

# THE EFFECT OF SIZE AND CRUMB RUBBER COMPOSITION AS A FILLER WITH COMPATIBILIZER PP-g-MA IN POLYPROPYLENE BLENDS AND SIR-20 COMPOUND ON MECHANICAL AND THERMAL PROPERTIES

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## Abstract

Having been researched the development of thermoplastic elastomer material of polypropylene and natural rubber SIR-20 compound with Crumb Rubber as the filler. Reinforced polypropylene with size 60 mesh with 1 mm, and the composition of the Crumb rubber (30, 40, and 50) wt%. Observed mechanical properties are tensile strength, fracture elongation, Young's modulus, tear strength and impact strength. Thermal properties are analyzed by DSC and DTA/TGA. It is acquired that for the size of 60 mesh crumb rubber tensile strength, fracture elongation, Young's modulus, tear strength and impact strength are bigger than 1mm size. The addition of 60 mesh crumb rubber increases but it decreases by adding of 50 weight%. While for crumb rubber 1 mm tensile strength, fracture elongation, tear strength and impact strength decreases. Based on analysis of DSC that the addition of crumb rubber does not make a difference boiling point significantly between samples containing crumb rubber and polypropylene Analysis TGA/DTA to an increase in enthalpy and decomposition temperature with the addition of crumb rubber used and thermal stability.

## Abstrak

**Pengaruh Ukuran dan Komposisi Serbuk Ban Bekas sebagai Filler dengan Kompatibiliser PP-g-MA pada Campuran Polipropilena dan Kompon SIR-20 terhadap Sifat Mekanik dan Termal.** Telah diteliti pengembangan bahan termoplastik elastomer dari polipropilena dan kompon karet alam SIR-20 dengan serbuk ban bekas sebagai bahan pengisi. Polipropilena yang diperkuat dengan serbuk ban bekas dengan ukuran 60 mesh 1 mm, dan komposisi serbuk ban bekas (30, 40, dan 50) %berat. Sifat mekanik yang diamati adalah kekuatan tarik, perpanjangan putus, Modulus Young, kekuatan sobek, dan kekuatan impact. Sifat termal dianalisis dengan DSC dan DTA/TGA. Dari hasil penelitian diperoleh bahwa untuk ukuran serbuk ban bekas 60 mesh kekuatan tarik, perpanjangan putus, modulus Young, kekuatan sobek, dan kekuatan impact lebih besar dibanding ukuran 1 mm. Penambahan serbuk ban bekas 60 mesh mengalami peningkatan namun mengalami penurunan pada penambahan 50 % berat. Sedangkan untuk ukuran serbuk ban bekas 1 mm kekuatan tarik, perpanjangan putus, kekuatan sobek, dan kekuatan impact mengalami penurunan. Dari analisis DSC diperoleh bahwa dengan penambahan serbuk ban bekas tidak menghasilkan perbedaan titik didih yang signifikan antara sampel yang mengandung serbuk ban bekas dan polipropilena. analisis TGA/DTA adanya peningkatan enthalpy dan suhu dekomposisi dengan adanya penambahan serbuk ban bekas dan terjadi stabilitas termal.

*Keywords: compound SIR-20, crumb rubber, mechanical, polypropylene, PP-g-MA, thermal properties*

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## 1. Introduction

Solid waste is an unwanted material presence, such as old tires. Vehicle tires will just end up in landfills and objects made of rubber causes serious environmental problems. More than one billion of vehicle tires in the world are discarded every year. People prefer to throw it away because the tires have a material that is not easily biodegradable.

When reviewed in chemical, waste consists of organic chemical compounds and inorganic compounds with a certain concentration and quantity, so we need the handling of waste tires. Destruction effort by burning them in the usual evidently produces harmful effects of pollution for it affects to human health [1]. There are two main ways to treat the used tires ie: recycle and reuse rubber tires and rubber reclaiming raw materials [2].

Used tires are thermoset materials in order to recycle materials such as thermoset needed special techniques to process used tires into crumb rubber and then it is devulcanized or partly devulcanisation by thermo-mechanical methods [3] and combine with thermoplastic materials to acquire elastomeric materials thermoplastic (TPE) [4]. Besides the quality of the mixture depends on the degree of phase separation and particle size of the dispersed phase. Incompatibility of the two materials result in low mechanical properties. Compatibilisation technique is often used to increase the quality of the mix and improve the mechanical properties.

