

## CHAPTER IV

### RESULTS AND DISCUSSIONS

#### 4.1 HIPS Scraps mix with Virgin HIPS

Typically, the scraps of Polystyrene from fabricators have been treated differently. Some is sold as scrap to the PS supplier for producing low grade product. The purpose of this section is to analyze the properties of mixtures of virgin HIPS and HIPS scrap. Various ratio of the virgin HIPS to HIPS scrap mixtures were prepared. As described in Section 3.2.1, 20% to 80% of virgin HIPS was added to HIPS scrap and tested according to Section 3.3 to 3.4.

##### 4.1.1 Mechanical Properties

###### 4.1.1.1 Tensile Properties

Figures 4.1 and 4.2 show the tensile strength at yield, tensile strength at rupture and the elongation of HIPS scrap mixed with virgin HIPS.

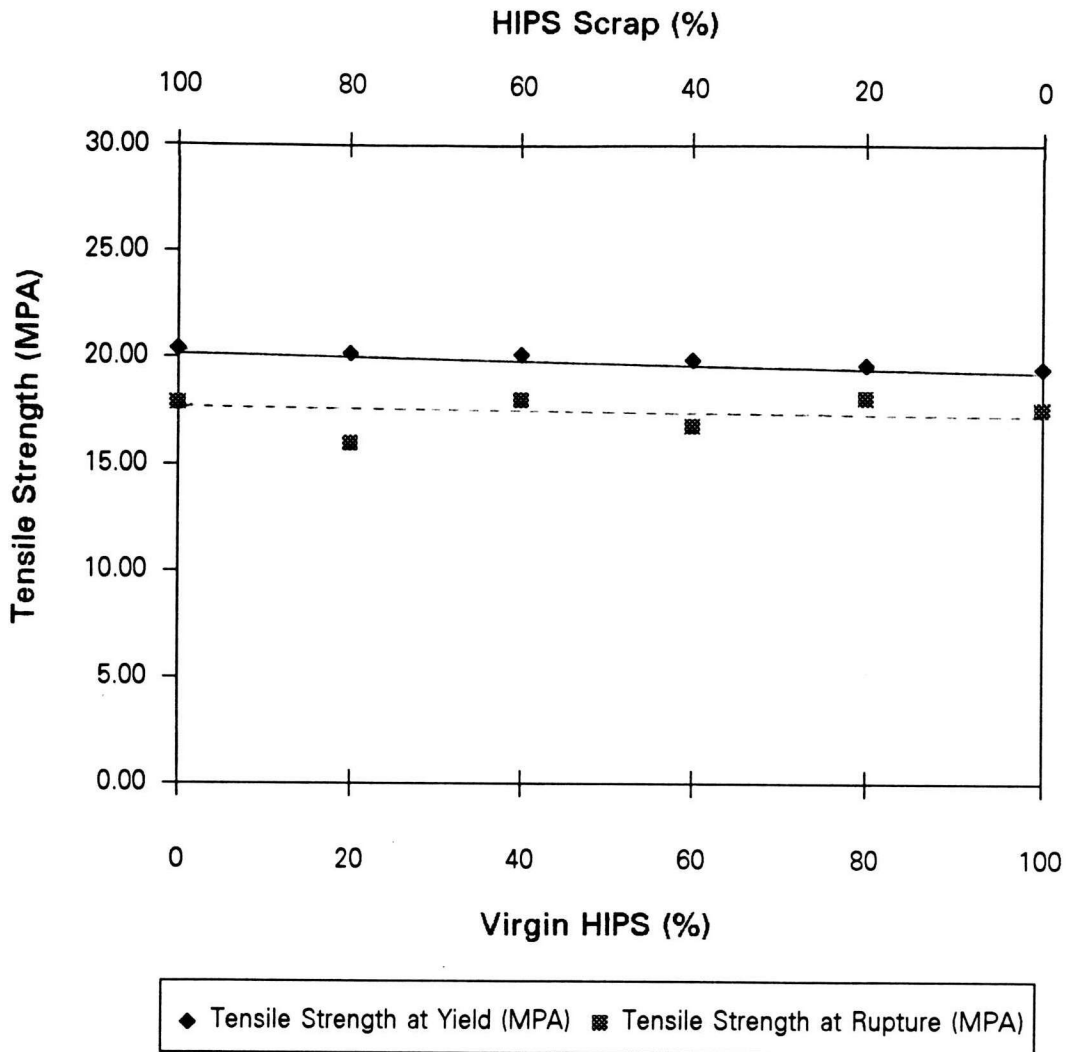


Figure 4.1 : The tensile properties of virgin HIPS/HIPS scrap mixture.

From Figure 4.1, an addition of virgin HIPS to HIPS scrap does not significantly effect the tensile strength at yield and the tensile strength at rupture. In fact, the plot shows that there is very little difference in the tensile properties, in terms of the yield and rupture strengths, between those of the pure HIPS scrap and the virgin HIPS. The tensile strength at yield decreased slightly with the amount of virgin HIPS. When adding virgin HIPS by 20 to 80%, the tensile strength at yield is decreased rather insignificantly by 1.3 and 3.92%. The tensile strength at rupture tends to decrease



very slightly with the amount of HIPS virgin. At an addition of 20 and 80% of HIPS virgin, the tensile strength at rupture decreased by 10.7% and increase by 1.06% respectively.

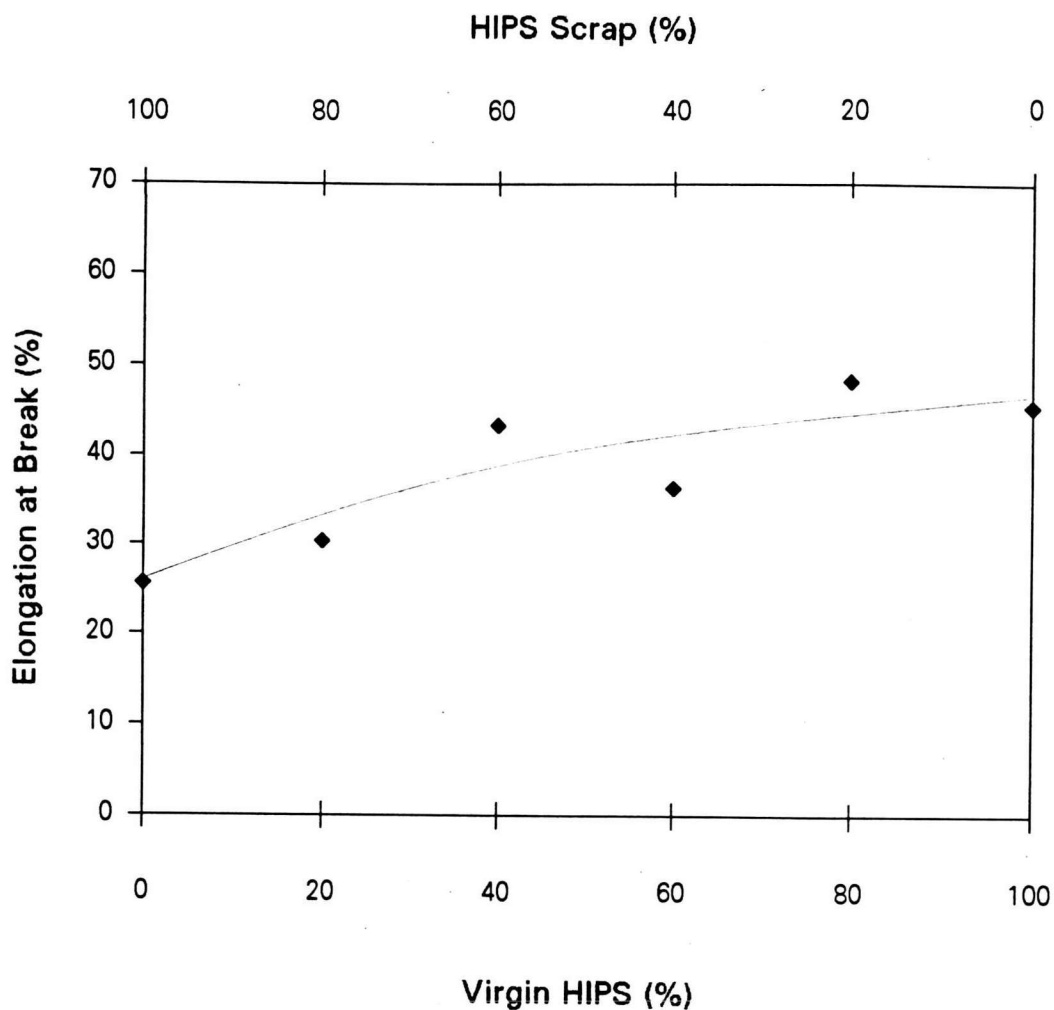


Figure 4.2 : The elongation of virgin HIPS/HIPS scrap mixtures.

Figure 4.2 shows an increase in the elongation with the amount of virgin HIPS. In other words, the elongation at break is at its minimum for 100% HIPS scrap. Having gone through prior processing, the scrap is likely to have been degraded to a larger extent than the virgin HIPS. The high shear stress during processing can lead

to chain breakage and hence molecular chain scission. An addition of 20 to 80% of virgin HIPS causes an increase in the elongation by 4.7% and 22.7% respectively.

#### 4.1.1.2 Izod Impact Strength

Figure 4.3 is a plot of the Izod impact strength against the concentration of virgin HIPS. The trend of the results shows that the higher the amount of virgin HIPS, the greater the Izod impact strength was found.

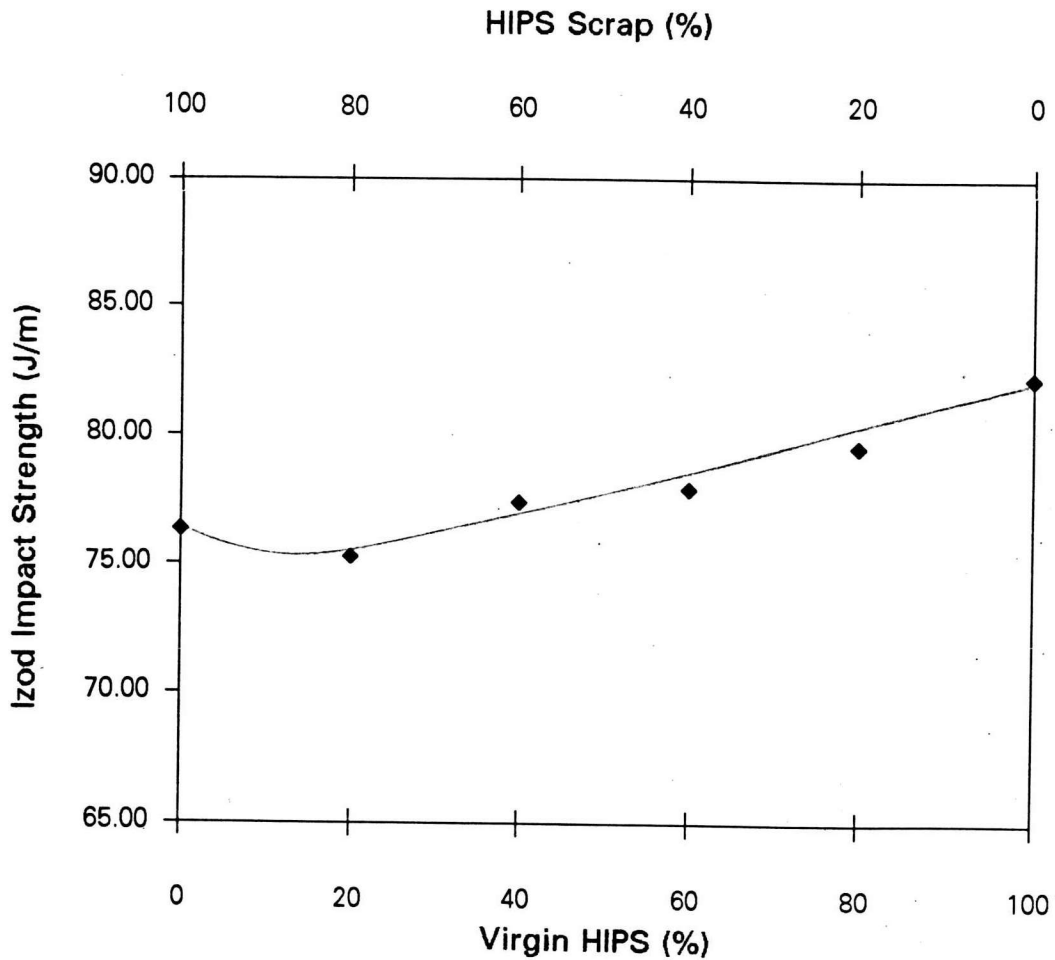


Figure 4.3 : The izod impact strength of virgin HIPS/HIPS scrap mixtures.

At 20% of virgin HIPS, the Izod impact strength was found to decrease slightly by 1.4%. It is not yet certain what could have caused the slight dip at 20% virgin HIPS. However, when the amount of virgin HIPS is increased upto 80%, the Izod impact strength increases by 4.2% when it is compared with that of the HIPS scrap.

#### **4.1.2 Thermal Properties**

##### **4.1.2.1 Melt Flow Rate**

The melt flow rate of HIPS scrap with various amount of virgin HIPS is shown in Figure 4.4.

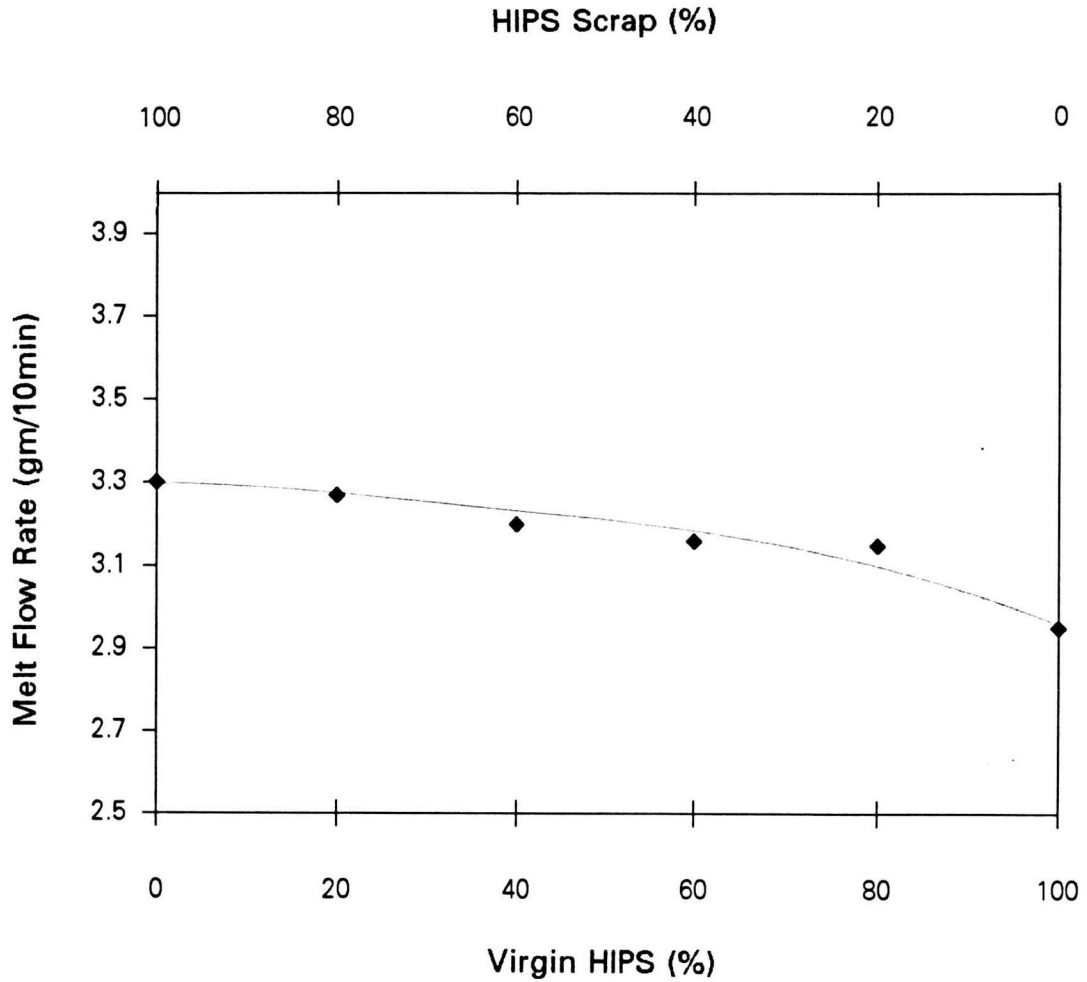


Figure 4.4 : The melt flow rate of virgin HIPS/HIPS scrap mixtures.

