

CHARTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Reclaimed Tire Rubber

Reclaimed tire rubber (RTR) and polypropylene (PP) were mixed at various ratios from 20/80 to 80/20 (RTR/PP) by using an internal mixer. The sulphur curing system was chosen for dynamic vulcanizations of these blends. In addition, a compatibilizer was also applied. The recipes used for the dynamic vulcanization are given in Tables 3.2-3.4 in section 3.3. Various mechanical property tests were performed in accordance with ASTM D256 and ASTM D412 for each blend. Furthermore, the difference between unvulcanized and vulcanized RTR was recognized through a solvent swelling study. The phase structure of the RTR/PP blends at various compositions was then assessed by mechanical and rheological properties and scanning electron microscopy (SEM) images.

4.1.1 Composition of reclaimed tire rubber

Reclaimed tire rubber (RTR) used in this study was taken from truck tire. Generally, the tread part is made of styrene butadiene rubber (SBR), while the side-wall and shoulder parts are made of natural rubber (NR) and styrene butadiene rubber (SBR)/butadiene rubber (BR), respectively. Since RTR was obtained from the devulcanization of ground tire rubber, the rubber part of RTR may be referred to as a miscible blend of NR, SBR and BR. It is also well known that the other major components in RTR are carbon black and calcium carbonate. In general, the amount of carbon black and the level of cross linking affect the temperature of mass loss [14]. When they increase, the temperature of mass loss will be higher.

The composition of RTR used in this study was clearly identified by its TGA thermogram as illustrated in Figure 4.1.

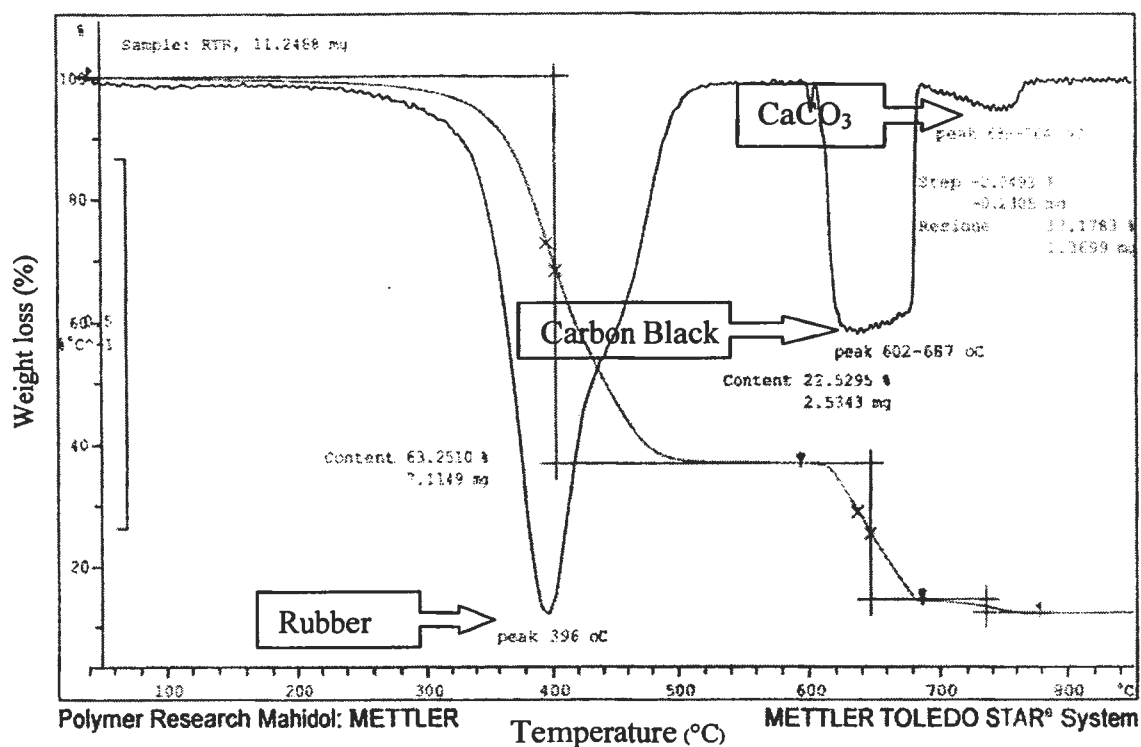


Figure 4.1 TGA thermogram of reclaimed tire rubber.

The first peak was arbitrarily assigned to SBR, NR and BR since the elastomer usually degraded between 300-500°C. The other major peak observed at 600°C which was in the range of the thermal degradation of carbon black, 400-1,600°C, indicated the presence of carbon black in RTR. The small peak appeared at 688-764°C was due to calcium carbonate [37]. Therefore, RTR comprised of 63.25% rubber, 22.53% carbon black, 4.66% calcium carbonate, and 7.52% residue as shown in Table 4.1.

Table 4.1 Composition of reclaimed tire rubber

Components	Amount (%)	Degradation temp. (°C)
Rubber	63.25	396
Carbon black	22.53	602-687
Calcium carbonate	4.66	688-764
Residue	7.52	>800

To further confirm the types of rubber in RTR the ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy was used. The ^{13}C NMR spectrum of the authentic NR sample was recorded and compared with the ^{13}C NMR spectrum of RTR as shown in Figure 4.2.