Some types of plastic that are widely used for making TPE include: Polyethylene (PE), polyvinylchloride (PVC) and polypropylene (PP) [5]. Polypropylene is the best option for mixing with thermoset materials as low softening temperature is at 150 °C and low glass transition temperature so that the two materials can easily unite. The properties of polypropylene is easily processed, melting point is relatively high 180 °C, low density and include the lightest among polymer materials, corrosion resistance, thermal, and electrical conductor, cost process is relatively inexpensive, easily available in the market, environmentally friendly as well as able to be recycled [4].

Crumb rubber is blended with polypropylene material which is expected to improve the composite mechanical properties, to reduce boarding materials and especially to utilize scrap tires and waste materials reduces environmental damage. The addition of filler materials such as crumb rubber into thermoplastic material polypropylene has high benefits because the power and flexibility of plastics can be improved. The main problem in the development of polymer blends is to assess the value of mixing miscibility. Polymer blend can not be fused immiscible due to the weakness of the tensile strength of the phase boundary, which can lead to phase separation. [5] To overcome the problem must be added compatible materials compatibilizer agent such as PP-g-MA [6].

The main objective of this study is to determine the effect of the addition of filler crumb rubber size and composition and mechanical properties of materials and compatibilizer the thermal properties of materials TPE.

## 2. Methods

**Materials.** The materials used in this study include, natural SIR-20 rubber, Crumb Rubber 60 mesh, and 1 mm from PT Santos Ruber Jakarta, polypropylene copolymer was obtained from Production Singapore. This polymer has melting point of 176 °C, and density of 0.896 g/cm<sup>3</sup>. Polypropylene grafted maleic anhydride (PP -g- MA) was obtained from Japan. Carbon Black N

330 was obtained from Cilegon Indonesia. Cabot Red Seal Zinc oxide was obtained from Aldrich. Sulphur and N-Isopropyl-N-Phenyl-p-phenylenediamine (IPPD) were obtained from Qingdao China. Tetra methy thiurea disulfarat (TMTD), marcapto benzhoathizole disulfide (MBTS), stearic acid were purchased from Sumi Asih Indonesia, and dicumyl peroksida (DCP) Trigonox from Japan.

**Instrumentation.** Two roll mixing mill of Internal Mixer Laboplastomil Model 30 R150, Hydraulic hot press, cold press of 37 ton from Genno Japan, Universal Testing Mechanic model Laryee Universal Testing Machine Wdw-10, DSC Mettler Toledo type 821, Setaram STA TAG 24 (DTA/TGA).

**Preparation of natural rubber compound.** Natural rubber compound was prepared by mixing natural rubber (SIR-20) mixed with blended using Two Roll Mixing Mill with the formula as shown in Table 1.

**Preparation of the sample** was commenced by grinding natural rubber for five minutes, to transform it into crumb, followed by addition of wax and carbon black. While the sample was continuously grinded for another five minutes, zinc oxide, stearic acid, IPPD, and sulphur were added into the mixture, followed by introduction of TMTD after the process last for 13 minutes and MBTS after 18 minutes. The process was completed after the whole mixture was grinded for five minutes. The compound obtained from this treatment was then used to prepare NR/PP blend loaded Crumb Rubber 60 mesh and 1 mm as filler.

**Preparation of Compound NR/PP blend.** To prepare coumpound NR/PP blend, the natural rubber compound previously prepared was mixed with PP, PP-g-MA, according to the composition as presented in Table 2. The mixture was blended using Laboplastomil Model 30 R150 internal mixer with a volume of 60 cc. The blending was carried out at temperature of 180 °C with rotor speed of 60 rpm for 10 minutes.

**Table 1. The Formula Used for Preparation of Natural Rubber Compound**

Ingredients	Quantity (phr)	Function
SIR- 20	100	Binder
Carbon BlackN 330	30	filler
Zinc oxide	5	Activator
Stearic acid	2	Activator
Sulfur	3	Curing agent
IPPD	2	Antioxidant
TMTD	1.5	Accelerator
MBTS	2.5	Accelerator

**Table 2. Composition of the Coumpound NR/PP Blends Size 60 mesh and 1 mm**

Sample	S <sub>0</sub>	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>
DCP	0	2	2	2
Crumb Rubber	0	30	40	50
PP-g-MA	5	5	5	5
PP	30	23	23	23
SIR-20 Compound	65	40	30	20

Mechanical properties measurement. Tensile strength measurement was performed according to JIS K 6781 standard using a Laryee Universal Testing Machine Wdw-10, at crosshead speed of 50 mm min<sup>-1</sup>. Young's modulus (E), ultimate tensile strength ( $\sigma_{max}$ ), and fracture elongation ( $\epsilon_f$ ) were determined from the stress-strain curves.