The addition of virgin HIPS results in a decrease in the melt flow rate. The melt flow rate is at its maximum for 100% HIPS scrap. The scrap had gone through the high shear stress and the heat during prior processing. Such history processing can lead to chain scission and results in greater melt flow rate. At 20, 40, 60 and 80% of virgin HIPS, the melt flow rate decreases by 0.9, 3.0, 4.2 and 4.5% respectively.

#### 4.1.2.2 Vicat Softening Point

The results of Vicat softening point is plotted against the amount of virgin HIPS in Figure 4.5.

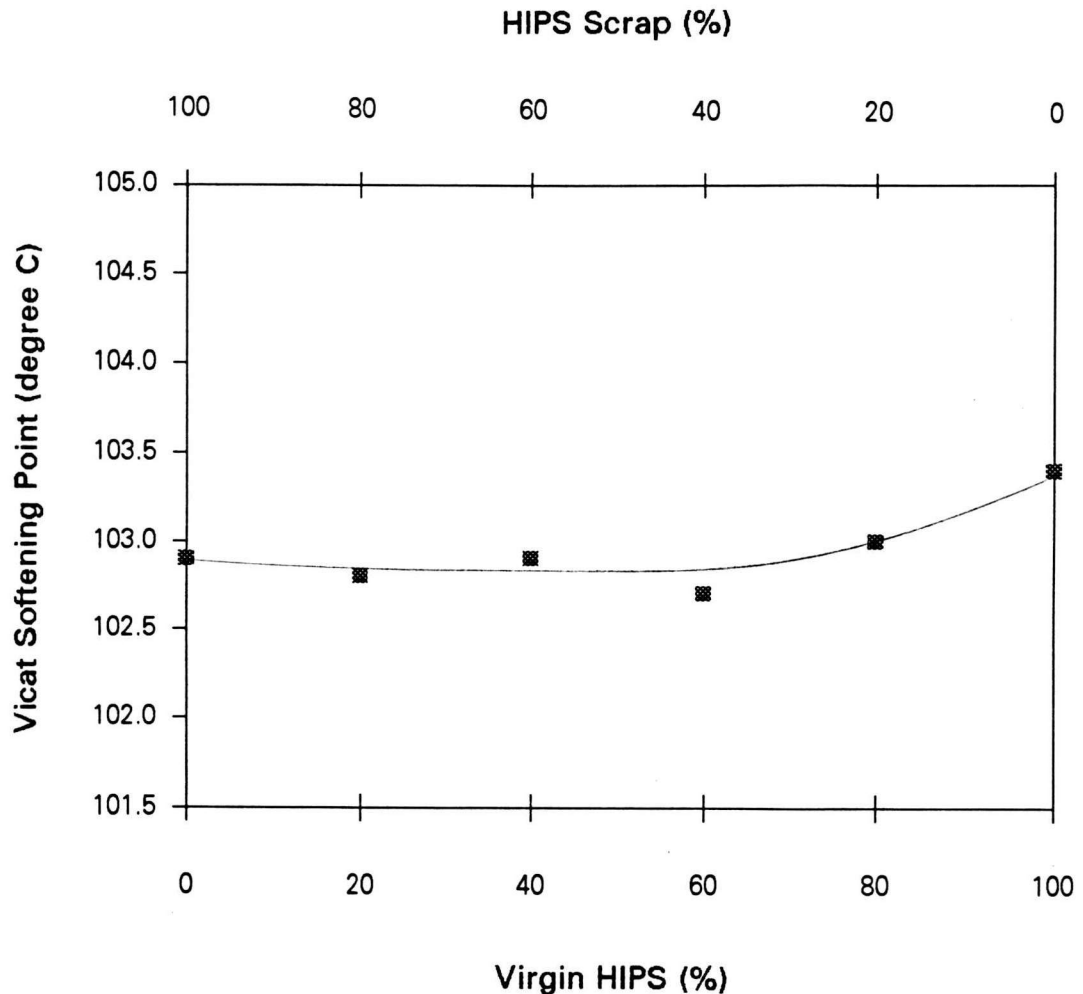


Figure 4.5 : The Vicat softening point of virgin HIPS/HIPS scrap mixtures.

Adding 20, 40, 60 and 80% of virgin HIPS, the Vicat softening point changes by  $-0.1^{\circ}\text{C}$ ,  $0^{\circ}\text{C}$ ,  $-0.2^{\circ}\text{C}$  and  $+0.1^{\circ}\text{C}$  respectively. The results clearly show that the Vicat softening point does not vary much. In fact, the percentage of change is less than 0.1% for any composition of the virgin HIPS.

The above results indicate that all properties of HIPS scrap was improved with the addition of virgin HIPS. However, the improvement is only slightly. A very large amount of virgin HIPS is needed to enhance the property of HIPS scrap. Even so, the enhancement was quite small. The results also indicate that HIPS scrap may have some deterioration induced by the intense shear stress and heat during its earlier processing step. Such deterioration is reflected in both the mechanical and thermal properties of the HIPS scrap. To use up the HIPS scrap, very large amount of virgin HIPS is needed and yet the improvement in the properties is only minor. The number of passes of HIPS scrap will highly effect the virgin properties. Property deterioration due to several passes of recycling of HIPS scraps will be presented in Section 4.2.

#### **4.2 Five Passes of Recycling**

This study is to explore how the various cycles of processing change the molecular weight, the mechanical properties and the thermal properties of HIPS.

One valuable factor for using HIPS scraps or return to reprocess is the knowledge of how reprocessing effect the HIPS scraps. This section intends to study the properties of recycle HIPS which has been reprocessed or reused from the first to the fifth pass. Results of all properties of HIPS scraps from the first to the fifth pass are described in Sections 4.2.1 to 4.2.3.

## 4.2.1 Mechanical Properties.

### 4.2.1.1 Tensile Properties

Figures 4.6 to 4.8 show the tensile strength at yield, tensile strength at rupture and the elongation at break of Scrap A and Scrap B after one to five passes of recycling.

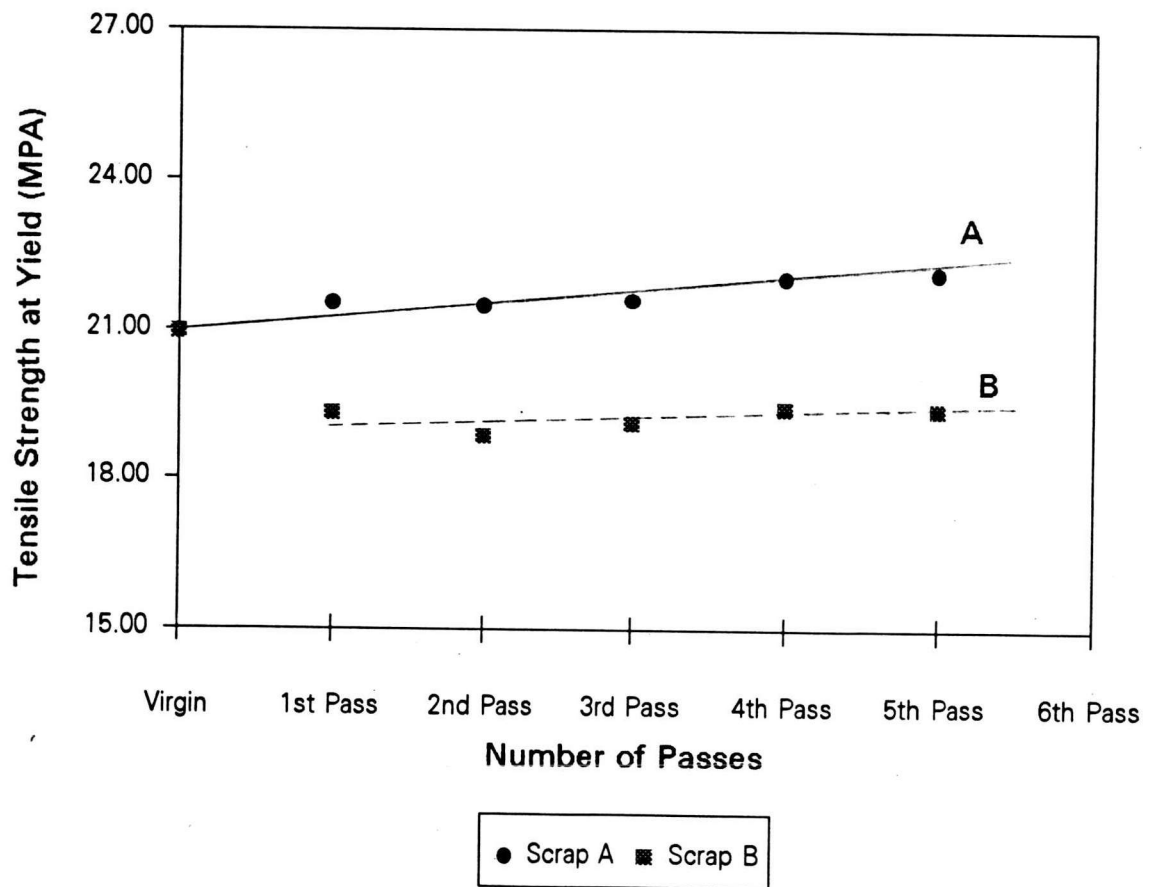


Figure 4.6 : The plot of tensile strength at yield with the various passes of recycling.

As shown in Figure 4.6, the five passes of recycling does not significantly effect the tensile strength at yield. The difference between the yield strength of virgin HIPS and those upto the fifth pass of recycling is more apparent in Scrap B than Scrap A.

The tensile strength at yield for Scrap A was increased by 2.82, 2.57, 3.10, 5.20 and 5.73% compared with virgin HIPS while those of the Scrap B were decreased by 7.78, 9.93, 8.69, 7.26 and 7.31%

For Scrap B, apart from the virgin HIPS, the general trend shows that the tensile strength at yield increased with the passes of recycling. The tensile strength at yield from the first pass to the second pass was decreased by 2.32%, which is the highest rate of change. Tensile strength at yield was increased by 1.38% from the second pass to the third pass, 1.57% from the third to the fourth pass and decreased by 0.05% from the fourth to the fifth pass.

Figure 4.7 shows the effect of tensile strength at rupture with several passes of recycling. The changes in the tensile strength at rupture of both Scrap A and Scrap B are not much. For Scrap A with the greater passes of recycling, the tensile strength at rupture increases by 4.32% for the first pass, 4.56% for the second pass, 6.67% for the third pass, 6.37% for the fourth pass and 7.87% for the fifth pass as compared with virgin HIPS. For Scrap B, apart from the first pass, all the tensile strength at rupture are higher than that of the virgin HIPS by 2.28%, 2.58%, 1.98% and 0.12% for the second, the third, the fourth and the fifth pass respectively. The abrupt drop in the tensile strength at rupture of Scrap B upon the first pass was initially assumed to have arisen from the testing error. However, the vast drop still exists and was consistent even if the experiment was repeated several times. In addition, processing of Scrap B after the first pass was found to be much more difficult than any other passes. The quality of the compressed sheets were sub-par. These problems of difficulty in compression molding and low tensile strength at rupture seem to disappear after the second pass onwards. The drastic change upon the first pass is



speculated to be the result of uneven dispersion of titanium dioxide therein. The high shear stress in further passes helped redistributing the titanium dioxide and even out the dispersion. As a result, the processing and mechanical property in terms of the tensile strength at rupture were restored to more or less close to those of the virgin one.

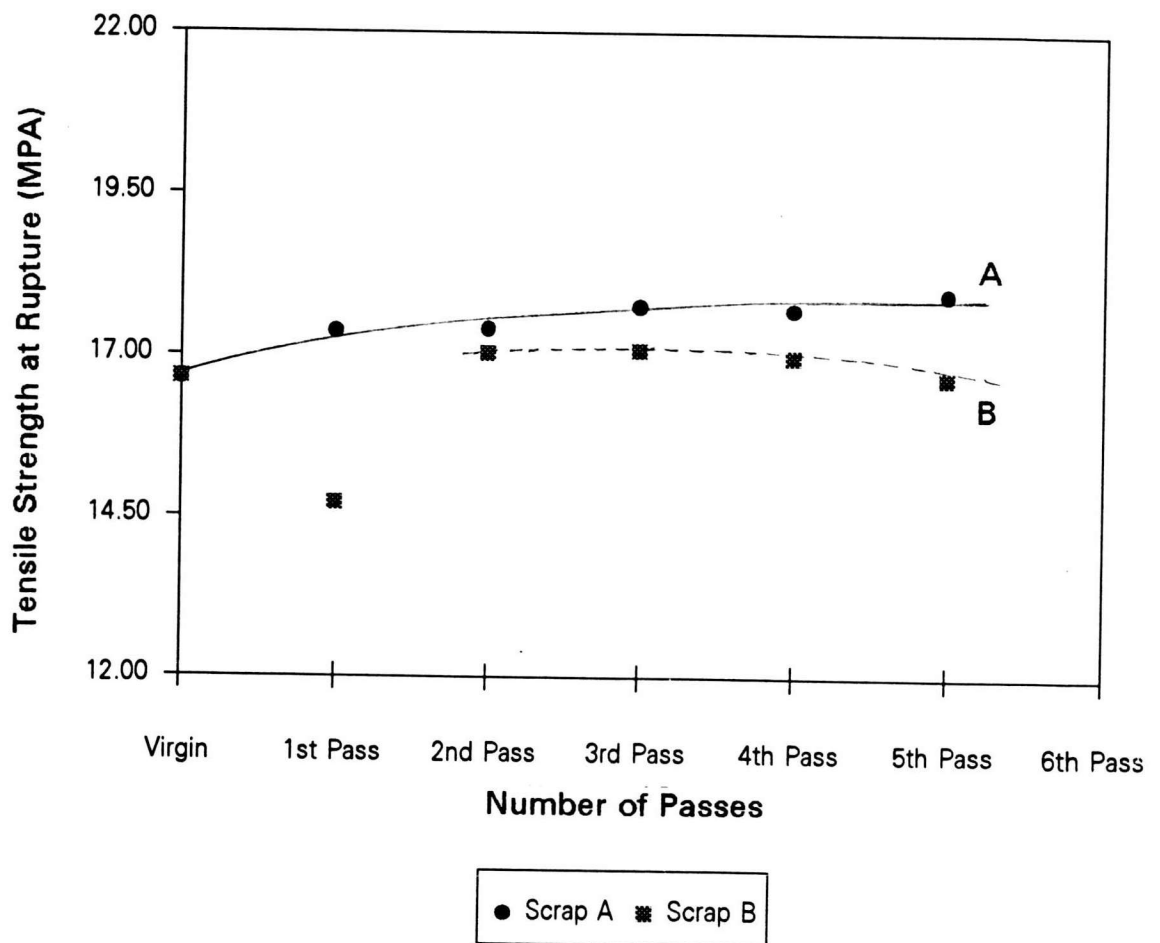


Figure 4.7 : The plot of tensile strength at rupture with the various passes of recycling.