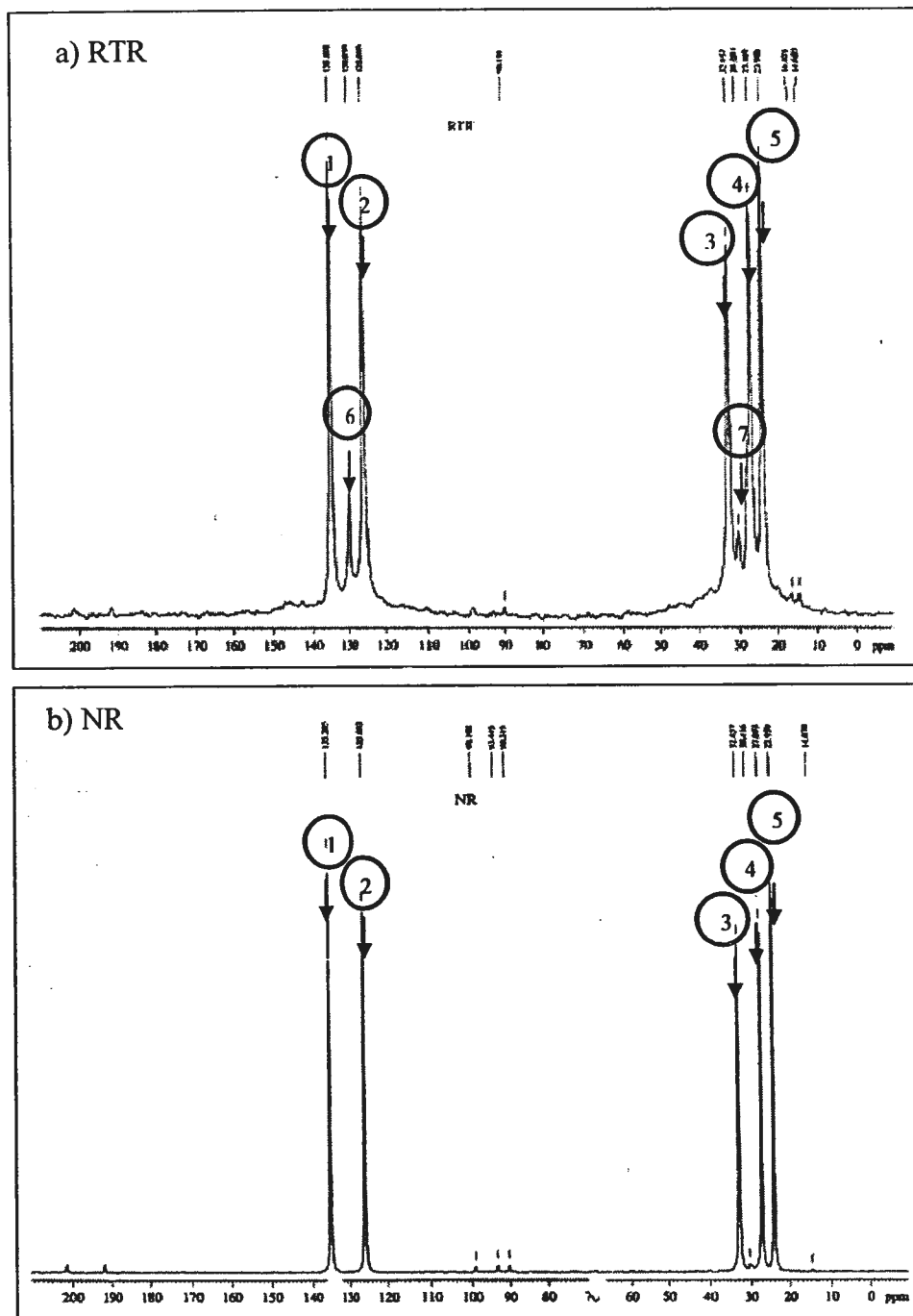


Figure 4.2 Solid state ^{13}C NMR spectra of (a) reclaimed tire rubber and (b) natural rubber.

In case of BR and SBR, their ^{13}C NMR spectral data were taken from the reference. Table 4.2 exhibits the comparison of the ^{13}C NMR spectral data of RTR, NR and SBR. The results obviously revealed that RTR was the mixture of NR and BR, but not SBR.

Table 4.2 ^{13}C NMR spectral data of RTR, NR and BR.

Peak ¹ No.	Chemical shift (ppm)		
	RTR ¹	NR ¹	BR ²
1	135.2	135.2	-
2	125.7	125.7	-
3	32.8	32.8	-
4	27.1	27.1	-
5	23.9	23.9	-
6	130.0	-	130.0
7	30.4	-	30.4

Remarks: 1. Refer to the ^{13}C NMR signals of RTR and NR as shown in Figure 4.2.

2. Taken from the reference [38].

4.1.2 Swelling test results

Prior to the blending study, the vulcanization capacity of RTR was investigated. Therefore the vulcanization of RTR with sulphur vulcanizing agent was carried out as described in section 3.3.1. Then the crosslink density of RTR, before and after vulcanization, was determined based on the solvent swelling test according to ASTM D471 [39]. Three measurements of each sample were taken and the average values were reported in Table 4.3.

Table 4.3 Swelling test results of unvulcanized and vulcanized RTR.

Samples No.	Swelling (%)	
	Unvulcanized	Vulcanized
1	287.9	71.1
2	300.1	70.2
3	297.0	71.2
Average	295.0	70.8
SD (%)	6.3	0.56

It can be seen that the swelling percentage of vulcanized RTR was considerably lower than the unvulcanized RTR. In other words, unvulcanized RTR could swell in toluene better than vulcanized RTR, indicating numerous double bonds in the structure of unvulcanized RTR were available. This means that unvulcanized RTR had low degree of crosslink density.

4.2 Effect of RTR Content on Reclaimed Tire Rubber/Polypropylene Blends

4.2.1 Mechanical properties of the blends

In general, plastics always have high tensile strength than rubber. The tensile strength of RTR was 5.03 MPa which was lower than RTR/PP blends containing RTR less than 70 phr as shown in Figure 4.3a. It clearly showed that the tensile strength of RTR/PP blend at 80:20 was lower than RTR. This might happen because this blend contained high amount of carbon black particles, which might coalesce to form somewhat brittle layers, which could not disperse properly into PP phase. The elongation at break of RTR (100 phr) was determined to be 57%, which was lower than reported by Abbas A. [28]. This was most likely due to the difference in quality of acquired RTR. Furthermore, the Young's modulus was measured to be rather small, 14.5 MPa, while an impact strength test could not be carried out due to the elastic nature of the material.

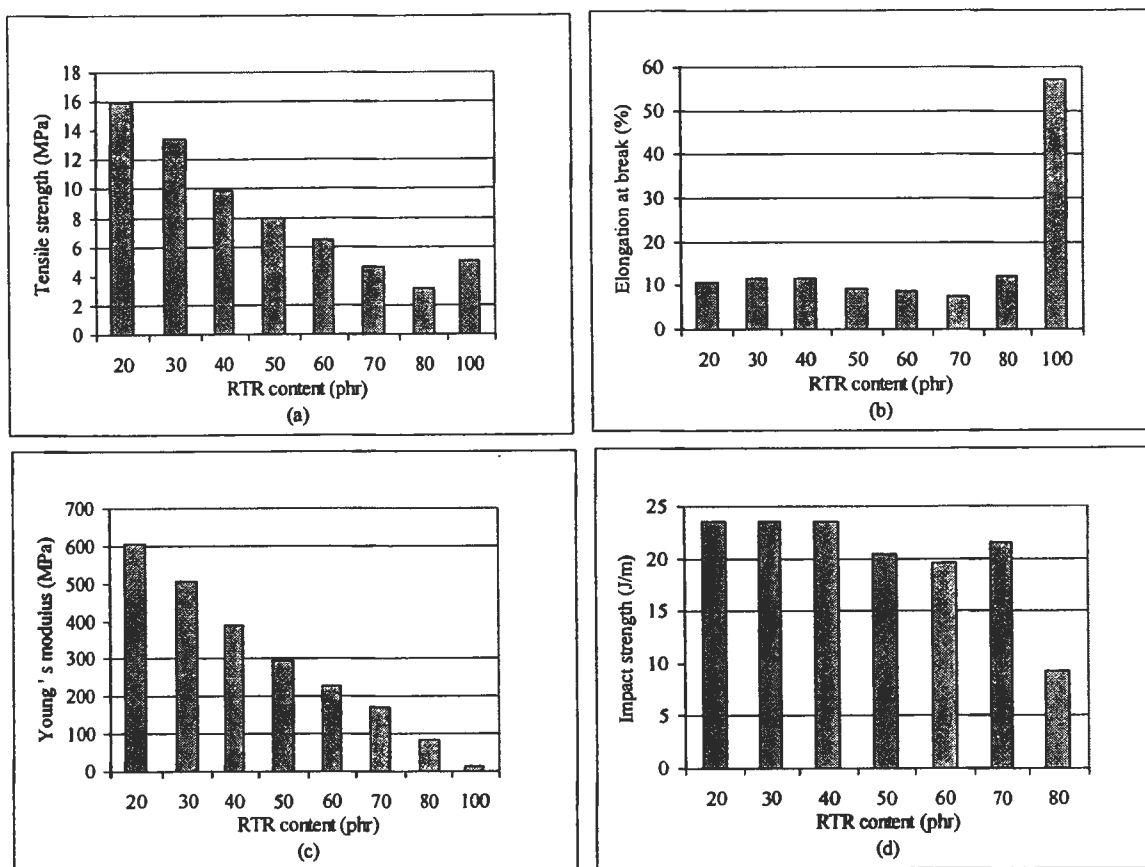


Figure 4.3 Effect of RTR content on mechanical properties of blends, (a) Tensile strength, (b) Elongation at break, (c) Young's modulus, (d) Impact strength.