Tear test. Sample to be tested is cut tear strength according to standard JIS K 6781 Type B. Specimen then placed on test equipment Co. Ltd Orientec Universal Testing Machine, Model UCT-5T at room temperature with a tensile speed of 20 mm/min -1.2% scale load cell of 100 kgf, test torn off.

Impact test. In impact test, impractor used in the form of a swinging pendulum from a height (h) and mass (m). The test sample was made to ASTM D-256, testing equipment used by Izod Impact Tester Walpert Type CPSA with pendulum arm angle formed 160°, weight 4 Kg.

Thermal Analysis. Thermal analysis was performed with a Mettler Toledo DSC 821 type, following the method described in ASTM D 3418-03, by weighing about 10-12 mg sample into 40 mL crucible. The analysis was carried out using nitrogen gas at a flow rate of 50 ml/min, with temperature program of heating-cooling-heating with the temperatures of -30 °C to 160 °C, -75 °C to 270 °C. The temperature ramp of -15 °C/min was applied for cooling process, and 15 °C/min for heating process.

Simultaneous thermal analysis (STA) was performed on TGA-DTA Setaram TAG 24, by scanning the sample over the temperature range of 50-600 °C using nitrogen gas with the flow rate of 50 mL/min and a heating rate of 20 °C/min.

### 3. Results and Discussion

Tensile Strength. One of the main criteria for thermoplastic elastomer material is that the tensile strength of more than 100%, so it should be investigated mechanical properties of TPE materials [7]. The effect of the filler with a size of 60 mesh and 1 mm on the

tensile strength of the material TPE sample shown in Figure 1. With the addition of crumb rubber 60 mesh sizes and (30, 40, 50) wt% can be found to increase the tensile strength of the sample, it was due to the addition of crumb rubber devulcanisation process will occur, in which the cross linking that occurs in crumb rubber due to sulfur will be interrupted during the process of blending at high temperatures. In order to obtain good adhesion between the polypropylene and crumb rubber that generate tensile strength increased by 197% compared to the sample without filler. From the images can be obtained that the smaller size of the fillers the greater tensile strength. In accordance with [8] if the particles of rubber are small enough and have well vulcanisation, the nature of the mixture is usually increased.

Generally, the tensile strength of PP will decrease with the addition of natural rubber, as immiscible and the mismatch between the polymer, it can be improved by the addition of a suitable compatibilizer so that adhesion between the two materials can be improved [9]. Addition of PP-g-MA increases the interaction between natural rubber and PP, improve adhesion and spread the filler system that is hydrophilic and hydrophobic matrix [10] and can increase and decrease the size of the phase homogeneity of natural rubber which are distributed so that the tensile strength increases [11]. The increase is also due to the tensile strength of adhesion derived from PP-g-MA which can react with the hydroxyl group (OH) on thermoset materials [12].

Fracture Elongation. Fracture Elongation properties are properties where the composite is pulled off. In Figure 2, fracture elongation properties are influenced by the size and composition of the filler. From the figure shows that for the size of 60 mesh filler increased elongation with the addition of fillers due to the good interaction between filler and matrix to filler size is quite small and there is good adhesion to the matrix, but for the size of fillers 1 mm, with increase in pollen composition tires will decrease elongation at break of the samples. The addition of copolymers can be used as a grafting material compatibilizer the polymer blend that can improve the mechanical properties of materials [13].

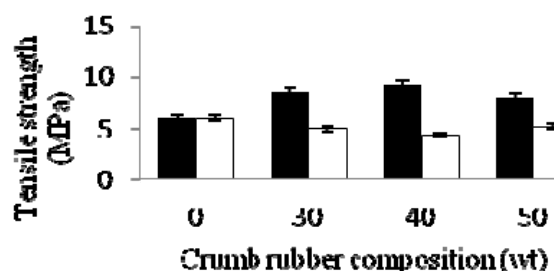
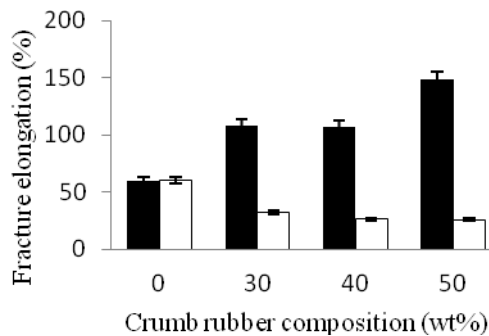
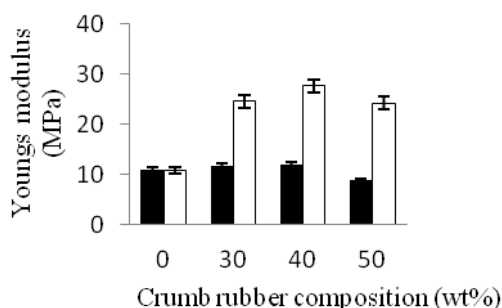