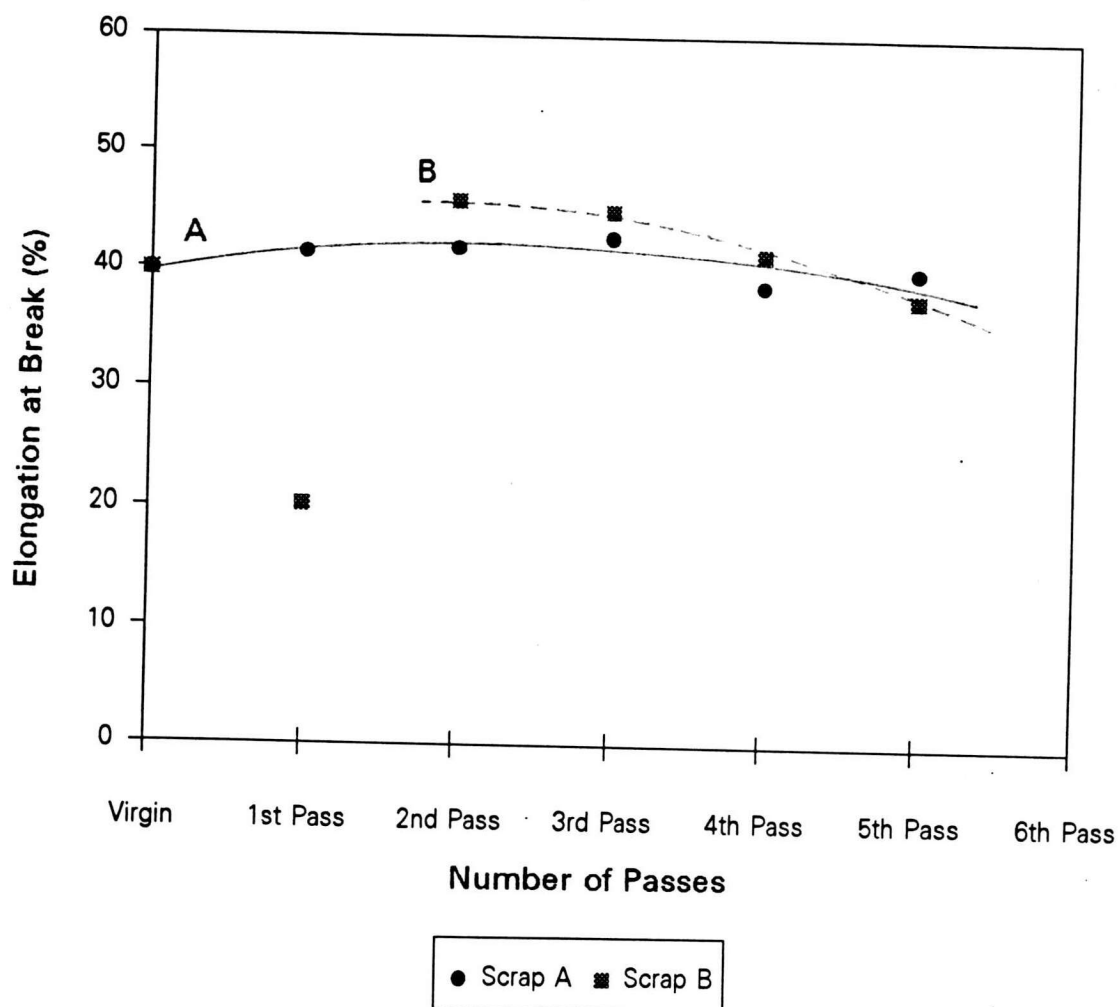


Figure 4.8 : The plot of elongation with several passes of recycling.

Figure 4.8 shows the tensile elongation at break of Scrap A and Scrap B with several passes of recycling. For Scrap A, the changes in the elongation at break is not much. The maximum percentage of decrease is 1.1% and that of increase is 2.9% compared with that of the virgin HIPS.

For Scrap B, the elongation of the first pass of recycling has dramatically decreased by 19.6% compared with that of the virgin HIPS. This is probably induced by the use of titanium dioxide, as discussed previously in the case of the tensile

strength at rupture. Although an important additive, titanium dioxide tends to deteriorate the properties of HIPS. As the scrap passed further processing passes, titanium dioxide was better dispersed and the mixture becomes more homogeneous within the materials. For the second to the fifth pass, it seems that the elongation at break does not change much with the passes of recycling.

#### 4.2.1.2 Izod Impact Strength

The effect of several passes of HIPS recycling on the Izod impact is shown in Figure 4.9.

The plot in Figure 4.9 shows the change in the impact property of recycled HIPS scraps. It is apparent from the plot that the Izod impact strength of the recycled HIPS are all lower than that of the virgin HIPS. The recycling of HIPS has significant effect on the Izod impact strength results. For Scrap A, the Izod impact strength decreases with the passes of recycling. At the first pass, the Izod impact is decreased by 7.6%. With more passes of recycling, the Izod impact strength is also decreased but less than that from the virgin to the first pass. At the second and the third pass of recycle, the Izod Impact is decreased by 8.19% and 9.36% compare with virgin. At the forth and the fifth pass, the decrease in Izod impact strength is almost at the same rate, i.e. 13.45% for the forth pass and 12.87% for the fifth pass.

For Scrap B, the trend of the results of the Izod impact strength which affects the HIPS recycling is the same as that of Scrap A. However, the percentage of change in Scrap B is about twice higher than that of in Scrap A. At the first pass of recycling, the izod impact strength of Scrap B decreases 11.12% when compared with

that of the virgin HIPS. At the second, the third, the fourth and the fifth pass of recycling, the Izod impact of Scrap B decreases by 16.37, 19.89, 22.22 and 21.64% respectively when compared with that of the virgin HIPS.

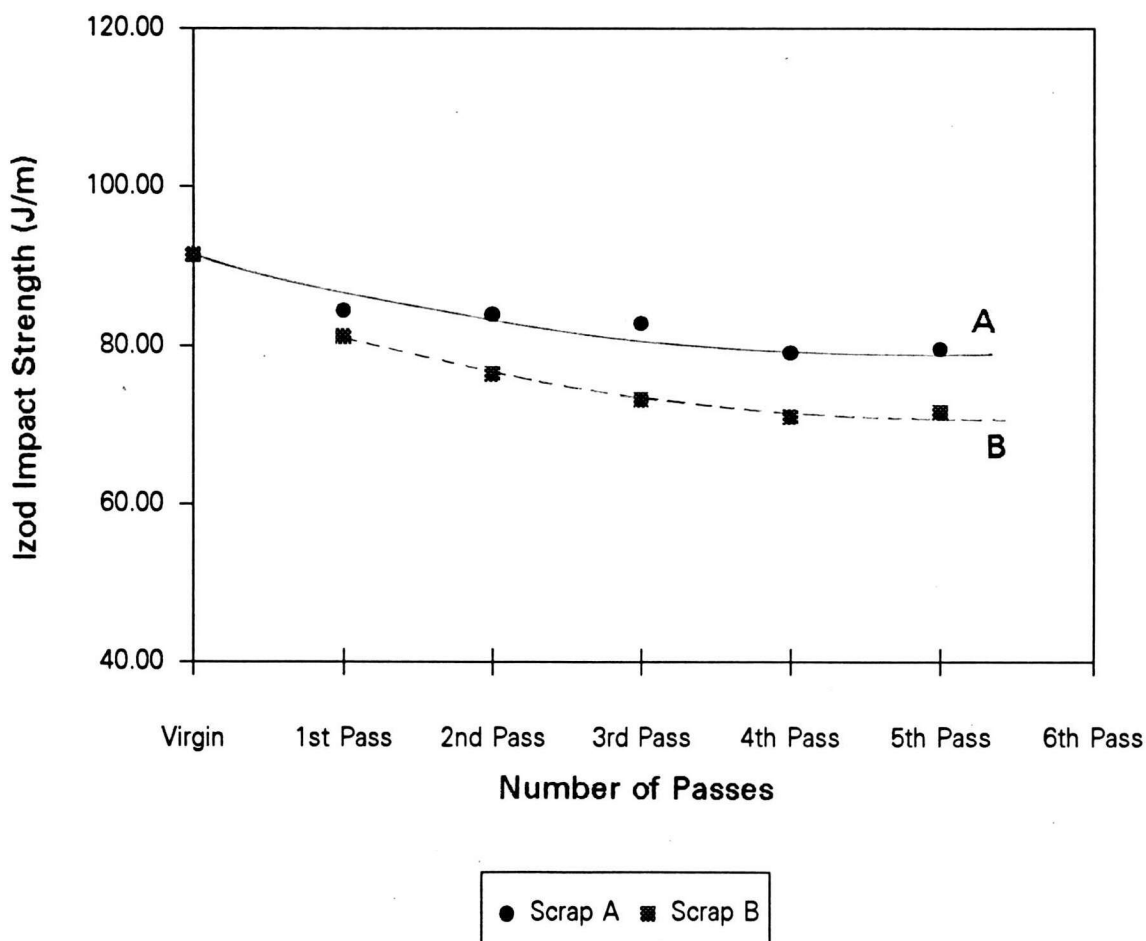


Figure 4.9 : The effect of several passes of recycling on the Izod impact strength.

It is apparent from the plot that the Izod impact strength decreases as the HIPS scrap undergoes the recycling process. Furthermore, the results evidently depicts the significance of the number of recycling passes on the impact properties of the recycled HIPS. The greater the number of recycling passes, the lower is the impact property. This is probably due to chain scission which occurs due to the high shear

stresses during processing, and hence decreasing the molecular weight with progressive processing. The impact properties are usually poorer after processing and recycling, this is shown in Figure 4.10 [11]. From this literature, the lowering of impact strength is substantial, down to one-half or less of its original value. The phenomena of possible chain scission is supported by the reduction in molecular weight as recycling progresses as will be discussed in Section 4.2.3.1.

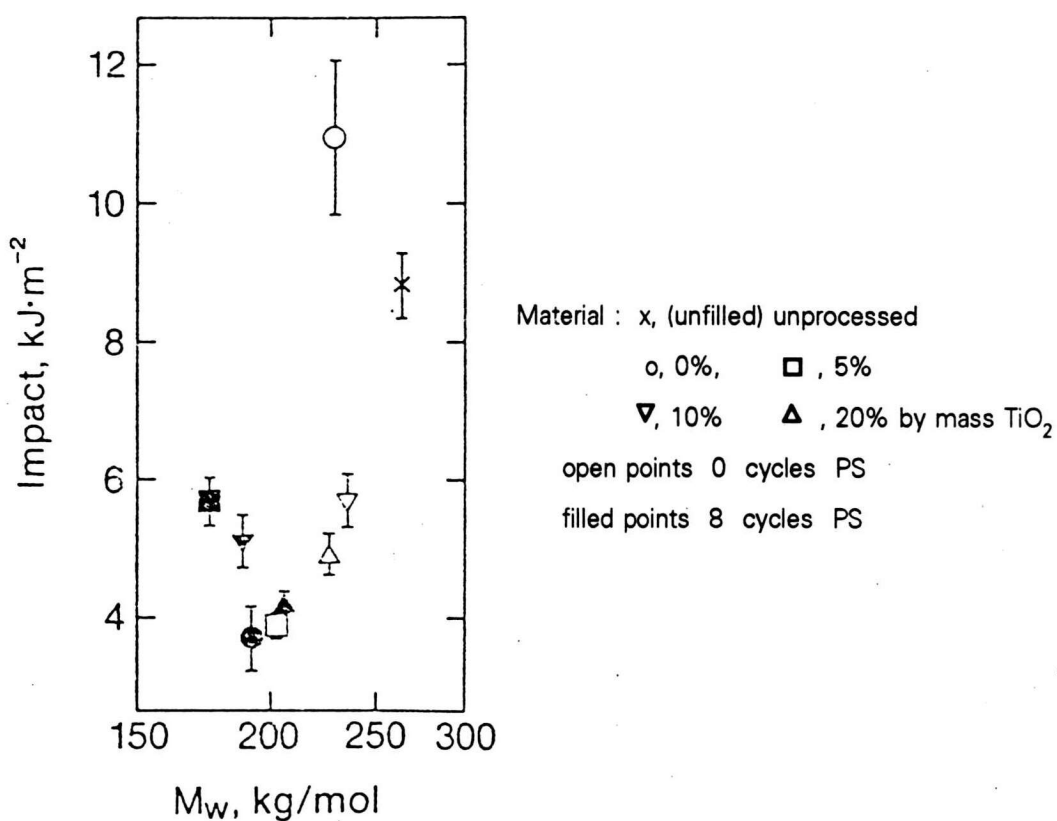


Figure 4.10 : Impact strength of PS plotted against the molecular weight.

Pigment such as titanium dioxide and other additives in Scrap B lower the Izod impact value. As a consequence, the results of several recycling show gradual deterioration on the Izod impact strength of both Scraps A and B.