The addition of RTR into the blends resulted in a reduction of the tensile strength and Young's modulus of the blends because its presence decreased a plastic phase. Every blend had the similar elongation at break which was lower than RTR. This indicated that reclaimed tire rubber had low adhesion with a plastic phase. This could be because it had passed a recycling process which caused shortening of the molecular chains. When these short-chained molecules were mixed with PP, a phase separation was likely to occur more.

Furthermore, the difference in impact strength of all the blends seemed to be small. As seen from the plot, for the RTR content of 20-70 phr, the impact strength was found to be in the similar level, between 19.7 to 23.6 J/m. On the other hand, the RTR content of 80 phr was lower than the others, about half. This could be because of the high amount of carbon black in the blend as explained earlier. The presence of these layers could possibly be responsible for lower energy adsorption, and hence

lower impact strength of the blend. Additionally, the maximum value of the impact strength was obtained when RTR content was at 20-40 phr.

In the research work by Tantayanon et al [22], they reported that the dynamic vulcanization of RTR/PP blends with sulfur crosslink agent had the highest impact strength at the ratio of 30/70 as well. It can be concluded that RTR plays an important role in toughening of PP through dispersion into the PP matrix.

4.2.2 Rheological properties of the blends

The plot of melt flow indices (MFI) of blends versus RTR contents is shown in Figure 4.4.

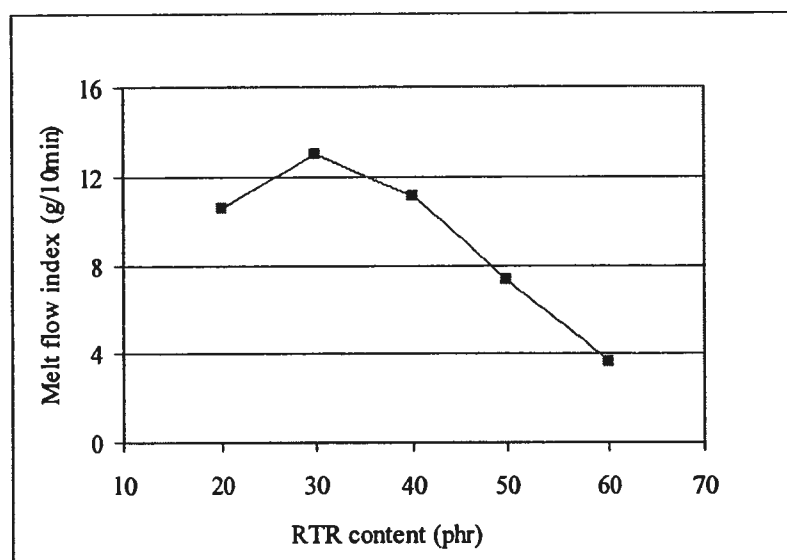


Figure 4.4 Effect of RTR content on melt flow index.

MFI values were found to be inversely proportional with RTR contents. This implied that the presence of RTR increased the flow resistance of the blends. The maximum MFI was obtained at the ratio of RTR to PP of 30:70. RTR/PP blend with this ratio was found to show the optimum properties. Here, MFI results were available for blends with the RTR content up to 60 phr because at the higher RTR content, the blends did not flow.

Rheological properties of blends with various RTR contents are shown in Figure 4.5. The complex viscosity of RTR/PP blends are shown in Figure 4.5a. The effect of RTR content was found to increase the complex viscosity. This was probably due to the fact that with an increasing degree of cross-linking, the viscosity of the

blends increased. It can be seen from the result that the complex viscosity was very similar between the blends with RTR content of 100, 80, and 70 phr. The blends with these ratios were also observed to have the highest viscosity values compared to the others with lower RTR content. The viscosity of the blends with lesser RTR was measured to vary proportionally with the RTR content. This observed relationship between the viscosity of the blend and its RTR content could be because there was a higher degree of freedom in the molecule chains as the amount of RTR was lower, i.e., less level of entanglement between the chains. As a result, the flow resistance was lower and so was the corresponding viscosity of the blends.

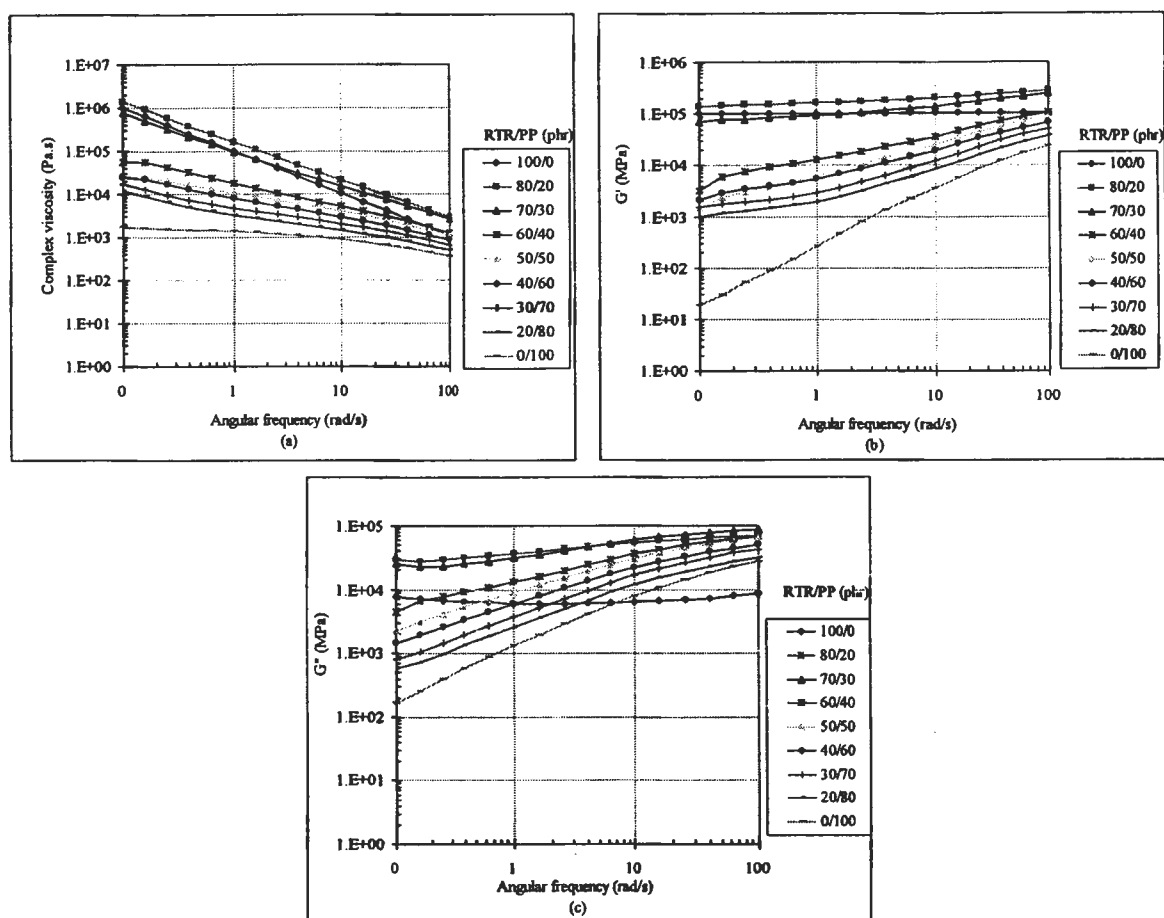


Figure 4.5 Effect of RTR content on rheological properties of blends

- (a) Complex viscosity, (b) Storage modulus, and
(c) Loss modulus.