Figure 1. Tensile Strength of the Samples Filler Crumb Rubber Size ■ 60 mesh and □ 1 mm



**Figure 2. Fracture Elongation of the Samples Reinforced with Crumb Rubber Size ■ 60 mesh and □ 1 mm**



**Figure 3. Young's Modulus of the Samples Reinforced with Crumb Rubber ■ Size 60 mesh and □ 1 mm**

Young's modulus. Young's modulus is a measure of a material, which means resistance to deformation elastic material. The greater the modulus is the smaller elastic strain generated due to the provision of voltage. In Figure 3, the effect of adding the amount of crumb rubber to the properties of the composite Young's modulus of PP/SIR-20 compound/crumb rubber. From the figure obtained by the Young's modulus maximum crumb rubber composition 40 wt% for the size of 60 mesh crumb rubber, this suggests that the resistance properties of the material is very good at filling material composition of 40 wt% which is in line with the results of tensile strength and tear strength, while results are in contrast to the fracture elongation. With the addition crumb rubber of more 50 wt% reduced young modulus corresponding to the tensile strength and the tear strength of the crumb rubber size 1 mm, Young modulus maximum obtained on the composition of 40 wt%, it is the opposite the tensile strength, fracture elongation and tear strength which obtained a minimum.

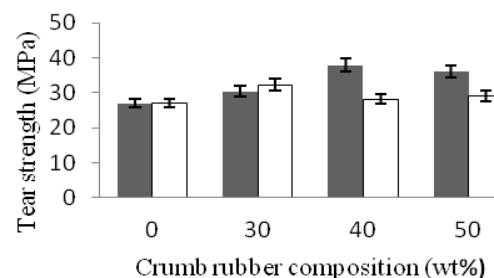
Tear Strength. Tear strength properties of the sample depends on dispersity and particle size of the dispersed phase and the vulcanization mixture [14] as shown in Figure 4. Maximum tear strength obtained on the composition of crumb rubber 40 wt % to 60 mesh size and to the size of 1 mm tear strength obtained on the

composition of 30 wt%. Compatibilisation between crumb rubber materials, compatibilizer, and non-polar materials can improve the morphology of the material as well as the phase of a homogeneous dispersion between natural rubber and the matrix can improve the mechanical the material [15] properties. Polypropylene does not belong to the polar groups in order to enhance the dispersion between the matrix and thermoset materials needed maleic anhydride (MA) were grafted with polypropylene (PP-g-MA) to increase the polarity of the polymer [16].

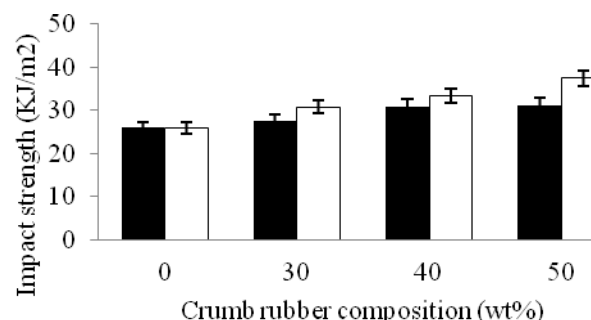
Impact Strength. The impact strength properties are based on resistance to impact imposed suddenly at high speed. In general, the strength properties in thermoplastic materials will increase with the addition of a rubber material, the rubber phase will strengthen the matrix. In Figure 5, showed that the addition of crumb rubber the size of 60 mesh or 1 mm will increase the impact strength of the sample, it is due to the blending thermoplastic material with rubber material will improve the impact strength, because it will strengthen

**Table 3. Melting Point of Each Composition**

Composition (wt%)	Melting point (°C)
30	164.20
40	159.98
50	161.35



**Figure 4. Tear Test of the Samples Reinforced with Crumb Rubber Size ■ 60 mesh and □ 1 mm**



**Figure 5. Impact Strength of the Samples Reinforced with Crumb Rubber Size ■ 60 mesh and □ 1 mm**

the rubber phase matrix [10]. Addition compatibilizer PP-g-MA can improve the mechanical properties of natural rubber and polypropylene blending with natural rubber modified phase OH group [14].