## 4.2.2 Thermal Properties

### 4.2.2.1 Melt Flow Rate

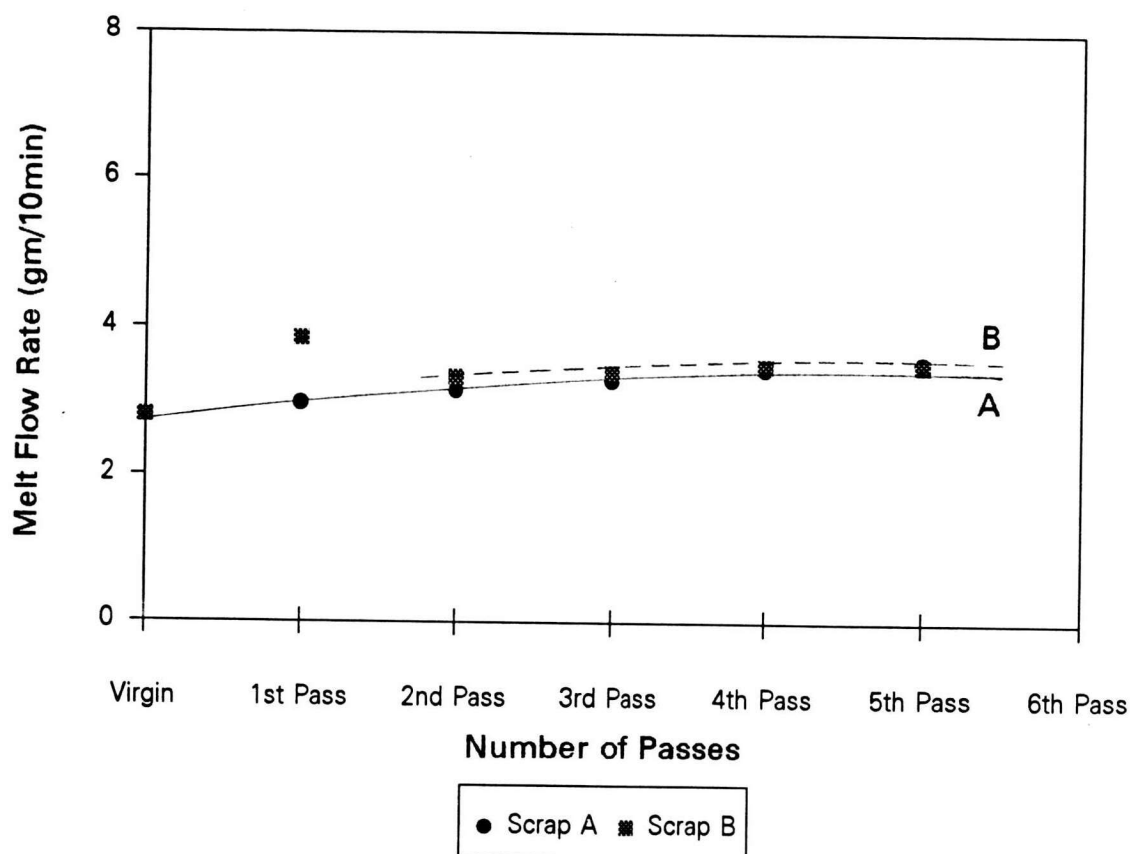


Figure 4.11 : The melt flow rate (MFR) of HIPS scraps upon gradual processing upto five passes of recycling.

As shown in Figure 4.11, the melt flow rate of recycled HIPS are all higher than that of the virgin HIPS. The melt flow rate of scrap A increases gradually. At the first pass of recycle, the melt flow rate is increased by 6.07%. With further passes of recycling, the melt flow rate also increases but at a slightly lower rate than the change between the virgin and the first pass. At the second, the third, the fourth and the fifth pass of recycling, the melt flow rate also increases by 12.14, 17.14, 22.5 and 26.07% respectively when compared with virgin HIPS.

For Scrap B, the melt flow rate of the first pass of recycling increases dramatically by 37.14% when it is compared with that of the virgin HIPS. This is in good agreement with the results found in Section 4.2.3.1 when the corresponding molecular weight was found to rise. A 13.54% decrease is found between the first pass and the second pass. At the second pass, the melt flow rate increases by 18.57% when compared with virgin HIPS. For the third pass to the fifth pass, the melt flow rate also increases but the change is much less than that between the first pass and the second pass of recycling. Apart from the first pass, all the melt flow rate increase slightly with the passes of recycling. For the second to the fifth pass, the melt flow rate increase by 1.81% for the third pass, 4.82% for the fourth pass and 5.12% for the fifth pass compared with that of the second pass.

From the above-discussed results, it is clear that the melt flow rate of the first pass of Scrap B shows a significant increase. This is believed to be the effect imparted by the titanium dioxide additive in Scrap B. Since coloring is one of the necessary steps in producing a finished plastic product, titanium dioxide is usually applied as an inorganic pigment. In this study, it is used as a white colorant for HIPS. The titanium dioxide used was fine, dry and white powder. The effect of titanium dioxide seems most prominent on the melt flow rate in the first pass. For the second pass, since the material was passed through a screw injection machine, it was possible that better dispersion of the titanium dioxide in the sample was achieved and resulted in the decrease of the melt flow rate.

From the experimental results of the melt flow rate, it seems that the increase in the melt flow rate, especially after several passes of recycling, is due to chain scission. The weight average molecular weight of the HIPS scrap after each pass, as

shown in Figure 4.13, decreases gradually upon further recycling. Chain scission is believed to be a degradative process and leads to a greater melt flow rate.

#### 4.2.2.2 Vicat Softening Point

The results of the Vicat softening point of HIPS scrap after processing upto five passes of recycling are shown in Figure 4.12.

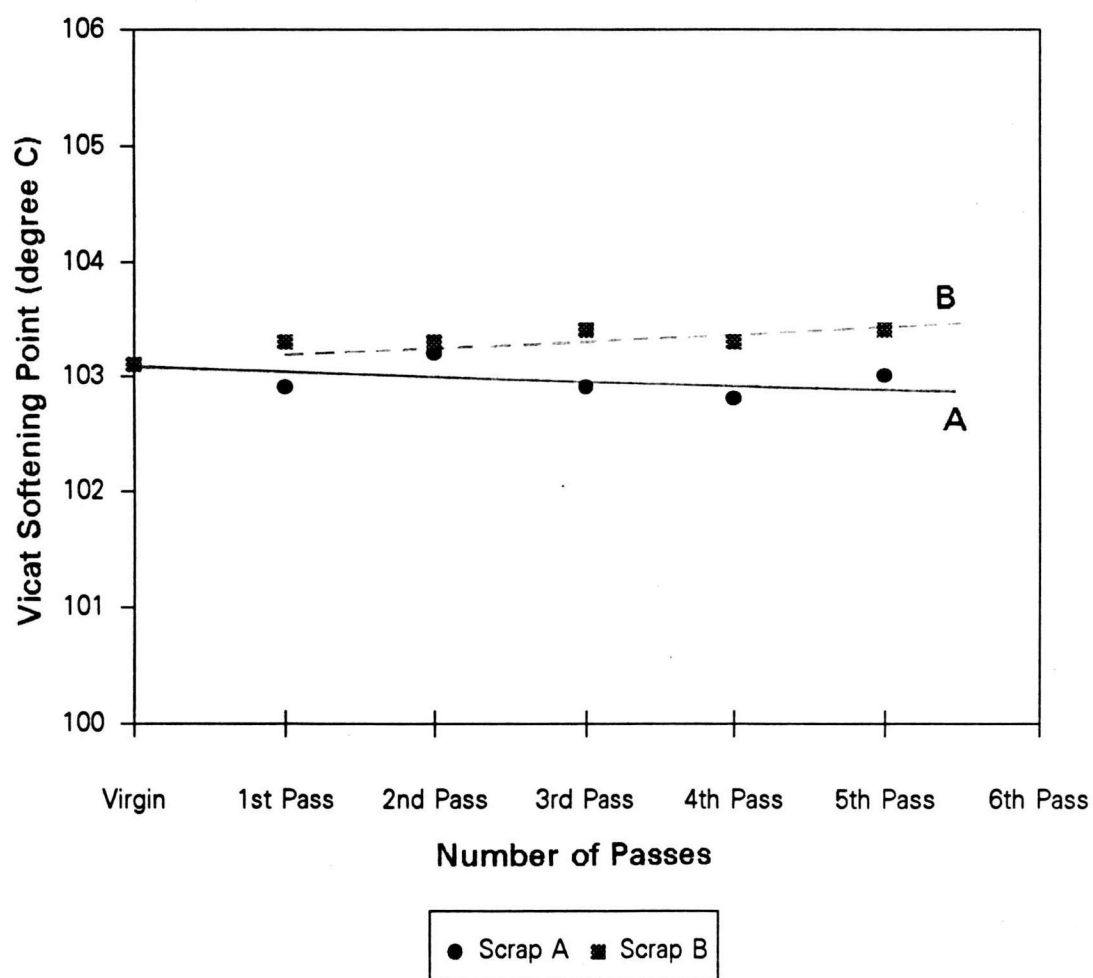


Figure 4.12 : The Vicat softening point of HIPS scraps upon gradual processing upto five passes of recycling.



The percentage of change in the Vicat softening point was calculated and compared with those of the virgin HIPS in the Table 4.1.

Table 4.1: The change in the Vicat softening point compared with that of the virgin HIPS.

	%Change of Vicat softening point (- decrease, + increase)				
	1st pass	2nd pass	3rd pass	4th pass	5th pass
Scrap A	-0.19	+0.10	-0.19	-0.29	+0.10
Scrap B	+0.19	+0.19	+0.29	+0.19	+0.29

The above results demonstrate that the number of recycling passes scarcely effects the Vicat softening point. The change found in the present study is less than 0.3% or 0.3 °C.

### 4.2.3 Physical Properties

#### 4.2.3.1 Molecular Weight

The weight average molecular weights of the first to the fifth pass of both Scrap A and Scrap B were determined from the size exclusion chromatograms. The results are plotted in Figure 4.13.

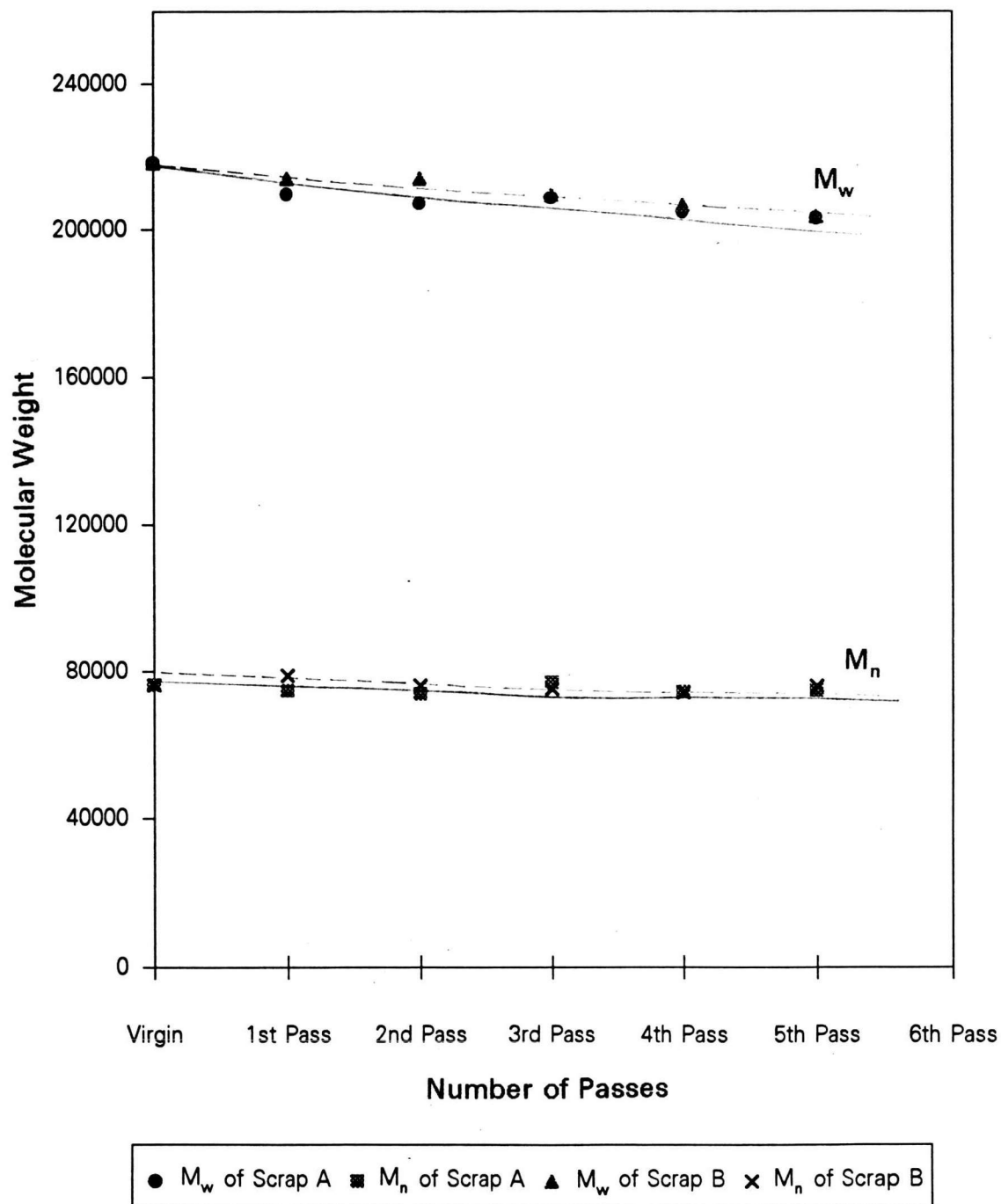
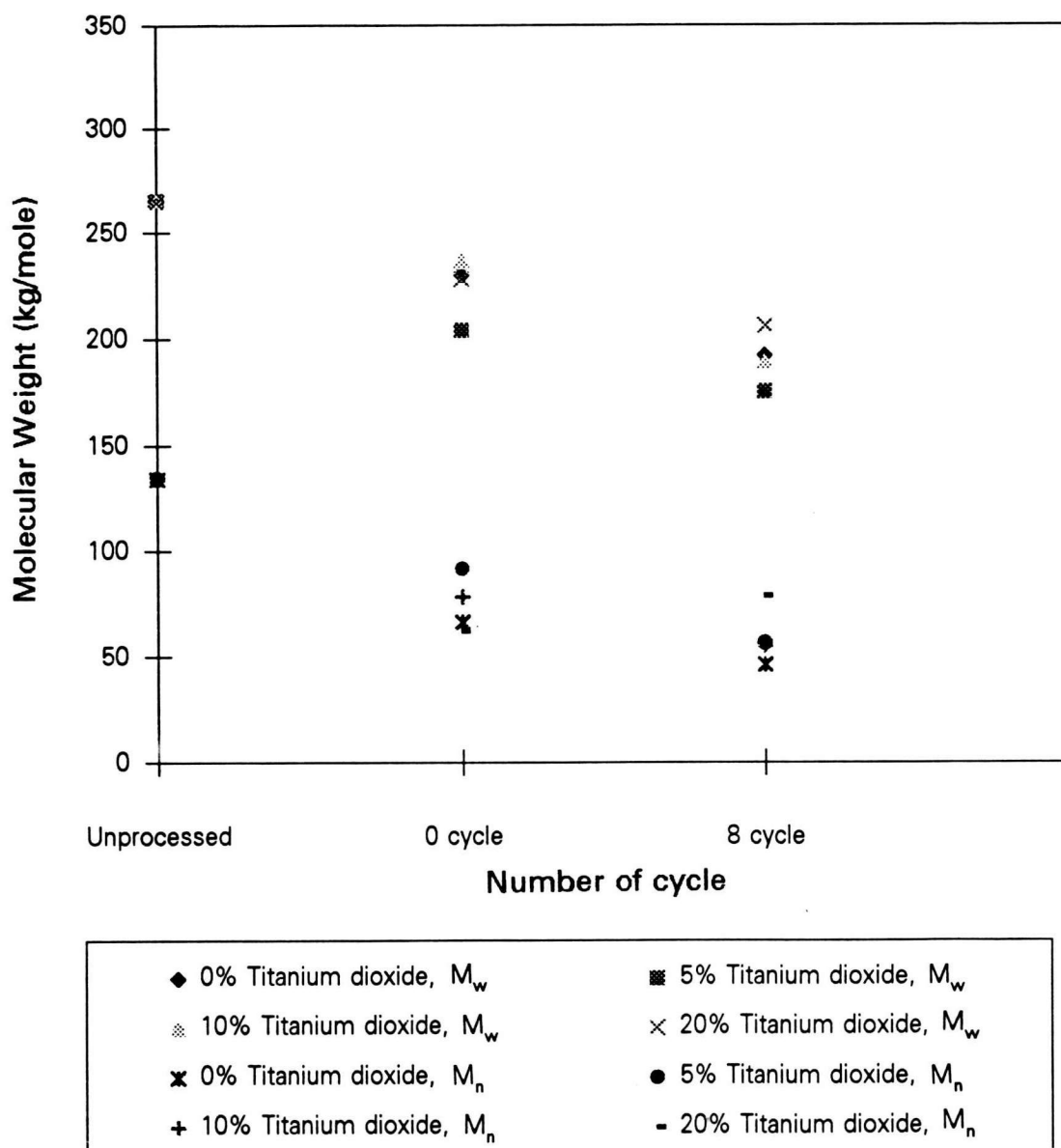


Figure 4.13 : The molecular weights of HIPS scraps upon gradual processing upto five passes of recycling.

