset{\text{CH}_3}{\text{CH}_3}$

Anhydride grafting

Chain Transfer

Termination

- Termination via combination of PP-PP

PM + Structure A → PM-P (Crosslinking or Branching)

- Termination via disproportionation of PP-PP

- Termination via combination of PP-Rubber

Scheme 4.3 The crosslink between PP and rubber by the corporation reaction of MA and DCP

The toughening of PP can be observed not only by impact strength measurement but also by elongation measurement. Which elongation at break can be calculated with the extension at breaks of specimen (change in gage length) divide by the original gage length and multiplies by 100. The elongation at break of 70/30 PP/RTR blend with addition of both MA and DCP showed upper 500 percent, whereas PP showed 350 percent. It can be noted that the compatibility of PP and RTR were occurred. From the higher in impact strength and elongation at break of PP/RTR blend with addition of both MA/DCP than PP indicated that the RTR could provided an increasing in toughness of PP.

4.7.1 Morphology of PP/RTR blends using MA/DCP

In this section, the dispersion and distribution of RTR in PP matrix phase was investigated by SEM technique. The molded samples of the blends were placed in liquid nitrogen, stained with osmium tetroxide (OsO₄) and sputter coated with gold, similar to the preparation for PP/RTR crosslinked with sulfur crosslinking agent.

Figure 4.13 shows the SEM micrographs of PP/RTR (70/30) crosslinked with MA/DCP system (RTR in white, PP in black). PP and RTR blended without any compatibilizer or crosslinking agents, S12, Figure 4.13(a) were not compatibilized as agglomeration of RTR was observed. This results in poor dispersion and distribution of RTR into PP matrix. Indeed, S12 had little higher impact strength than PP. The dispersion and distribution of RTR into PP matrix of all PP/RTR blends using MA/DCP may be seen similarity. However, the higher agglomeration of RTR in PP/RTR blend using only MA (S13) or DCP (S14), which could be lower improved in impact strength.

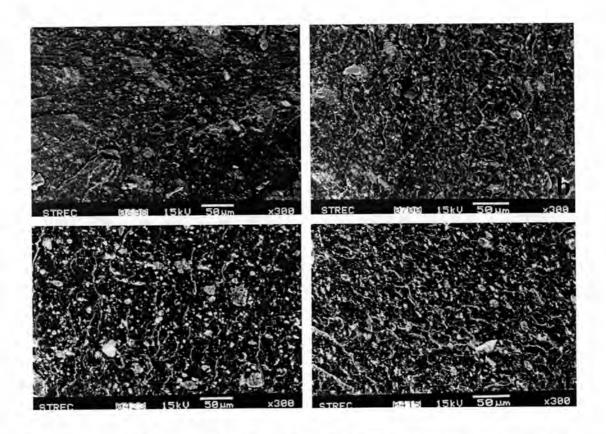


Figure 4.13 SEM micrographs of 70/30 PP/RTR blends: (a) no added, (b) with MA (c) with DCP, (d) with both MA and DCP.

4.7.2 Thermal properties of PP/RTR blends using MA/DCP

Thermal properties of PP/RTR blends using MA/DCP, such as melting temperature and percentage crystallinity of PP, were determined from the DSC curves, the same techniques with studied the effect of RTR loading on thermal properties of PP/RTR blend using sulfur crosslinking agent in section 4.5.1.3.

Table 4.9 shows the thermal analysis of 70/30 PP/RTR blend with MA/DCP crosslinking system and the DSC thermographs is shown in Figure 4.14.

Table 4.9 Thermal analysis of 70/30 PP/RTR blends using MA/DCP.

Composite No.	T _{onset}	T _m (°C)	$\Delta H_{\rm f}$ (J/g _{composite})	ΔH _f (J/g _{PP})	Crystallinity (%)
РP	147.13	161.33	85.52	85.52	45.01
S12 (PP/RTR)	147.80	162.34	57.30	81.85	43.08
S13 (PP/RTR/MA)	150.30	163.34	51.40	73.43	38.65
S14 (PP/RTR/DCP)	151.90	162.67	49.11	70.16	36.92
S15 (PP/RTR/MA/DCP)	152.47	164.00	48.30	69.00	36.32

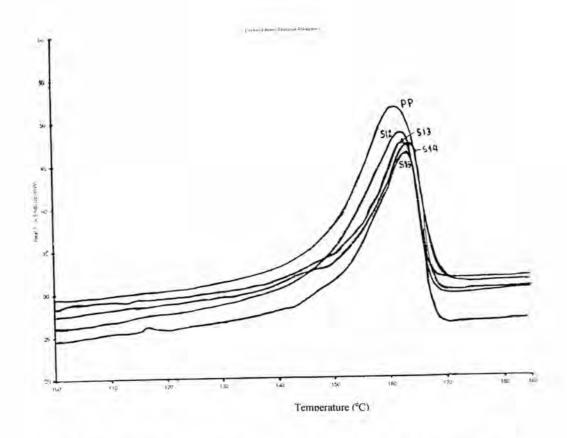


Figure 4.14 DSC thermographs of 70/30 PP/RTR blends using MA/DCP.