**Thermal properties.** In this study, thermal characteristics of the samples were evaluated by analyzing the samples with differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) and DSC. In Figure 6, obtained the melting point of each composition as shown in Table 3. From the figure shows PP crystals

begin to melt from a temperature of 140 °C to 180 °C. According to showed a transition endothermic chemical reaction in the presence of DCP, compatibilizer material and filler material do not interfere with the integrity of the PP matrix structures, although there is PP degradation results from the decomposition of DCP at high temperature and cutting on the melting process, identical melt temperature that gives the impression that it significantly PP-g-MA is limited by the cross linking reaction of the PP matrix and crumb rubber [17].

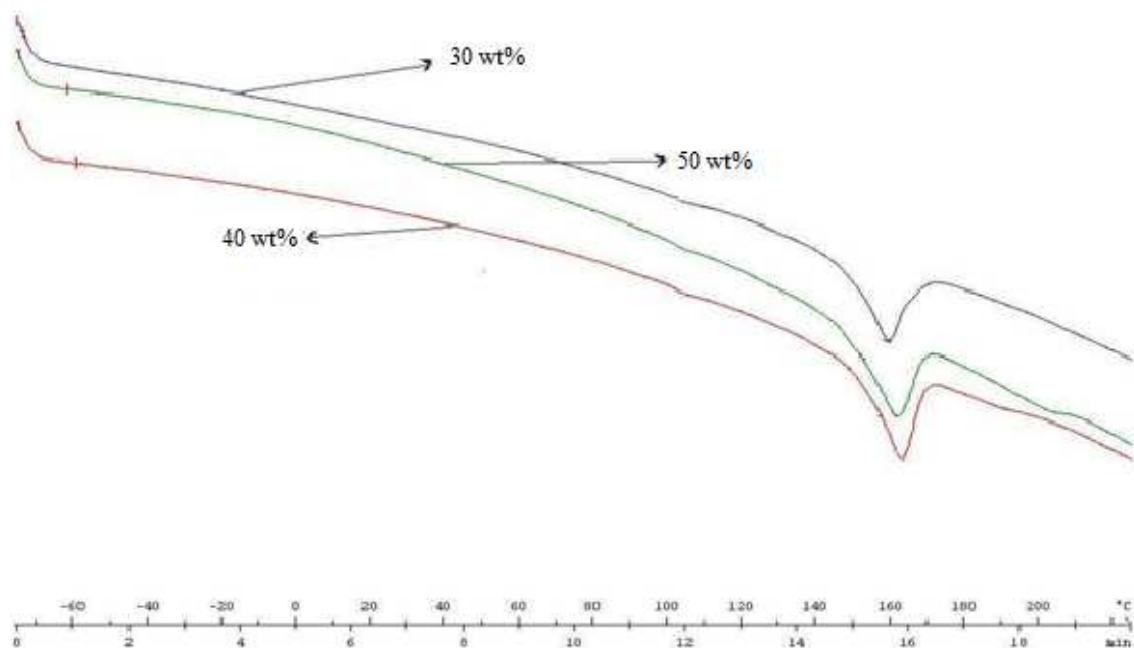


Figure 6. DSC Thermogram of the Samples Filled with Crumb Rubber (30, 40, and 50) wt% Size 60 mesh