The weight average molecular weight shows that the molecular weight of both Scrap A and Scrap B decreases with the passes of recycling process. As recycling progresses from the first to the fifth pass, the weight average molecular weight decreases by 3.94%, 5.09%, 4.44% 6.14% and 7.01% respectively for Scrap A. The decrease by 1.97%, 1.97%, 4.08%, 5.36% and 6.83% respectively is found for Scrap B. The additives in Scrap B seems to have no effect on the change of weight average molecular weight of Scrap B. The weight average molecular weight of both Scraps A and B decreased with passes of recycling. The weight average molecular weight of Scrap B in each pass of recycling is closed to that of Scrap A.

The decrease in the weight average molecular weight is believed to be the result of chain scission. However, the extent of the scission can be dependent on the type and the condition of processing. From the study of Ho Yin Tang [11], recycling at 200 °C through an extruder upto eight passes was found to lower the molecular weight by 16.52%. Tang's results [11] are plotted against the number of passes and shown in Figure 4.14.



$M_w$  = weight average molecular weight

$M_n$  = number average molecular weight

Figure 4.14 : The weight and the number average molecular weight of Polystyrene upto eight passes of recycling with and without additives.

Springer et al [12] found a reduction in the molecular weight by 3.5% per extrusion at 230 °C. Hornsby and Sothern [13] reported that chain scission occurred and the reduction of the molecular weight was by 1.5, 2.3 and 2.1% respectively when recycling was performed at 130-165 °C at 9 rpm, 130-165 °C at 24 or 60 rpm and 140-190 °C at 9 rpm. The results found in the present study are in good agreement with earlier findings [11,12,13] on the change in the weight average molecular weight of Polystyrene.

The number average molecular weight shows that the molecular weight of both Scraps A and B does not change with the passes of recycling. Even though there are some additives in Scrap B, there is no effect in the number average molecular weight.

The result of the number average molecular weight in the present study does not vary in the same order with Tang's results [11] which is shown in Figure 4.14. Tang reported that the number average molecular weight ( $M_n$ ) is not considered a good representative for the material in his study. It is greatly influenced by the smallest molecules, which may degrade to oligomers and volatilize in a random way in the several passes of the experiments. Tang [11] showed that pure chain scission must have lowered the  $M_n$  since the total mass remains constant while the number of molecules increases. But from the present results, the number average molecular weight is relatively constant, i.e. relatively unchanged as shown in Figure 4.13 which is in good agreement with Springer et al [12] on the constancy of the  $M_n$  after extrusion while the two findings, Hornsby and Southern [13] and La Mantia et al [14] reported lowering of the  $M_n$  after extrusion.

#### 4.2.3.2 Color

Figures 4.15 and 4.16 respectively show the “Lightness index” and “Yellowness index” of Scrap A and Scrap B after the several passes of recycling.

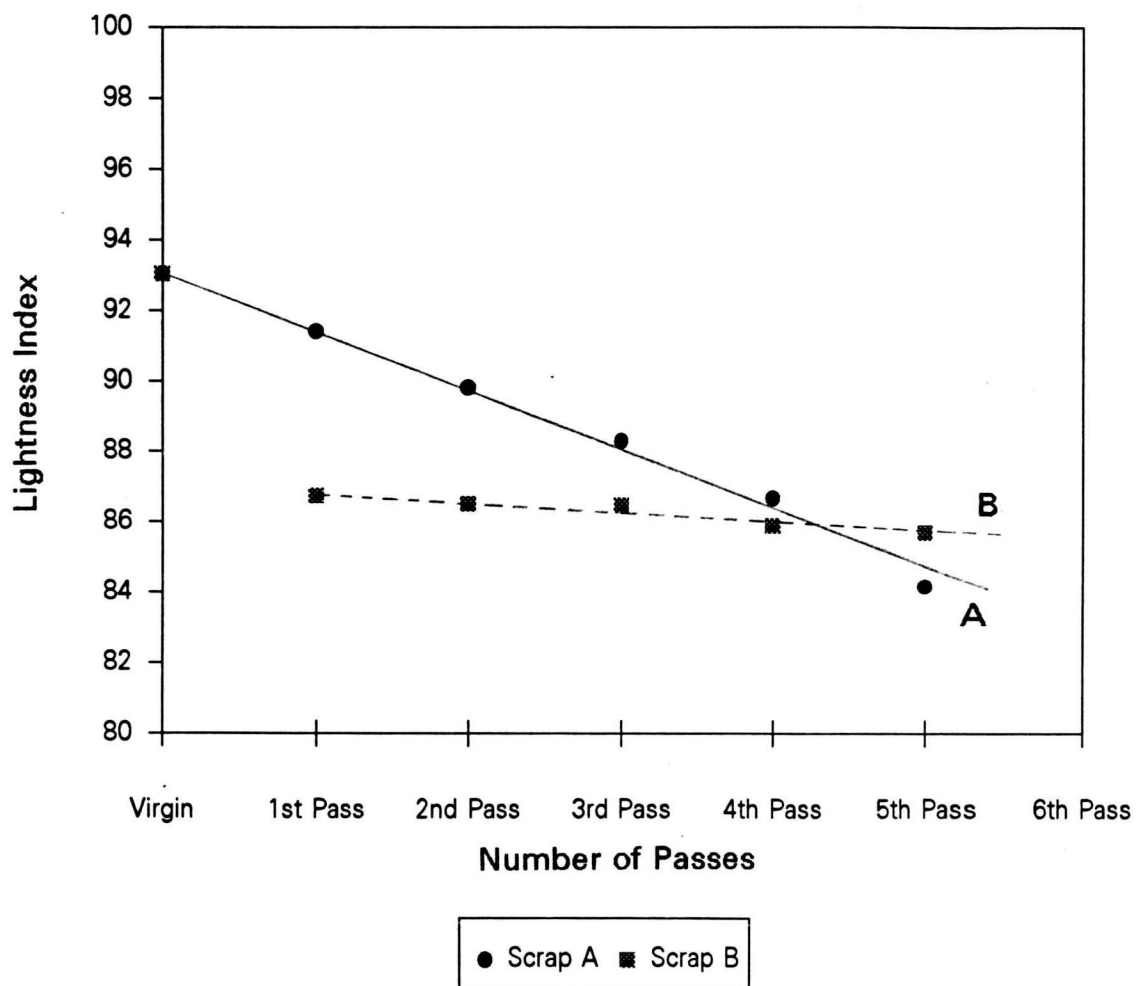


Figure 4.15 : The plot of “Lightness index” with several passes of recycling of HIPS scraps.

Figure 4.15 shows that the more the number of passes of recycling, the greater the decrease in the Lightness index. This is found in both Scrap A and Scrap B. The Lightness index of Scrap A decrease progressively as the scrap undergo further passes of recycling. However, the Lightness index of Scrap B drops drastically upon the first pass and remains relatively constant throughout the first to the fifth pass.

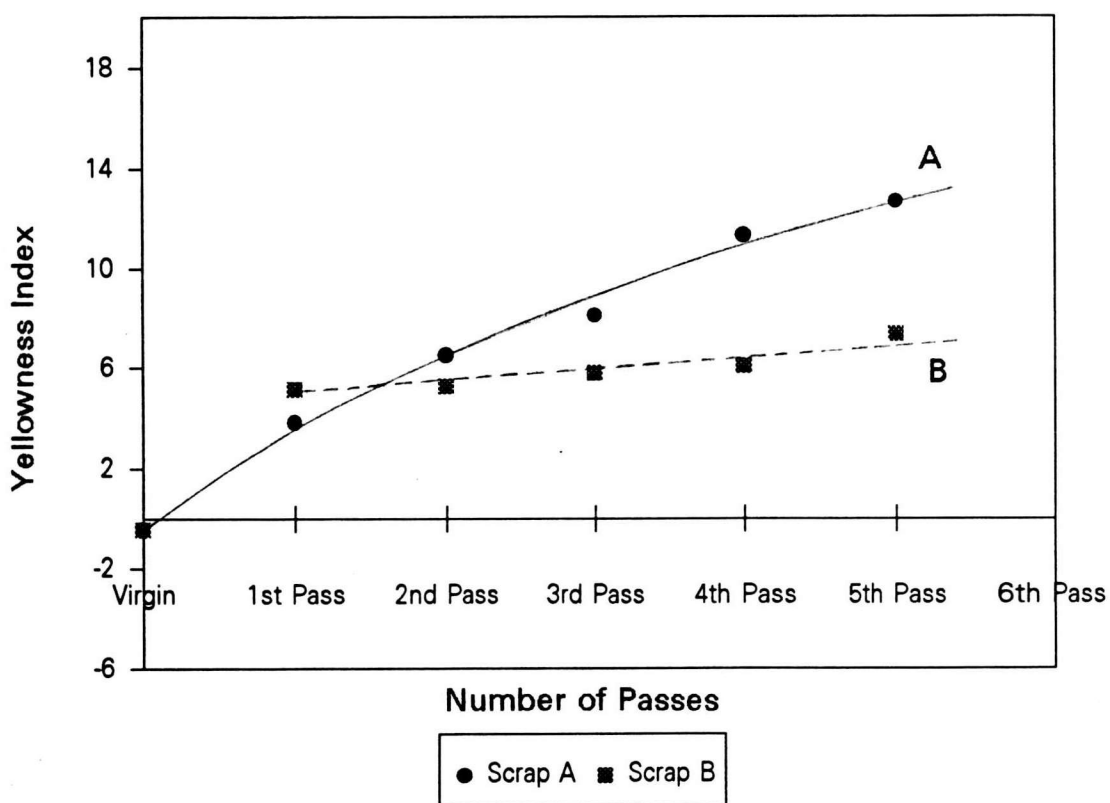


Figure 4.16 : The plot of “Yellowness index” with several passes of recycling of HIPS scraps.

The Yellowness index, as shown in Figure 4.16, shows the same trend for both Scraps A and B. However, the change in Scrap A was higher than that in Scrap B. The Yellowness index increases with the more passes of recycling. For Scrap A, the

Yellowness index changes from -0.47 of virgin HIPS to 12.65 of the fifth pass of recycling. For scrap B, the Yellowness index changes from -0.47 to 7.32.

Beyond the first pass, the color of Scrap B does not change very much. This is probably due to the influence of the whiteness imparted by the titanium dioxide pigment which was added in Scrap B before it became scrap.

This study indicates that the processing and recycling have significant effect in the color of the recycled plastics. The results provide a good indication of the deterioration in color due to processing and recycling. The color of Scrap B was shown to be better than that of Scrap A due to the prior addition of titanium dioxide.

To reuse any scraps, some color modification should be made to reduce the effect of the color change towards greater yellowness in recycled plastics.

### **4.3 Enhancing Properties by Adding an Impact Modifier**

It is apparent from Figure 4.9 that the Izod impact strength of recycled polystyrene decreases upon further recycling. So, an impact modifier seems to be an appropriate additive for recycled HIPS scraps.

The impact modifiers used in this study are Styrene Butadiene Styrene Block Copolymer of two types, SBS-I and SBS-II as described in Section 3.1.3.

Various amount of SBS-I and II were added separately to each of the HIPS scrap to form a series of composition as described in Section 3.2.3. Then properties were



tested accordingly with the details given in Sections 3.3 to 3.6. The results are presented and discussed in the following sections.

### 4.3.1 Mechanical Properties

#### 4.3.1.1 Tensile Properties

One of the most extensively used mechanical tests for polymers is the tensile or "Stress-Strain" test. It is usually done at a specified rate and temperature. The sample configuration is similar for all polymers. Typical stress-strain curves for HIPS is shown in Figure 4.17.

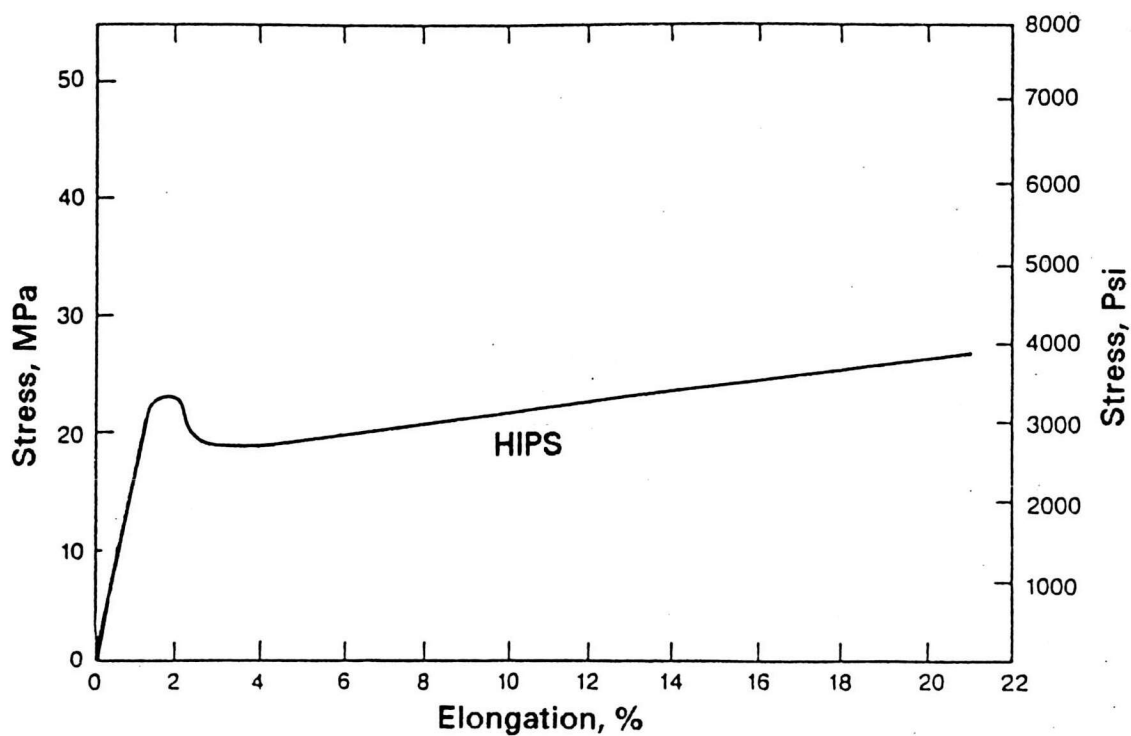


Figure 4.17 : Stress-strain curves of HIPS.