In this study, it was found that the melting temperature (T_m) or onset temperatures (T_{onset}) are not significantly different from PP. The percentage crystallinity of PP in the composite No.S15, using both MA and DCP, is lower than the blends using only MA or DCP. In addition, composite blend with MA alone (S13) shows a higher degree of crystallinity than when does blend with DCP alone (S14). It can be indicated that the addition of both MA and DCP in PP/RTR blend gave a higher disturbance in crystallinity of PP than the addition of DCP and MA alone, respectively. This disturbance in crystallinity occurs by the formation of the crosslinking in these composites.

4.7.3 MFI of PP/RTR blends using MA/DCP

The results of MFI of 70/30 PP/RTR blends using MA/DCP show in Table 4.10. Figure 4.15 shows the percentage MFI of these composites, comparing with PP.

Table 4.10 The MFI of 70/30 PP/RTR blends using MA/DCP.

Composite	Melt Flow Index: MFI (g/10 min.)				
No.	Average	SD	%Variation		
PP	3.15	0.01	0.32		
S12 (PP/RTR)	2.90	0.00	0.00		
S13 (PP/RTR/MA)	1.85	0.01	0.54		
S14 (PP/RTR/DCP)	1.73	0.01	0.58		
S15 (PP/RTR/MA/DCP)	1.56	0.02	1.28		

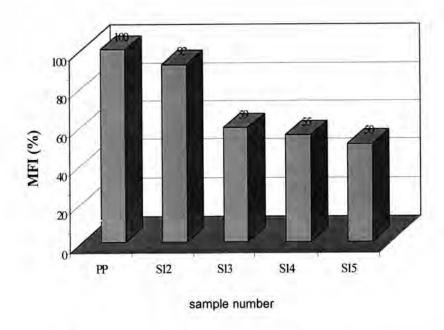


Figure 4.15 Percentage MFI of 70/30 PP/RTR blends using MA/DCP.

The addition of MA and DCP can improve the impact strength of the composites, while the MFI of each composite is decreased. The 70/30 PP/RTR blend using both MA and DCP (S15) exhibites a larger drop in MFI (~50%), comparing with PP. The addition of DCP (S14) results in a 45% drop in MFI while the addition of MA (S13) gives a decrease in MFI which is less than S14 blend. This result is similar to 70/30 LLDPE/GRT blend [35], the addition of only MA results in a small change in viscosity but with a major increase in viscosity when addition of only DCP.

The larger drop in MFI, higher viscosity, of S15 blend is due to crosslink between PP and rubber. Generally, crosslink can restrict the melt flow of polymer, which leads to lower MFI. In case of S15 blend, the three types of crosslink between PP-PP, PP-rubber and rubber-rubber, were performed, which produce the higher adhesion and leads to lower MFI. Whereas S13 and S14 produce these crosslinks less than S15, thus S15 had lowest MFI.

4.8 Reproducible melt-mixing of PP and RTR

In this research work, melt-mixing had been carried out very carefully. The manipulation was controlled to be at the same condition and designed to ensure totally well mixing. Eventhough each blend had been prepared only one time, it is assumed to be a well-mixed blend. However, 70/30 PP/RTR using the combination of MA and DCP was chosen to be repeated. By measuring notch-Izod impact strength of three blends (Table 4.11) which are in the proximity to each other, this indicates the reproducible melt-mixing.

Table 4.11 The notch-Izod impact strength of three blends of 70/30 PP/RTR using MA/DCP.

Mixing No.	notch-Izod impact strength (kJ/m²)	elongation at break
1	8.07	Ce.
2	7.96	>500
3	8.00	>500

4.9 Applications and Economics

Rubber-toughened PP have experienced a fairly rapid growth rate over a number of years, exceeding those of traditional rubbers and commodity plastic, as a new applications are found for them. TPNR (thermoplastic natural rubber) is one type of these materials that has a correspondingly broad range of applications. Rubbery grades can be used as replacements for vulcanized rubber and flexible plastics. In general TPNR is suitable in applications not requiring the superior strength and elasticity of vulcanized NR. It is important to note that it is many of these areas that plasticized PVC and EVA copolymers have been used. Examples are footwears, sports goods, glazing seals and some types of hose. An advantage of TPNR is that it has a higher softening temperature than PVC or EVA or styrene-butadiene-styrene block copolymers. This is due to the high melting point of PP and stable crosslinks in the NR phase, so that it has a relatively low compression set and, consequently, a high service temperature. Another advantage is that it does not harden at low temperature to the extent of PVC. Hard grades of TPNR will meet most automotive specifications for bumpers and related impact-resistant components.

In this study, reclaimed tire-rubber (RTR) toughened polypropylene (PP) is the one type of thermoplastic elastomers in which RTR was used instead of natural rubber (NR), although RTR has slightly lower properties, such as elongation and tensile strength, than NR. It is interesting that RTR has a two point lower cost than NR. The notch-Izod impact strength of 70/30 PP/RTR blend with combination of MA/DCP has a 8.07 kJ/m², whereas high flow polypropylene impact copolymer resin (Pro-fax SW 834) of HMC Polymers Co.,Ltd., which was used for making washing machine tub, electrical appliances and automotive parts, has a 6.84 kJ/m² notch-Izod impact strength. This exhibited that 70/30 PP/RTR blend with combination of MA/DCP may use to produce things like automotive parts, motorcycle parts and industrial containers.