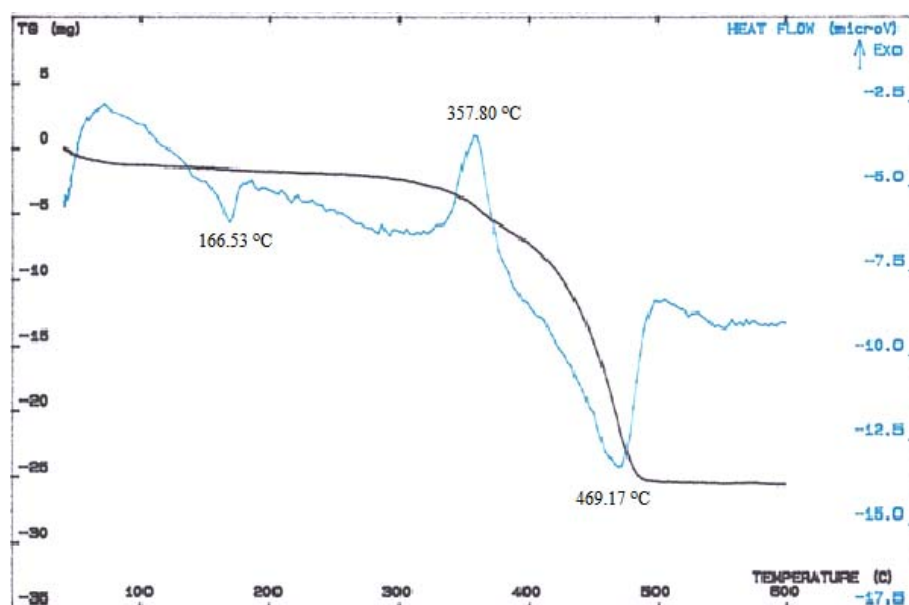


Figure 7. TGA/DTA Thermograms of the Samples Filled with Crumb Rubber 30 wt% Size 60 mesh

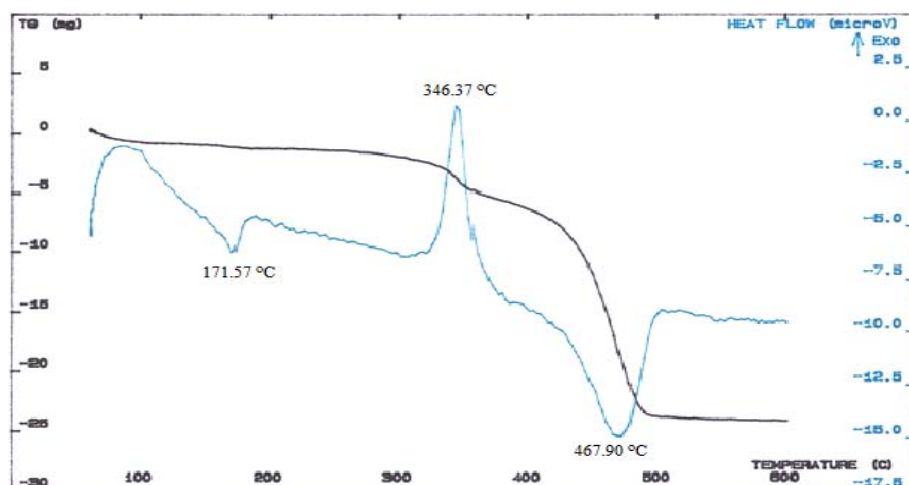


Figure 8. TGA/DTA Thermograms of the Samples Filled with Crumb Rubber 40 wt% Size 60 mesh

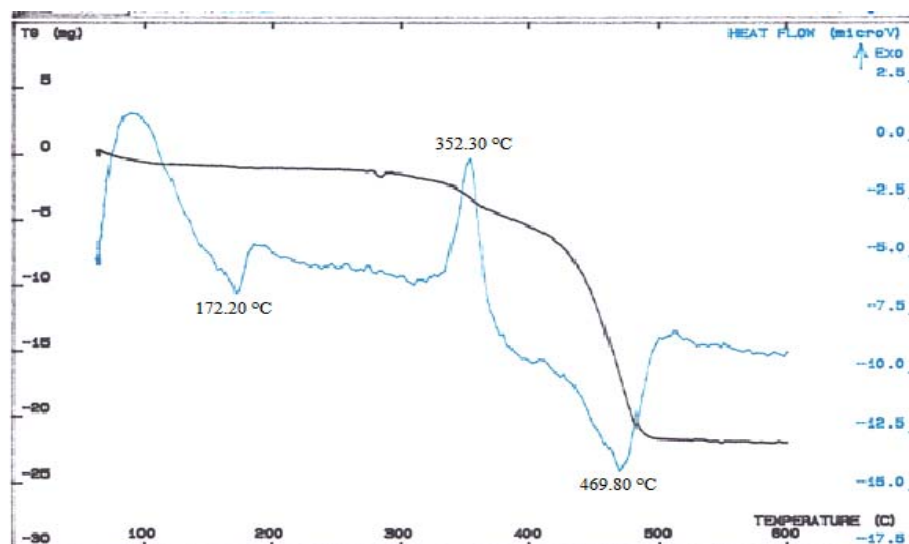


Figure 9. TGA/DTA Thermograms of the Samples Filled with Crumb Rubber 50 wt% Size 60 mesh