The effect of the two additives, SBS-I and SBS-II, on the tensile strength at yield, tensile strength at rupture and the elongation on Scraps A and B is shown in Figures 4.18 to 4.20 respectively.

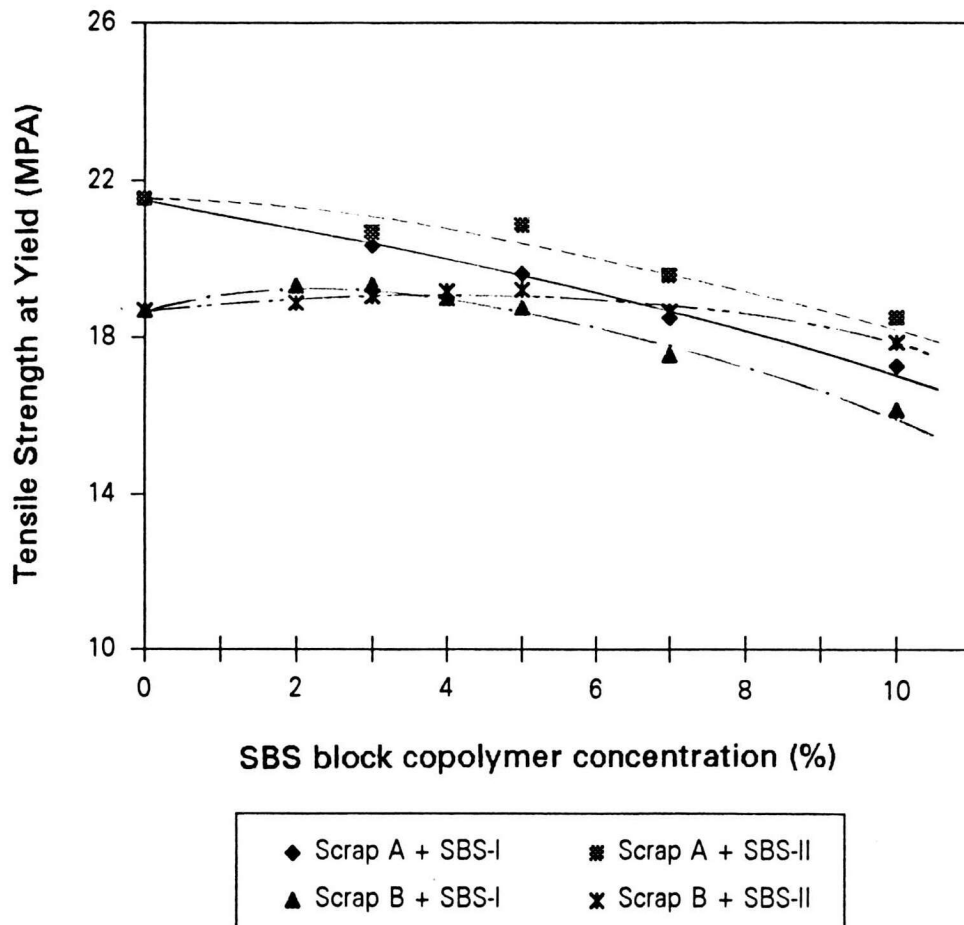


Figure 4.18 : The tensile strength at yield of HIPS scraps mixed with SBS block copolymer concentration.

As shown in Figure 4.18, the tensile strength at yield has not changed significantly over the applied range of 0 - 5% of SBS-I and SBS-II block copolymers. But beyond 5%, the tensile strength at yield decreases at a far greater rate than that at the lower amount of SBS block copolymers.

Both SBS-I and SBS-II give the same trend of results. However, the change of strength at yield when SBS-I was used is greater than that in the case when SBS-II was applied.

For Scrap A, the higher the amount of SBS-I and SBS-II, the more rapid is the drop in the tensile strength at yield. At 3, 5, 7 and 10% of SBS-I and SBS-II, the tensile strength at yield decreases by 5.53, 8.92, 14.17 and 19.88% for SBS-I and 4.04, 3.25, 9.15 and 14.17% for SBS-II.

For Scrap B, when 2-5% of SBS-I and SBS-II was added, the tensile strength at yield is elevated. At 2, 3, 4 and 5% of SBS-I and SBS-II the tensile strength at yield increases by 3.32, 3.43, 1.61, 0.32% for SBS-I and 1.07, 1.87, 2.62 and 2.78% for SBS-II. For the range studied, when the amount of SBS-I and SBS-II is increased upto 7 to 10%, the tensile strength at yield is found to be lower. At 7% and 10% of SBS-I and SBS-II, the tensile strength at yield decreases by 6.21 and 13.70% for SBS-I and 0.21, 4.50% for SBS-II. From the above results, the increase in the tensile strength at yield was very little over the range of SBS block copolymer of 2-5%. Greater change is observed when the SBS-I and SBS-II is used by 7% or higher.

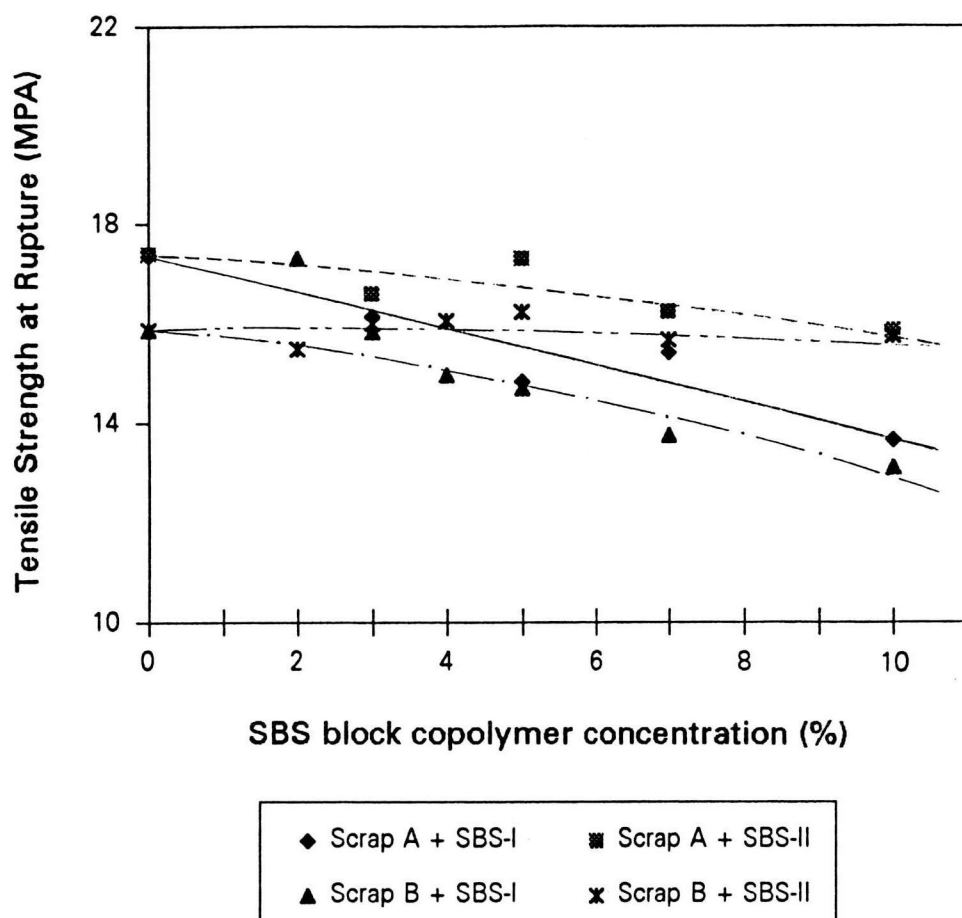


Figure 4.19 : The tensile strength at rupture with HIPS scraps mixed with SBS block copolymer concentration.

The tensile strength at rupture is shown plotted against the amount of the two SBS block copolymers in Figure 4.19. Most results depict a similar trend to that from the tensile strength at yield, i.e. the tensile strength at rupture decreases when the concentration of the SBS block copolymer increases. Both SBS-I and SBS-II give the same trend.

For tensile strength at rupture, the results of Scraps A and B show a different pattern. For Scrap A, with 3, 5, 7 and 10% of SBS-I and SBS-II, the tensile strength

at rupture decreases by 7.20, 14.68, 11.40 and 21.47% for SBS-I and 4.55, 0.52, 6.68 and 8.86% for SBS-II. For Scrap B, with the higher amount of SBS-I, a lower tensile strength at rupture was found in the mixture. With 2% the tensile strength at rupture was decreased by 9.02%. With 3, 4, 5, 7 and 10% the tensile strength at rupture was decrease 0.25, 5.74, 7.44 13.43 and 17.40% respectively.

Scrap B with SBS-II did not show a clear pattern of change in the tensile strength at rupture with the various amount of SBS-II. However, the change of the tensile strength at rupture is not significant. With 2% of SBS-II, the maximum change was only 2.46% decrease.

The different trends observed in the change in the tensile strength at rupture of Scraps A and B in the presence of SBS block copolymers are probably due to the existence of other additives which had been added to the plastic B before it was used as Scrap B. However, the trends observed at various concentrations of SBS block copolymer is that the tensile strength at rupture decreases when more SBS block copolymer was added.

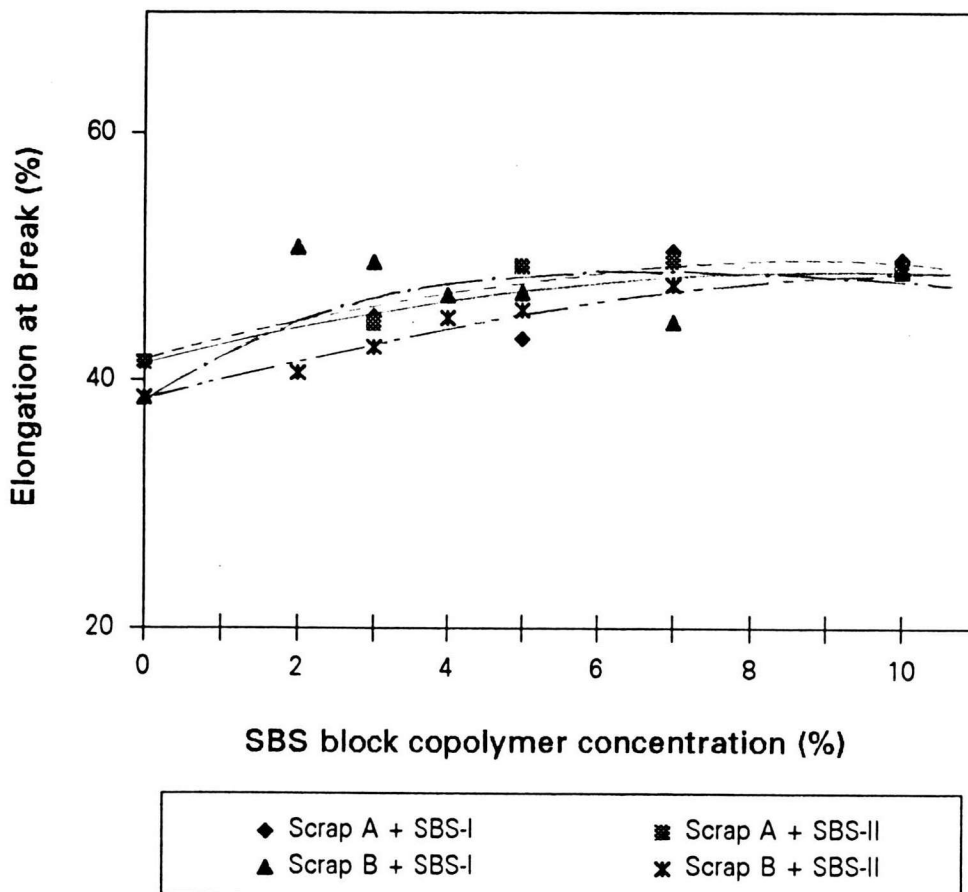


Figure 4.20 : The elongation at break of HIPS scraps mixed with SBS block copolymer concentration.

As shown in Figure 4.20, the elongation at break of the HIPS scrap with SBS-I and SBS-II are all higher than that of the pure scrap. This is a clear evidence that the scrap has become more ductile when SBS block copolymer was added even at a tiny amount. For Scrap A, with 3, 5, 7 and 10% of the SBS-I, the elongation at break increases by 9.18, 4.83, 21.74 and 20.05%. For SBS-II, the increase is found to be 7.73, 18.84, 19.81 and 18.36%.

For Scrap B with 2, 3, 4, 5, 7 and 10% of SBS-I, the elongation at break increases by 31.35, 28.24, 21.5, 22.02, 15.80 and 26.42%. With SBS-II, the elongation at break increases by 5.18, 10.62, 16.84, 18.39, 23.58 and 26.94%.

For the range studied, the elongation at break increases with the amount of the SBS block copolymers. Both SBS-I and SBS-II are effective additives in enhancing both the elongation at break and the Izod impact strength. However, the increase in toughness is at the expense of a decrease in the tensile strength at yield and the tensile strength at rupture.

#### 4.3.1.2 Izod Impact Strength

Typically, the mechanical and the physical properties are the most important properties to the use of HIPS. They can be used to define the end applications. In addition they are vital information for the process of product and mold design.

Izod impact properties is one of the important mechanical properties which is directly related to toughness of plastics. The Izod impact test was performed at room temperature according to the details described in Section 3.3.2. The test is particularly useful in assuring the energy required to break a notched specimen. The high value of the Izod impact strength is an indication of the more impact resistance the HIPS is.

Figure 4.21 is a plot of the Izod impact strength against the concentration of SBS block copolymers. The addition of SBS block copolymer to the HIPS scraps improves the Izod impact strength significantly.