This tendency was more notable for the blends with the higher RTR amounts, i.e., with higher degree of crosslink. The viscosity enhancement effect was more obvious at the lower shear rate.

Furthermore, the viscosities of blends with low RTR amounts tended to show non-Newtonian flow behavior with an increasing shear rate. Pure PP displayed a Newtonian flow behavior at low shear rate.

The viscosity of PP was seen to be almost constant within a low frequency range 10^0 - 10^1 rad/s. This independence of corresponding viscosity from the applied shear rate indicated a Newtonian behavior. However, as a higher frequency range was approached, i.e., greater shear rate, a decline in viscosity could be detected. It could be said that PP behaved in a non-Newtonian behavior in other words, it had exhibited a shear thinning behavior at this higher range of frequency. This noticed drop in viscosity with an increasing shear rate was possibly owing to a better arrangement of molecular chains resulting from a higher applied shear force. Properly organized molecular chains would then result in a lower flow resistance of PP blend and thus lower viscosity values as measured.

The results of storage modulus (G') measurement on several RTR/PP blends are shown in Figure 4.5b. G' is a modulus property which depends on ω^2 and can be employed to assess the elasticity of the relevant materials. It can be seen from the graph that the greatest values of G' were similarly measured from the blends with RTR content of 100, 80, and 70 phr. Nonetheless, an overall values of G' for the other blends with lower RTR content was found to decrease according to the RTR content of each blend. This result might suggest that the RTR content had a strong indication on the corresponding elasticity of the blends.

The loss modulus (G'') of RTR/PP blends series are shown in Figure 4.5c. G'' is a modulus property which depends on ω and can be employed to assess the viscous flow behaviour of the relevant materials. For RTR, a very negligible change in G'' was seen within the range of shear rate studied. This could be because a slip among the polymer chains did not occur permanently during a shear procedure.

It can be seen that the addition of RTR contents in the blends resulted in an enhancement of complex viscosity and storage modulus. These properties were increasing due to the higher degree of entanglement between the RTR molecular chains.

The interfacial tension between the matrix and the dispersed phase would tend to resist the applied external forces in order to maintain the shape of domain. When the dynamic and viscous forces became larger than the interfacial forces, the domain deformed and eventually broke into a smaller domain [41]. Since the increase in viscosity was probably due to the entanglement of molecular chains of RTR, this entanglement could severely impede the flow in melt at low shear rates. Consequently, the viscosity became higher [42]. However, the disentangling effect was much greater than the entangling one at high shear rates. This could be because the repulsion between RTR chain and the hard segments of PP arose from incompatibilization of both of them.

4.3 Reclaimed Tire Rubber/Polypropylene Blends with Additives on Mechanical properties

RTR/PP blend with a ratio of 30:70 was found to show the optimum properties. This was because, at this particular ratio, the optimum value of MFI was measured while the corresponding mechanical properties were also relatively superior compared to the other ratios.

The poly-octene-ethylene (POE) was used as the compatibilizer in 30/70 RTR/PP blends. These types of additive were chosen for this study because it was reported that the compatibility between RTR and PP was promoted by the presence of copolymers. It was explained that the function of these additives was to reduce the interfacial tension and then improve the phase dispersion and adhesion at the polymer/polymer interface through both interpenetration and entanglement mechanisms [8].

The tensile strength of blends was an important characteristic of polymeric material because it indicated the maximum magnitude of stress that can be sustained by the relevant material in most applications. The tensile strength of 30/70 RTR/PP blend was found to be dependent on the added amount of both compatibilizer as shown in Figure 4.6. The comparison of the effects of two different compatibilizers on mechanical properties of RTR/PP blends can be found in Figure 4.6. In order to study the significance of polarization in the compatibilizers, a maleic anhydride grafted polypropylene (MA-g-PP) was chosen to represent the polarized additive.

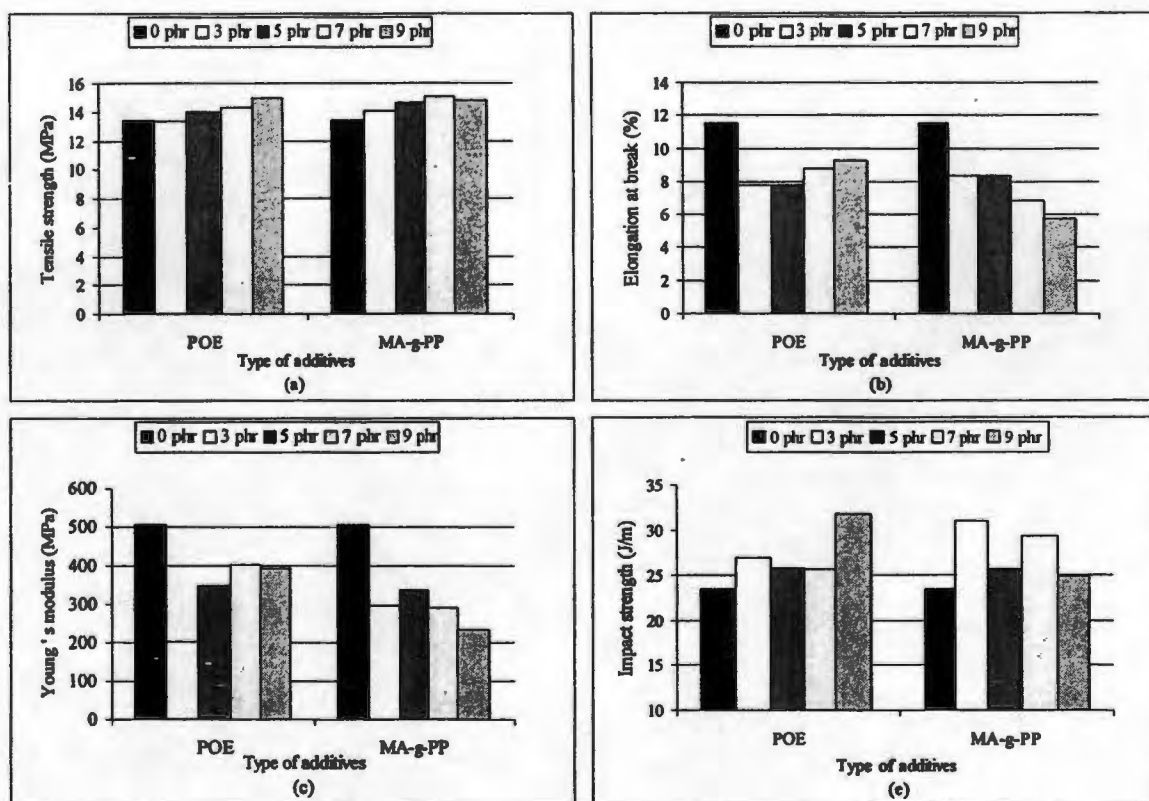


Figure 4.6 Effect of additives on mechanical and rheological properties of 30/70 RTR/PP blends, (a) Tensile strength, (b) Elongation at break, (c) Young's modulus and (d) Impact strength.