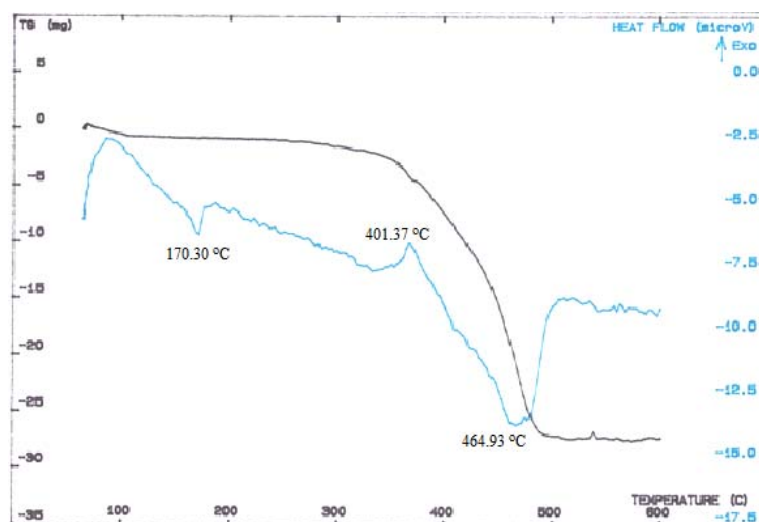


Figure 10. TGA/DTA Thermograms of the Samples Filled with Crumb Rubber 30 wt% Size 1 mm

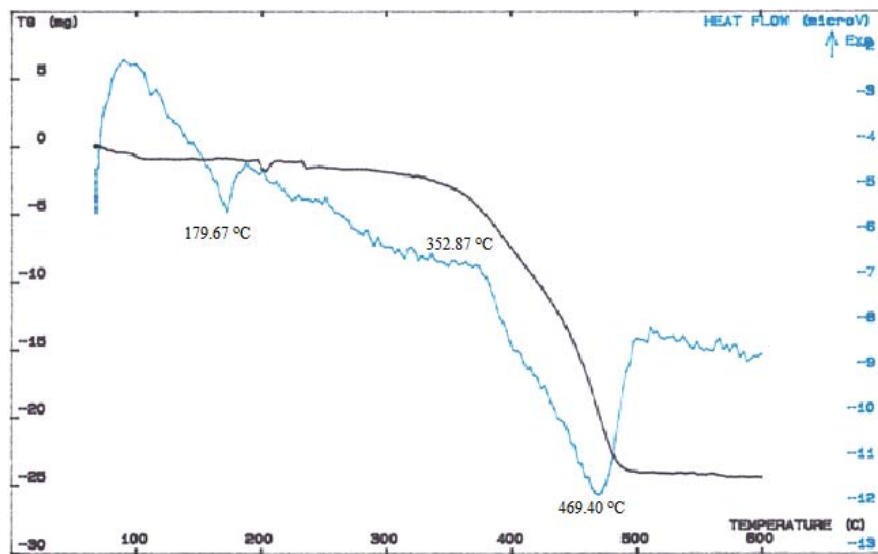


Figure 11. TGA/DTA Thermograms of the Samples Filled with Crumb Rubber 40 wt% Size 1 mm

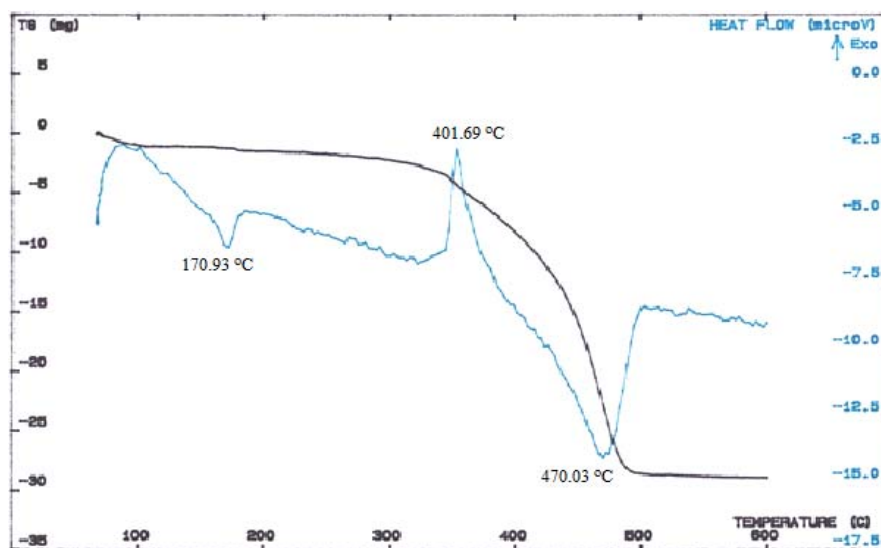


Figure 12. TGA/DTA Thermograms of the Samples Filled with Crumb Rubber 50 wt% Size 1 mm