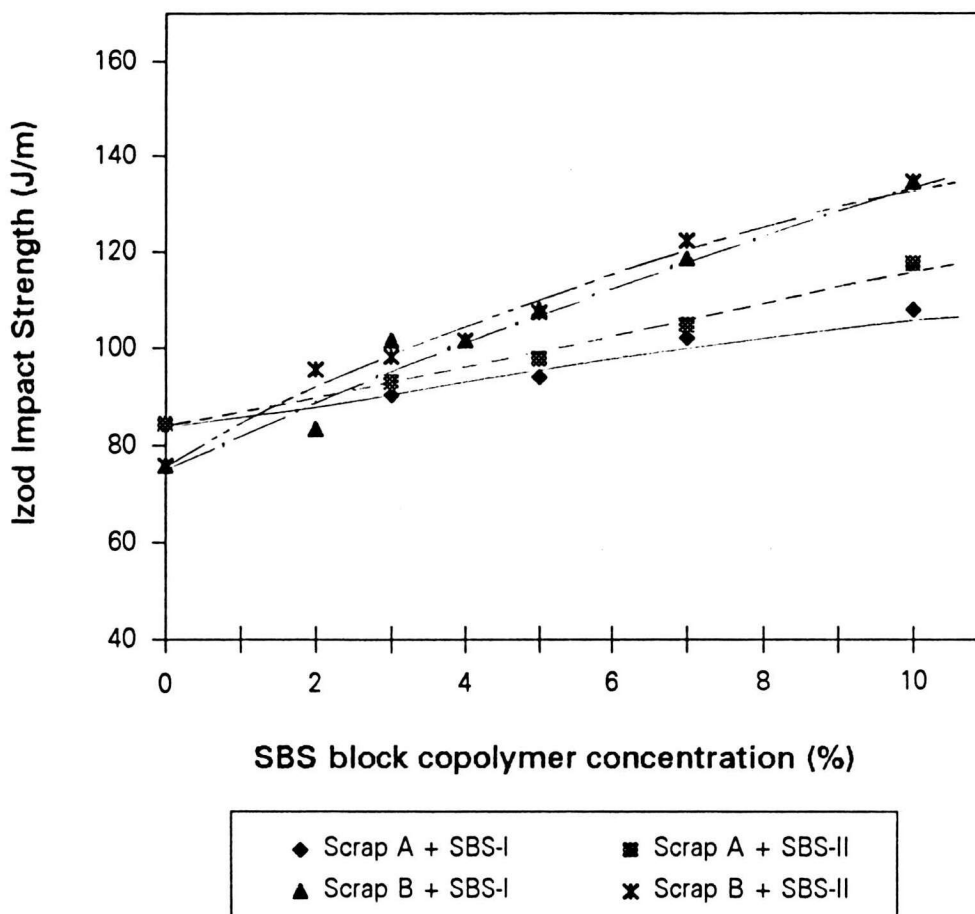


Figure 4.21 : The Izod impact of HIPS scraps with and without SBS-I and SBS-II block copolymer concentration.

An addition of SBS-I by 3, 5, 7 and 10% leads to an increase in the Izod impact strength of Scrap A by 7, 11.4, 20.9 and 27.8% and of Scrap B by 33.8, 42.2, 56.3 and 77.5%. For SBS-II, when used by 3, 5, 7 and 10%, the Izod impact strength of Scrap A is increased by 10.1, 15.8, 24.0 and 39.2% and for Scrap B by 29.6, 41.5, 61.3 and 77.5%.

The enhancement in the Izod impact strength when SBS block copolymer is present is an advantageous effect believed to be imparted by the butadiene in the



block copolymer. As one might intuitively expect, the incorporation of butadiene rubber particles within the matrix of plastics enormously improves their impact resistance. This is apparent in the present study. Indeed, the impact resistance imparted by the rubber is the principal reason for its incorporation [15] in rubber-plastic grafts.

The degree of impact resistance obtained depends both on the quantity of the butadiene rubber incorporated and the method of forming the polyblend. The effect of these two variables on the Izod impact strength of polybutadiene/ polystyrene blends was observed in earlier investigations [16] and shown in Figure 4.22. When the polymers are mechanically blended together, or when styrene is graft-polymerized in solution onto the dissolved rubber, an improvement in the impact strength is observed. The greater improvement is noted for the graft polymer. In general, an optimum rubber concentration and phase domain size exists, the values depends on the polymer and rubber concerned. For the range studied using both SBS-I and SBS-II whose rubber content is identical i.e. 69% by weight of the copolymer, an addition by 10% of the SBS block copolymer is most desirable as this is the concentration at which the toughness is enhanced the most.

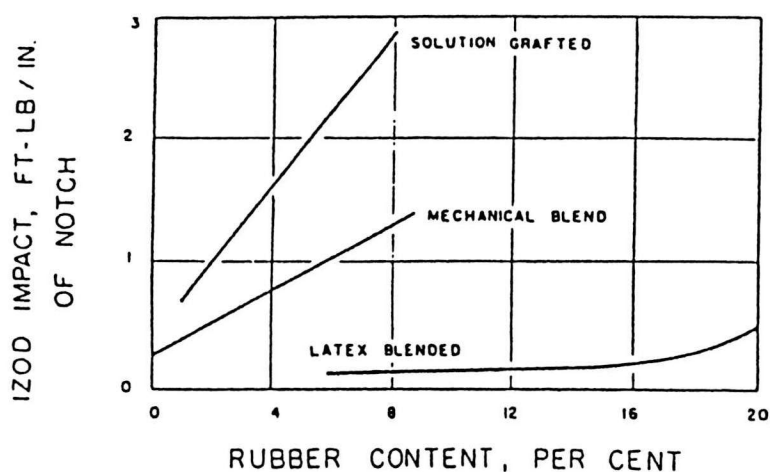


Figure 4.22 : The effect of blend type and the rubber content on Izod impact resistance of polybutadiene/polystyrene blends.

Materials having values of impact strength about 1.0 ft-lb/in of notch or greater are generally classified as impact resistant. Material used in this study have an impact strength in the range of 1.34 to 2.52 ft-lb/in thus can classified as impact resistant. A major factor in impact strength appears to be the ability to yield and undergo cold-drawing at the high rates of loading concerned. Such a correlation is also supported by the measurements of stress-strain behavior during actual impact tests by using an impact tester equipped with a suitable transducer to measure force as a function of time. For example, Bucknall et al. [17] noted three types of fracture behavior in HIPS tested at temperatures between  $-100$  and  $+70$  °C as shown in Figure 4.23.

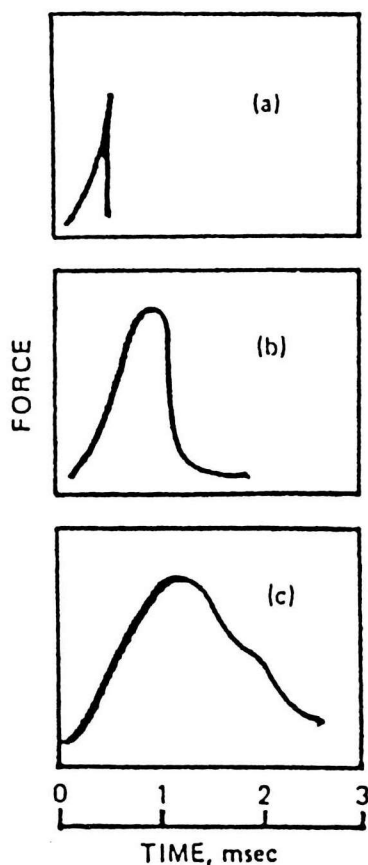


Figure 4.23 : Schematic indicating the three types of fracture during an impact test of HIPS at different temperatures:

(a) Type I ( $-70^{\circ}\text{C}$ ), brittle throughout, (b) type II ( $+10^{\circ}\text{C}$ ), some yielding and ductility during crack initiation, and (c) type III ( $+50^{\circ}\text{C}$ ) general yielding and ductility.

The plot of force against time in Figure 4.17 (a) or type I demonstrates no yielding and no stress-whitening. The fracture is typically brittle fracture for the temperature range between  $-100$  to  $-68^{\circ}\text{C}$  and the impact strength is less than  $0.5$  ft-lb/in of notch. Figure 4.17 (b) or Type II shows some yielding and stress-whitening during crack initiation. When the crack propagated, the fracture is brittle for the temperature range between  $-68$  to  $+10^{\circ}\text{C}$ . The impact strength rises with

temperature, from 0.5 to 1.5 ft-lb/in of notch. Figure 4.17 (c) or Type III demonstrates yielding and stress-whitening throughout the fracture process. The fracture is rather ductile failure for the temperature range +10 to +70 °C. The impact strength rises with temperature, from 1.5 to 4.5 ft-lb/in of notch.

## 4.3.2 Thermal Properties

### 4.3.2.1 Melt Flow Rate

In general, the melt flow rate of a polymer is an indication of relative processability. It reflects the cycle time for processing of that particular polymer. The higher the melt flow rate, the easier the polymer is to be processed under the conditions chosen. Higher melt flow rate resins are generally used in injection-molding applications. Tougher resins with lower melt flow rates are used for extrusion.

The melt flow rate of each scrap and scrap with SBS block copolymer was studied in Section 3.4.1. The results are plotted against the amount of SBS block copolymers as shown in Figure 4.24.

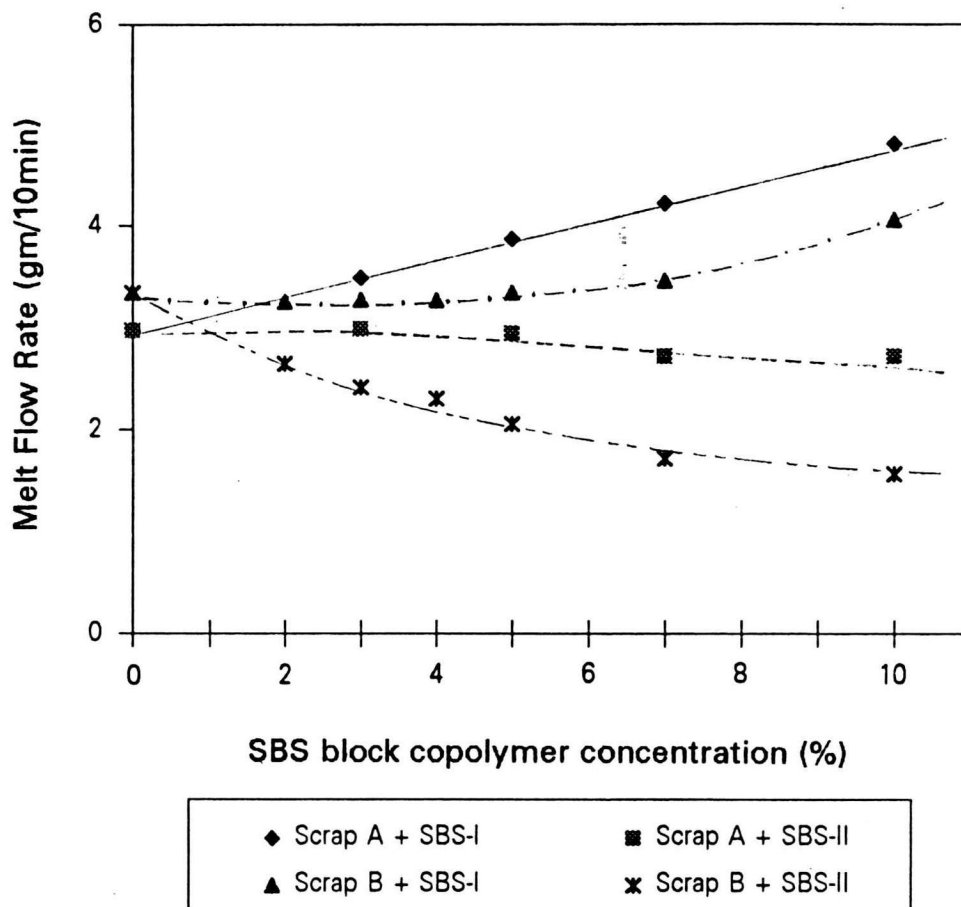


Figure 4.24 : The melt flow rate of the scraps with SBS block copolymer plotted against the SBS block copolymer concentration.

For SBS-I, the higher the amount of SBS-I added to the HIPS scraps, the higher the melt flow rate is observed in the mixture. This trend was found in both types of scraps, A and B respectively. At 3% of SBS-I, the melt flow rate increases by 17.5% for scrap A and decreases by 2.1% for Scrap B when compared with pure HIPS scrap. For pure Scrap B, the melt flow rate is 3.34. This is higher than that of the virgin HIPS by 19.3%. The melt flow rate of the HIPS used in the present study is 2.8, those of the pure HIPS Scrap A and B are 2.97 and 3.34 gm/10 min respectively. The significant increase in the melt flow rate may be caused by the additive in Scrap B.

The most likely contribution for the increase in the melt flow rate for Scrap B is titanium dioxide which is normally applied in the powder form. Hence, the plastics can still melt and flow easily. However, for Scrap B, the higher the amount of SBS-I added to Scrap B, the greater the melt flow rate was found. At 5% SBS-I, the melt flow rate increases by 30.3% for scrap A and 0% for scrap B, which equals to the value of the melt flow rate of pure Scrap B. At 7%, the melt flow rate increases by 42.09% for Scrap A and by 3.59% for Scrap B. At 10% SBS-I, the melt flow rate increases by 62% and 21.6% for scrap A and B respectively.

The addition of SBS-II as an impact modifier has, however, a different effect on the melt flow rate of both scrap systems. The higher the amount of SBS-II, the lower is the melt flow rate. At 3, 5, 7 and 10%, the melt flow rate decreases by 0.34, 1, 8.75 and 8.75% for scrap A and by 27.84, 38.62, 48.8 and 53.29% for scrap B respectively. From the above results, the rate of change in the melt flow rate of Scrap B was higher than that of Scrap A. The different results obtained from Scraps A and B may have arisen from the different component or processing additives in each of the scrap itself. However, the general trend demonstrated by the results of both sets of scrap is that as the amount of SBS-II increases, the melt flow rate decreases.

#### **4.3.2.2 Vicat Softening Point**

The Vicat softening point is used to predict the temperature at which a fabricated part will distort under a specified load. The results of the Vicat softening point is plotted against the amount of SBS block copolymers in Figure 4.25.