The tensile strength of blends was increased slightly as the amount of POE was raised. This was clearly the role of POE which caused a higher interfacial tension between RTR particles and PP phase.

In case of MA-g-PP, the percentage of elongation at break seemed to display a declining trend as opposed to the amount of MA-g-PP in the blend increased. The effect of MA-g-PP on elongation at break was more pronounced than POE. This was probably because there was a higher degree of a phase separation in the blends added with MA-g-PP compared to those containing POE. Moreover, a slight increase in the elongation at break with the content of the POE was possible because the additive itself had no polarity. This could lead to a better interaction between RTR and POE which resulted in a POE-encapsulated structure in a few RTR particles [26]. Nonetheless, even with an improvement in elongation at break of the blends with increasing POE content, the elongation results of the blends were still not quite close to that found without the POE.

Adding the compatibilizers into RTR/PP blends was also resulted in a reduction in Young's modulus. Similar to the elongation at break results, this decreasing trend was more evident in the MA-g-PP filled specimens than those filled with POE. In addition, the Young's modulus of the blends filled with POE was found to increase slightly with higher additives content. This was probably due to an increase in a plastic phase following the rising amount of POE.

For the impact strength, the blends with no compatibilizer exhibited lower impact strength than the blends added with both additives. The function of compatibilizers was to provide a better means to dissipate the impact energy into the whole bulk material. The highest impact strength was measured at 9 phr and 3 phr for the blends containing POE and MA-g-PP, respectively.

4.4 Reclaimed Tire Rubber/Polypropylene Blends with Natural Rubber

4.4.1 Effect of NR on mechanical properties of the blends

In this section, natural rubber (NR) was added into the RTR/PP blends in order to investigate its effect on the blends properties. The blend ratio employed in this part was 30 RTR to 70 PP. The comparison of experimental results are displayed in Figure 4.7.

The tensile strength of the blends containing each of the NR went down as the amount of the rubber was increased. This might be because an introduction of a rubber phase could have resulted in a reduction of a plastic phase in the blends. Conversely, the effect of NR on elongation was more significant than that of blends without NR. This was probably because NR comprised of structures that were similar to those in RTR. The blends with NR content of 30 phr gave much higher impact strength than the others blends by at least 57%.

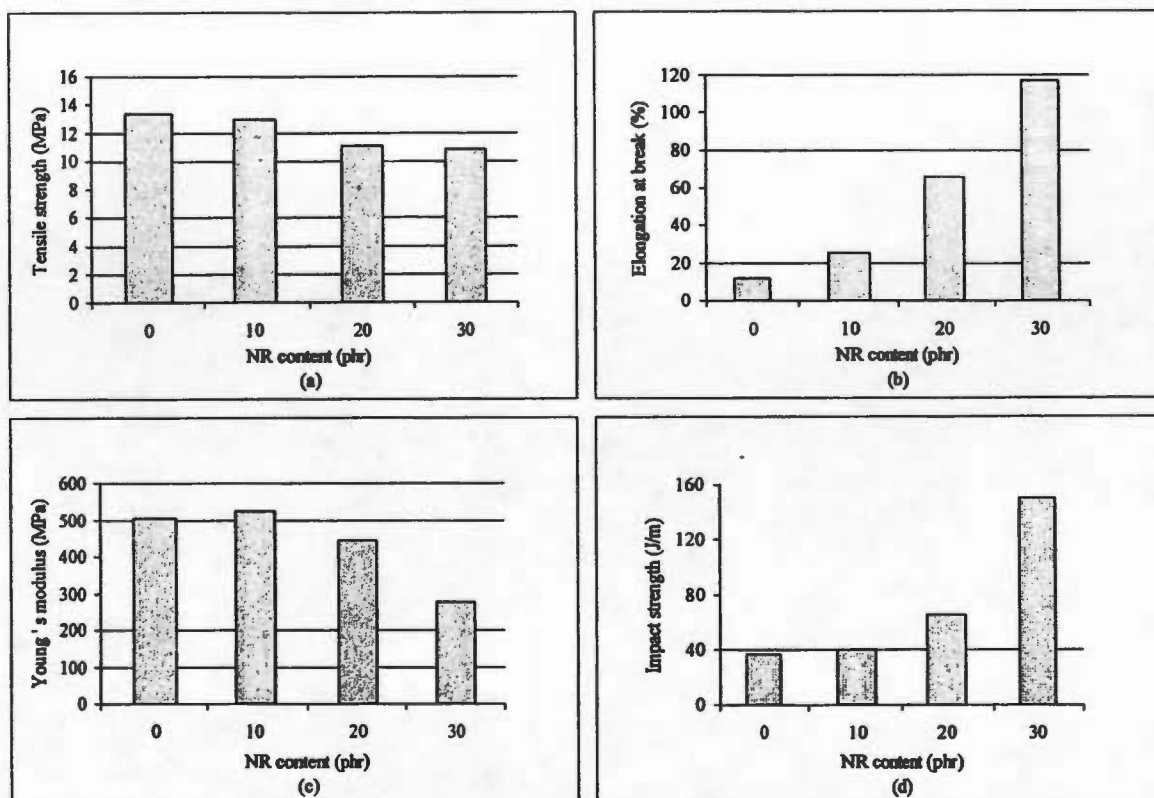


Figure 4.7 Effect of NR on mechanical properties of blends, (a) Tensile strength, (b) Elongation at break, (c) Young's modulus and (d) Impact strength.

4.4.2 Effect of NR on rheological properties of the blends

Rheological properties of blends with various virgin rubber amounts were shown in Figure 4.8. The complex viscosity of RTR/PP/NR blends are shown in Figure 4.8a. The effect of RTR amount was to increase the complex viscosity. This was probably due to the fact that with increasing the degree of cross-linking, the viscosity increased.