Table 4. Print Out Thermograms TGA/DTA of PP /PP-g-MA/ SIR-20 Coumpound/Crumb Rubber Size 60 mesh Blends

Sample	30 wt%	40 wt%	50 wt%
Melting Point (°C)	155.23-166.53	141.60-171.57	134.93-172.20
MassVariation (mg)	-0.23	-0.40	-0.25
Enthalpy (mJ/mg)	-1.077	-7.400	-16.407
Cross linking (°C)	337.43-357.80	329.47-346.37	336.87-352.30
MassVariation (mg)	-3.94	-3.52	-2.76
Enthalpy (mJ/mg)	3.363	18.128	8.267
Decomposition (°C)	433.03-469.17	437.77-467.90	429.83-469.80
MassVariation (mg)	-17.41	-17.19	-15.76
Enthalpy (mJ/mg)	-12.464	-14.909	-32.204

**Table 5. Print Out Thermograms TGA/DTA of PP/PP-g-MA/SIR-20 Coumpound/Crumb rubber size 1 mm Blends**

Sample	30 wt%	40 wt%	50 wt%
Melting Point (°C)	159.00-170.30	152.73-179.67	151.97-170.93
MassVariation (mg)	-0.04	-0.37	-0.16
Enthalpy (mJ/mg)	-3.043	-3.684	-5.008
Cross Linking (°C)	354.80-401.37	345.80-352.87	393.70-401.69
MassVariation (mg)	-5.42	-4.48	-5.21
Enthalpy (mJ/mg)	-0.329	6.168	-4.697
Decomposition (°C)	433.07-464.93	442.70-469.40	425.47-470.03
MassVariation (mg)	-19.51	-18.09	-16.23
Enthalpy (mJ/mg)	-39.622	-19.711	-22.760

With the addition of compatibilizer will increase the Temperature melting ( $T_m$ ), and enthalpy of the PP melting. This indicates that the macro chain compatibilization limit movement of molecules due to the interaction between the phases that produce high enough Temperature melting [18]. In the amorphous portion of PP, where the glass transition temperature ( $T_g$ ) can not be detected by DSC, because DSC is only sensitive to the scope of the molecules motion larger than the micro-Brownian motion which causes the loss of dynamic peaks [19].

The melting temperature is an important parameter for thermoplastics because it represents the minimum temperature required for processing of polymers. Melting behavior highly depends on the chemical structure of the material along with the size and regularity cristalitasion found in the crystalline phase. TGA/DTA thermograms of Figure 7-9, and Table 4 to size 60 mesh, show the increase of melting point by addition of fillers as well as the changes of entalphy and processes, while the changes of decomposition temperature don't change significantly, but the mass variation decreased with increasing composition.

The improvement of thermal stability of mixed PP/PP-g-MA/SIR-20 compound/crumb rubber is caused by the presence of strong interfacial adhesion among the matrix polypropylene filler that comes from the addition of malead anhydride functional groups, [20] where the group functionalization maleated anhydride in PP-g-MA increases the bond between the face fillers and polypropylene matrix. Polymers are considered heat stable or heat-resistant, if the polymer is not biodegradable under 400 °C temperature and it must maintain its useful at temperatures close to the decomposition temperature.

TGA/DTA thermogram of Figure 10-12 and Table 5 for the size of 1 mm on the composition of 30 wt% to 50

wt% does not significantly change the melting point but an increase in the mass variations well as enthalphy.

For cross linking the temperature decreases to 40 wt% composition as well as for variations in mass. Temperature increases in the process of decomposition but the enthalphy process decreases. In general, the melting point for the size of 1 mm is higher than 60 mesh as well as on the cross linking while the decomposition temperature differences are not significant, it is caused by increasing adhesion between the front crumb rubber between the polypropylene matrix and SIR-20 compound [21]. The rise degree of temperature can be caused by the interaction of the hydroxyl group of molecules between the filler and the carbonyl group from materials compatibilizer resulting hydrogen bonds can decrease the polymer mobility.

#### 4. Conclusions

The result showed that for the size of 60 mesh crumb rubber tensile strength, fracture elongation, Young modulus, tear strength and impact strength greater than 1 mm. The addition of 60 mesh crumb rubber have increased but decreased on the addition of 50 wt%. While for size 1 mm tensile strength, fracture elongation, tear strength and impact strength decreased. Obtained from DSC analysis that the addition of crumb rubber used do not produce significant difference in melting point between the samples containing crumb rubber used and polypropylene. Analysis TGA/DTA result enthalpy and decomposition temperature in the increase with the addition of crumb rubber and occurs thermal stability.

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