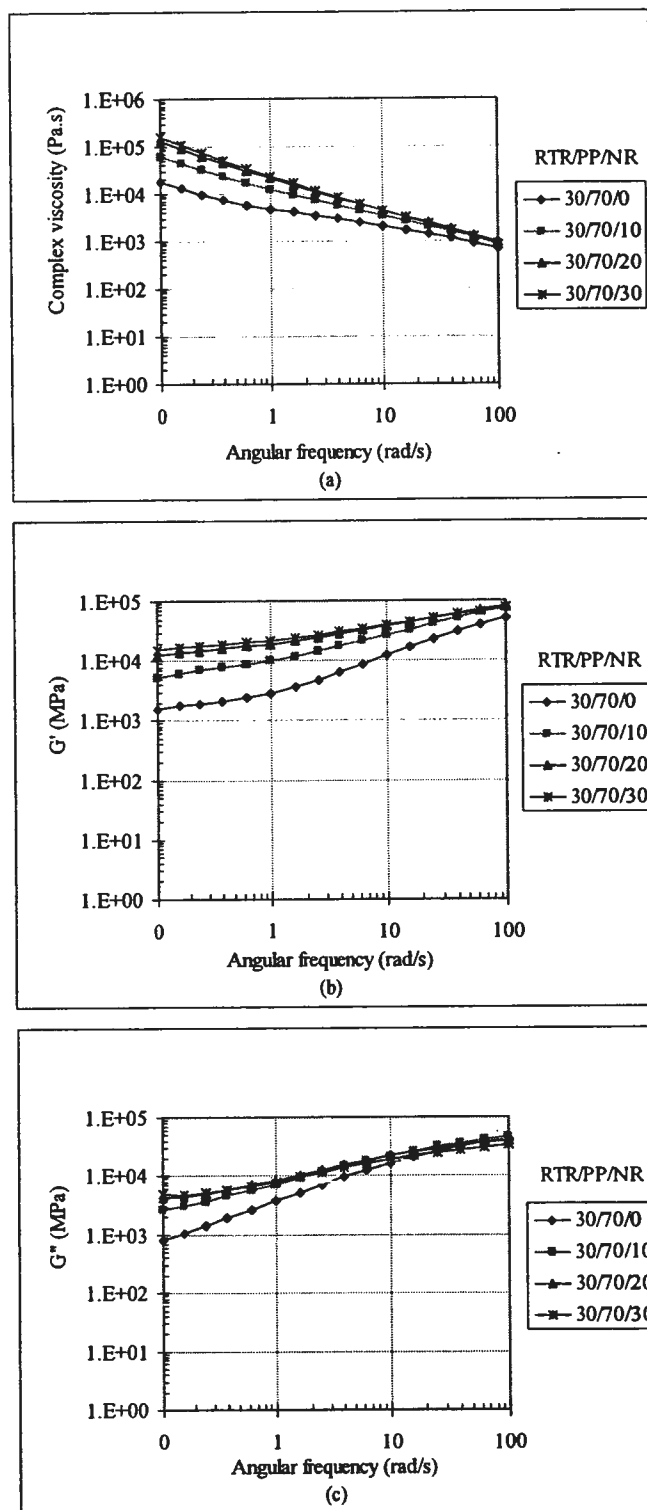


Figure 4.8 Effect of virgin rubber content on properties of blends, (a) Complex viscosity, (b) Storage modulus, and (c) Loss modulus.

The addition of virgin rubber in the blends increased complex viscosity, storage modulus and loss modulus. The increase in viscosity is due to the entanglement of the molecular chains of both RTR and PP caused particularly by NR. Because of the enough long and flexible molecular chains, NR chains can entangle among themselves and also with the RTR chains. This entanglement impedes severely the flow of the melt at low shear rates, and consequently, the viscosity becomes higher. The chains of NR in the RTR/PP blends are easy to adhere with NR. At high shear rate, all the results of blends ratio are not different but the loss modulus of the blends without NR is lower than them. NR is increasing due to the entanglement of the rubber molecular chain. An additional NR did not significantly the loss modulus (G'') of the blends.

4.4.3 Phase Morphology of RTR/PP and RTR/PP/NR

In dynamic vulcanization, the RTR phase changes from a viscous fluid to an elastic solid. The elastomer becomes rigid as a result; this phase breaks up into micron-sized elastomer particles. Because in the most RTR/PP blends the elastomer phase was the major component, this phase was continuous in the initial state. Due to the continuing curing and mixing, phase inversion takes place and the elastomer becomes dispersed.

Coran et al. [11] found that it was important that the elastomer phase was well mixed before the onset of the vulcanization reaction and that the mixing should continue until the dynamic vulcanization was completed. If the cured elastomer phase was continuous, the resulting compound could not be processed [12]. To observe the effect of virgin natural rubber on blend morphology RTR/PP blend at ratio of 30/70 and RTR/PP/NR blend at ratio of 30/70/30 were compound. The samples were fractured in liquid nitrogen, stained with osmium tetroxide (OsO_4) and coated with carbon for the study. Their scanning electron micrographs are shown in Figure 4.9.

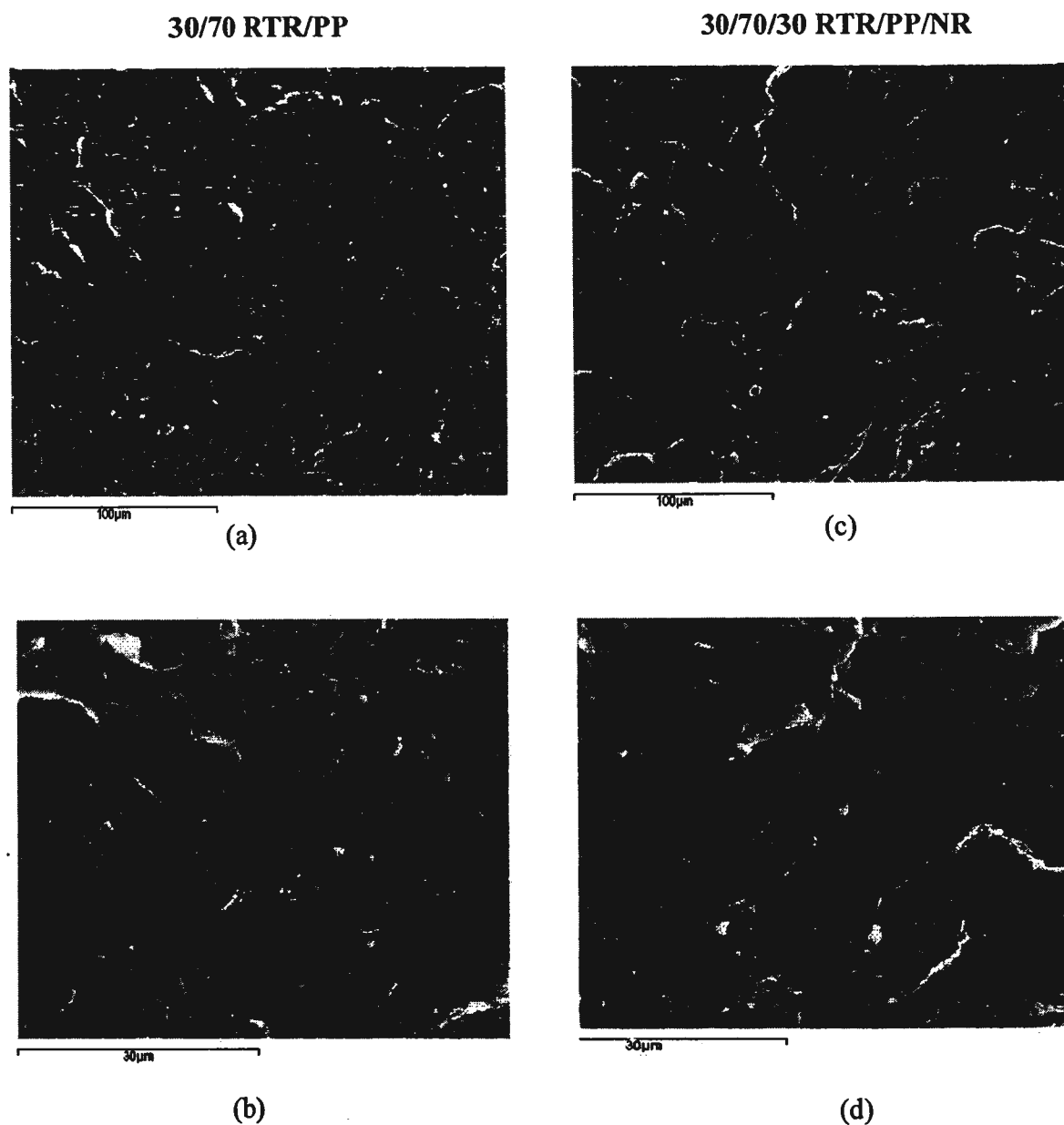


Figure 4.9 SEM micrographs of 30/70 RTR/PP blends a) X 500, b) X 2000 and 30/70/30 RTR/PP/NR blends c) X 500, d) X 2000.

Morphological analysis suggested that the RTR phase was well dispersed in the PP phase. The formation of RTR particles was reduced significantly and distribution of vulcanized particles was more uniform in the RTR/PP/NR blends than that in RTR/PP blends. The average size of elastomer particles in RTR/PP blend was about 1.8 μm and of elastomer particle in RTR/PP/NR blend was about 1.34 μm . Therefore, it was remarkable that the properties of these materials.

The morphology plays a key role in the mechanical properties and it has been the subject of many studies. The results of add NR in good dispersion and distribution of RTR into PP matrix which could be higher improved in mechanical and elastic properties.

4.4 Comparison of Natural Rubber and Ethylene Propylene Diene Monomer on Mechanical Properties of Reclaimed Tire Rubber/Polypropylene/ Blends

In this section, natural rubber (NR) and ethylene propylene diene rubber (EPDM) were separately added into the RTR/PP blends in order to investigate their effect on properties of the blends. The comparisons of experimental results are displayed in Figure 4.10.

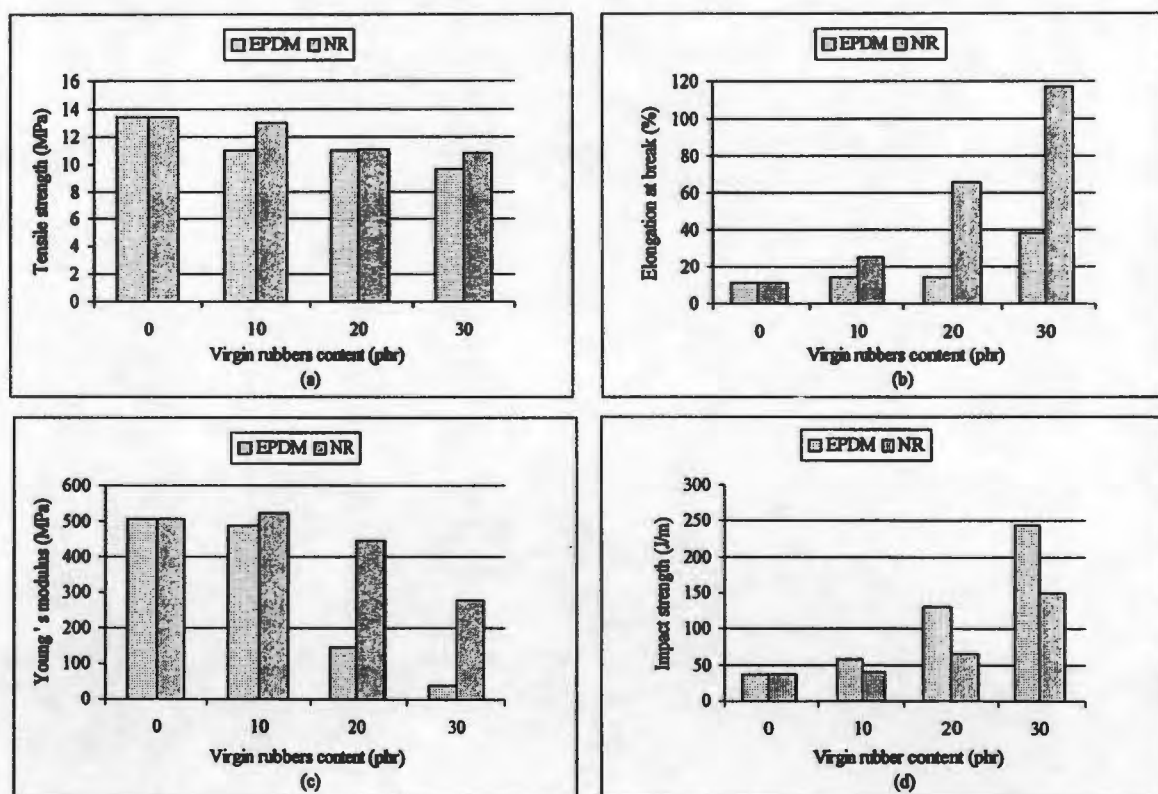


Figure 4.10 Effect of virgin rubber on mechanical properties of blends,

- (a) Tensile strength, (b) Elongation at break, (c) Young's modulus and
(d) Impact strength.

It can be seen from Figure 4.10 that the effect of NR on elongation at break was more significant than that of EPDM. This was probably because, in contrast to EPDM, NR comprised of structures that were more similar to those in RTR.

Even though a similar trend of increment, via an addition of rubber, was generally observed for the impact strength results, EPDM was found to be more influential than NR. The results of impact strength additional EPDM were higher than NR because they transferred energy of break to EPDM more than NR. Mechanisms of energy absorb first sent to plastic and after that energy transfers to rubber. This results show that the interaction between PP with EPDM was more than that of PP with NR. The relationship between the morphology and impact strength for the blends of PP with two kinds of RTR had different EPDM content. The blends had high EPDM content resulted in thickening of interfacial region between PP domain and EPDM phase, because this PP had good energy transfer to EPDM. This thickening of the interfacial region caused the enhancement of impact strength.

4.6 Reprocessing of the Blends

An important advantage of RTR/PP blends over the conventional thermosetting rubbers was that blends can be reprocessed by all common equipment for plastics processing, such as extruders, injection molders, and blow molders without significantly changing the physical properties of blends.

4.6.1 Reclaimed tire rubber/polypropylene/natural rubber blends

To illustrate the reprocessing ability of the 30/70/30 RTR/PP/NR blends, the blends were reprocessed four times by compression molding of the ground blending material. The mechanical properties were measured after each cycle, as shown in Figure 4.11.

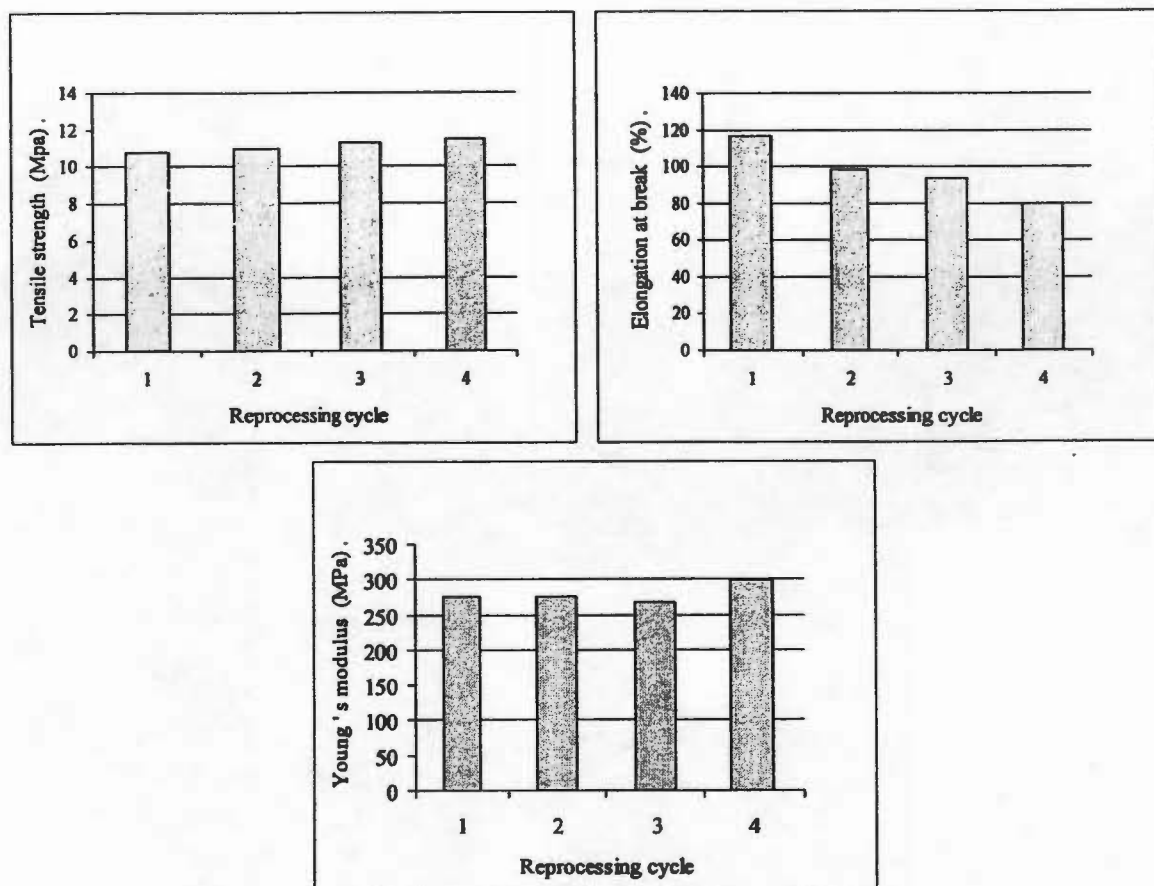


Figure 4.11 Mechanical properties of reprocessed RTR/PP/NR blends, (a) Tensile strength, (b) Elongation at break and (c) Young's modulus.

The tensile strength of blends was decreased slightly as the number of reprocessing cycles. The elongation at break was consecutively decreased as reprocessing cycles at 45 %. The Young's modulus of blends was unchanged as amount of reprocessing cycles. This was clearly the role of thermoplastics which caused reprocessing property.

4.6.2 Reclaimed tire rubber/polypropylene blends

To investigate this reprocessing ability of the 30/70 RTR/PP blends, the blends reprocessed four times by compression molding with the product being reground after each molding cycle. The mechanical properties were measured after each cycle, as shown in Figure 4.12.

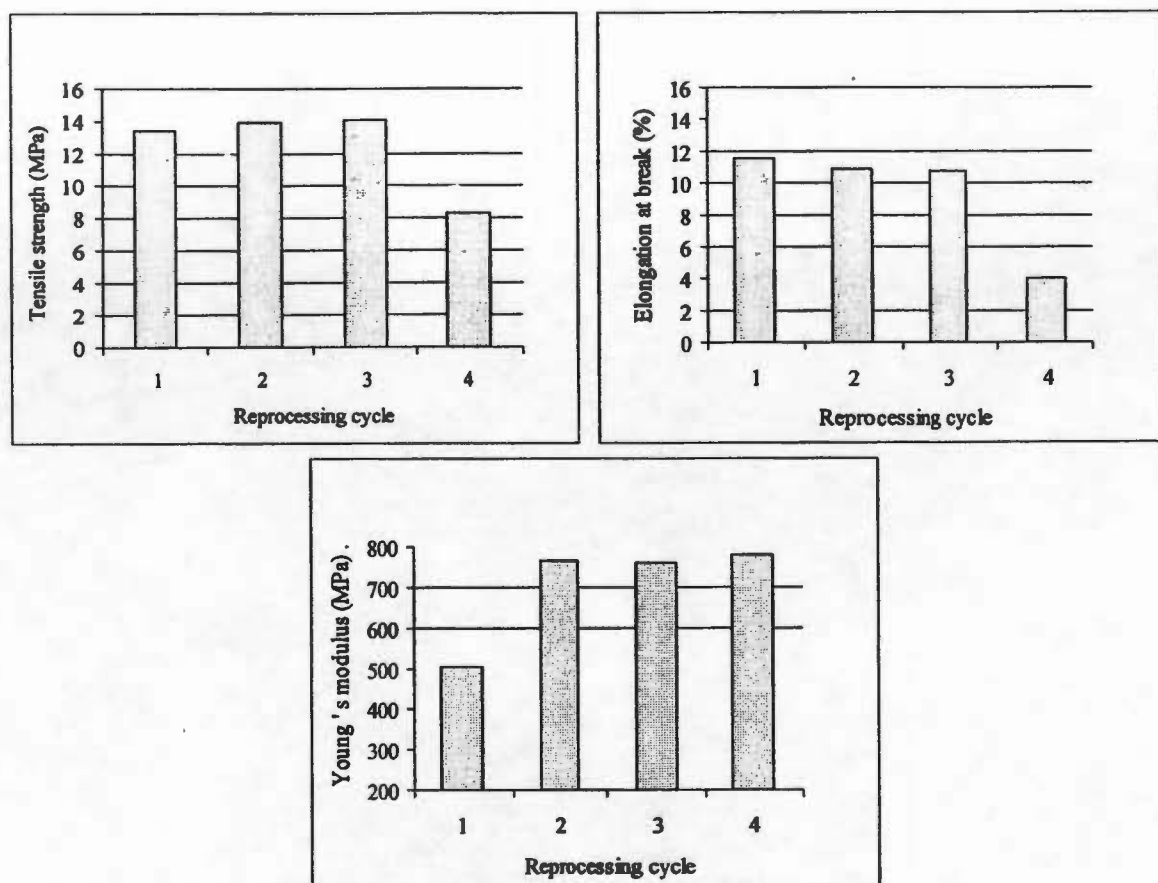


Figure 4.12 Mechanical properties of reprocessed RTR/PP blends, (a) Tensile strength, (b) Elongation at break and (c) Young's modulus.

It was found that the mechanical properties were significantly decreased after four cycles. The effect of tensile strength and elongation at break were decrease at least 35 % and 64 % consecutively. Young's modulus of the blends were increased after reprocessing for two cycles and was unchanged from 2-4 cycles. This indicates that the blends have good reprocessing ability up until 3 cycles.