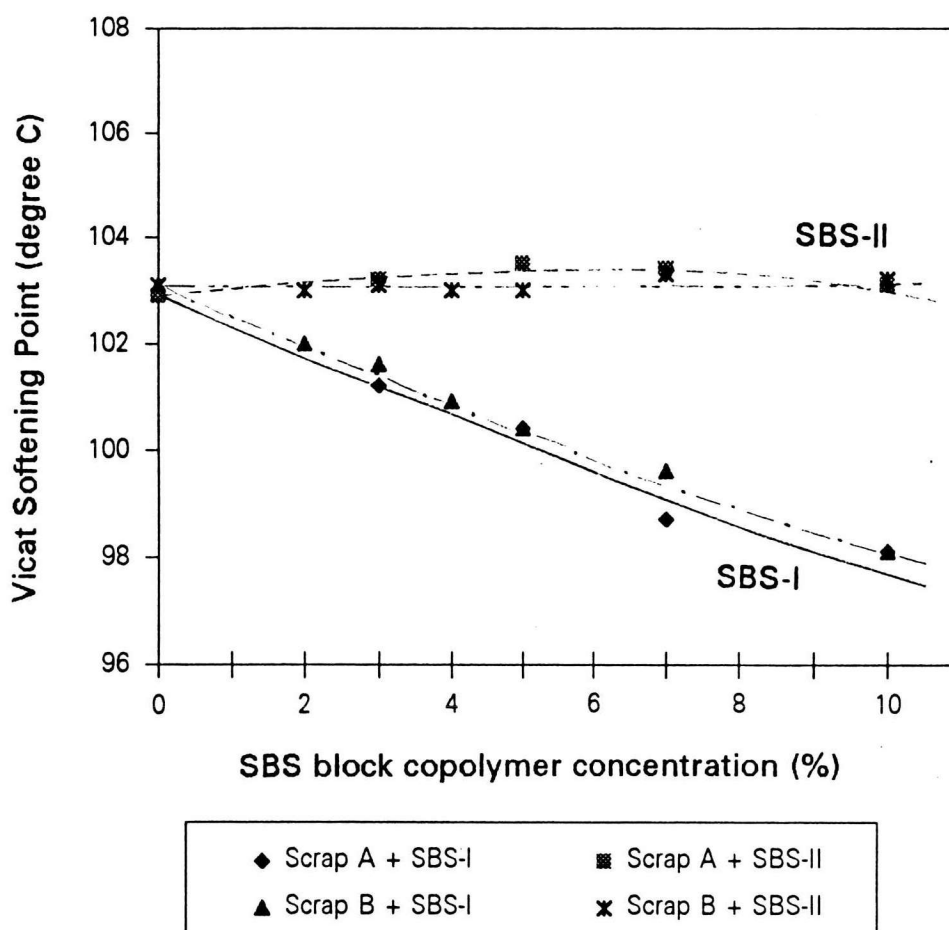


Figure 4.25 : The Vicat softening point of the scraps with SBS block copolymer plotted against the SBS block copolymer concentration.

From Figure 4.19, the amount of SBS-II additive does not have much effect on the HIPS scraps. Only upto 0.4% of change was found in the Vicat softening point when the SBS-II was varied from 0 to 10%. For SBS-I, the addition of SBS-I to the HIPS scraps causes a higher decrease the Vicat softening point. At 5% of SBS-II, the Vicat softening point decreases from 102.9 to 100.4 °C (2.4%) for scrap A and 103.1 to 100.4 °C (2.5%) for scrap B. At 10% the Vicat softening point decreases by 4.7% and 4.8% for Scrap A and Scrap B respectively.

The major difference in the effect of SBS block copolymer on the Vicat softening point is believed to be due to the plasticizer in the HIPS scrap. The plasticizer is defined as nonvolatile solvents added to high polymer to soften and render them plastic. Plasticizer reduce the energy required to induce slippage of polystyrene chains. So, the addition of plasticizer causes some decrease in the Vicat softening point. SBS-I generally contains 29% of plasticizer while SBS-II does not have any plasticizer at all. Hence, the decrease in the Vicat softening point of the mixture occurred only when SBS-II was added to the HIPS scraps.

### **4.3.3 Physical Properties**

#### **4.3.3.1 Color**

The effect of color variation in terms of Lightness index (Color L\*) and the Yellowness index with the various amount of SBS block copolymer was measured by a spectrophotometer. The results are shown in Figure 4.26 and 4.27 respectively.



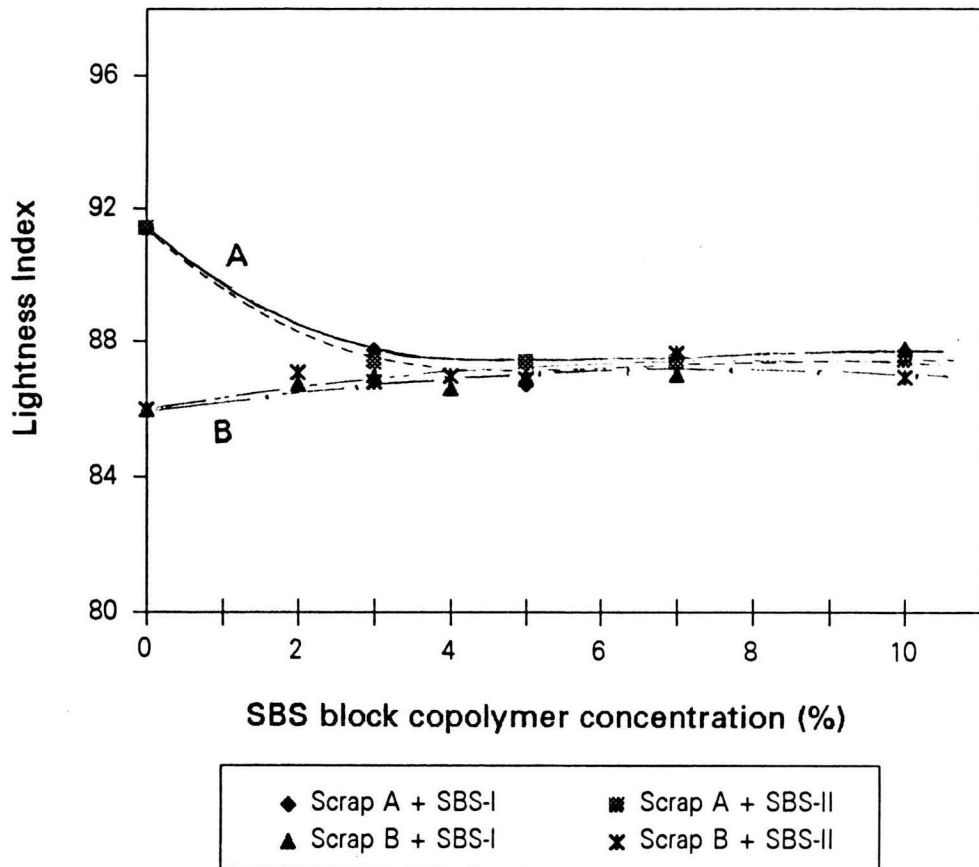


Figure 4.26 : The “Lightness index” of the scraps with SBS block copolymer plotted against the SBS block copolymer concentration.

As illustrated in Figure 4.26, the SBS block copolymer decreases the Lightness index of Scrap A regardless of the amount of SBS block copolymer and slightly increases the Lightness index of Scrap B. For addition of SBS block copolymers, either SBS-I or SBS-II into the HIPS scrap, the Lightness decreases by 4 to 5% for Scrap A and increases by 1 to 2% for Scrap B at any concentrations of additive over the range studied from 2 to 10% of SBS block copolymers.

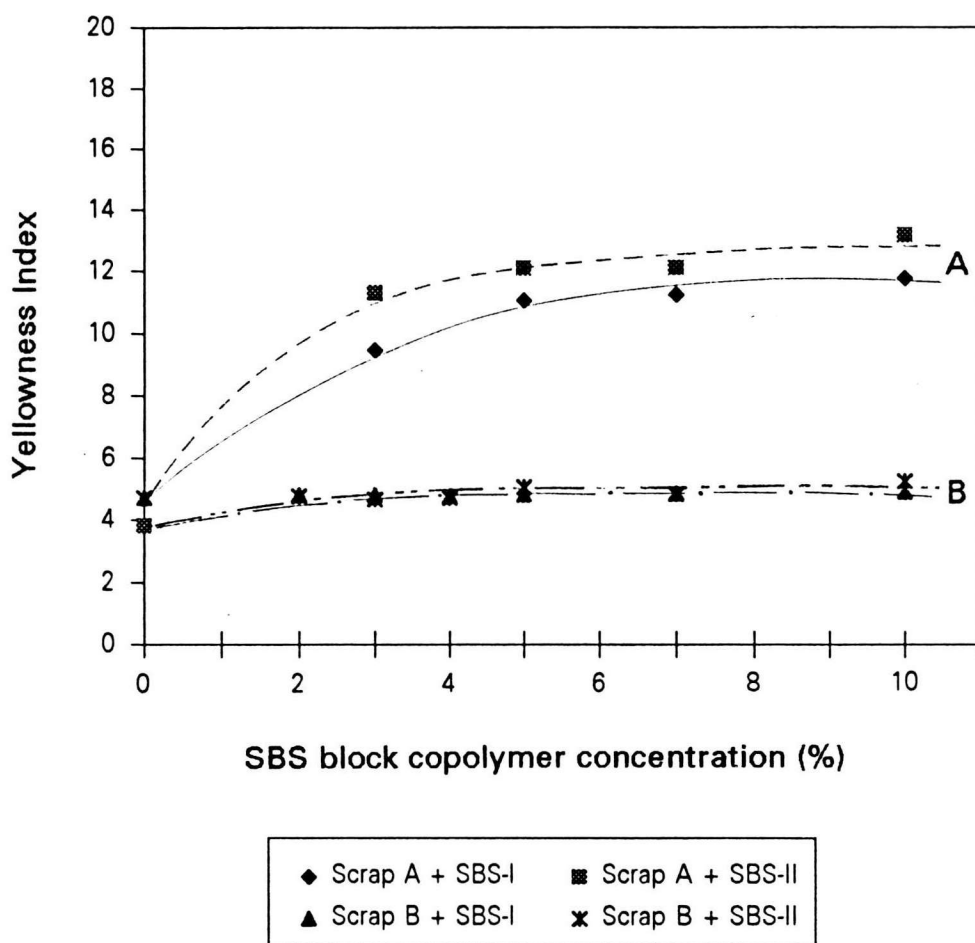


Figure 4.27 : The “Yellowness index” of the scraps with SBS block copolymer plotted against the SBS block copolymer concentration.

In Figure 4.27, the Yellowness index was changed significantly by adding the SBS block copolymer to Scrap A. The index of all scrap A with SBS block copolymer present is found to increase quite dramatically by at least 140% when compared with the pure scrap. However, the maximum change in the yellowness index among the various concentrations of SBS block copolymers is at 24.2% for SBS-I and at 16.4% for SBS-II.

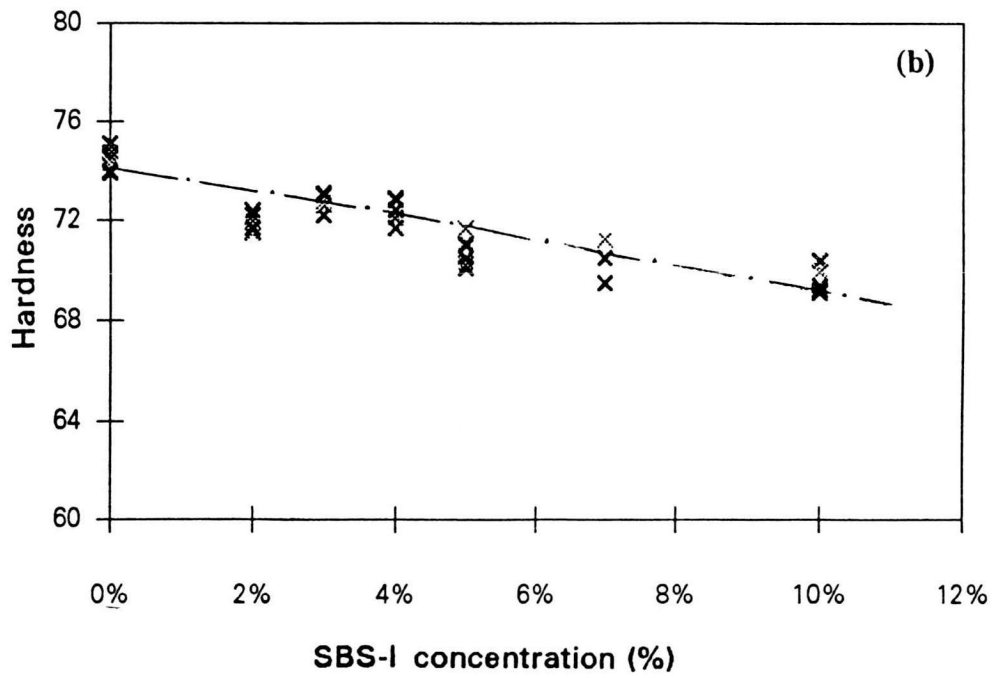
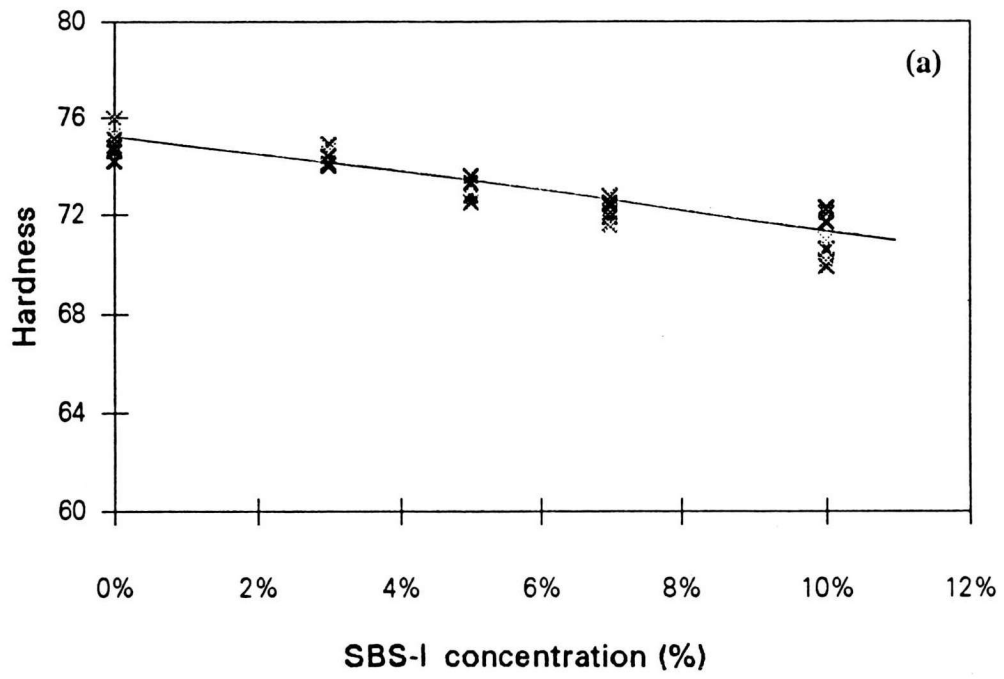
For Scrap B, an addition of both SBS-I and SBS-II does not change the yellowness index of the mixtures. For the range studied, the yellowness index of Scrap B is relatively constant.

No significant difference is detected between the effect of both kinds of SBS block copolymers with the color of the mixture. There are, however, some differences in the change of color in both Scraps A and B. The color change is non significant in Scrap B. The color additive, titanium dioxide, in Scrap B is an important factor. It was originally added as a color pigment to the virgin HIPS. The existence of titanium dioxide in the mixture results in a constant value of the yellowness index for Scrap B throughout all concentrations of the SBS-I and SBS-II studied. While the HIPS was re-compounded, titanium dioxide is believed to be better dispersed and distributed within the mixture. Hence the lightness is enhanced.

All of the above results are the quantitatively measurement of color using a spectrophotometer. This is a very sensitive method applied to indicate the color difference in terms of Lightness and Yellowness Index. Although, when observed visually, the color of the series of mixture is not different and can not be detected by naked eyes.

#### **4.3.3.2 Hardness**

The effect of SBS block copolymer on the hardness of HIPS scrap is shown in Figures 4.28 (a) to (d). Figure 4.28 shows the hardness of Scraps A and B at various amounts of SBS-I and SBS-II.



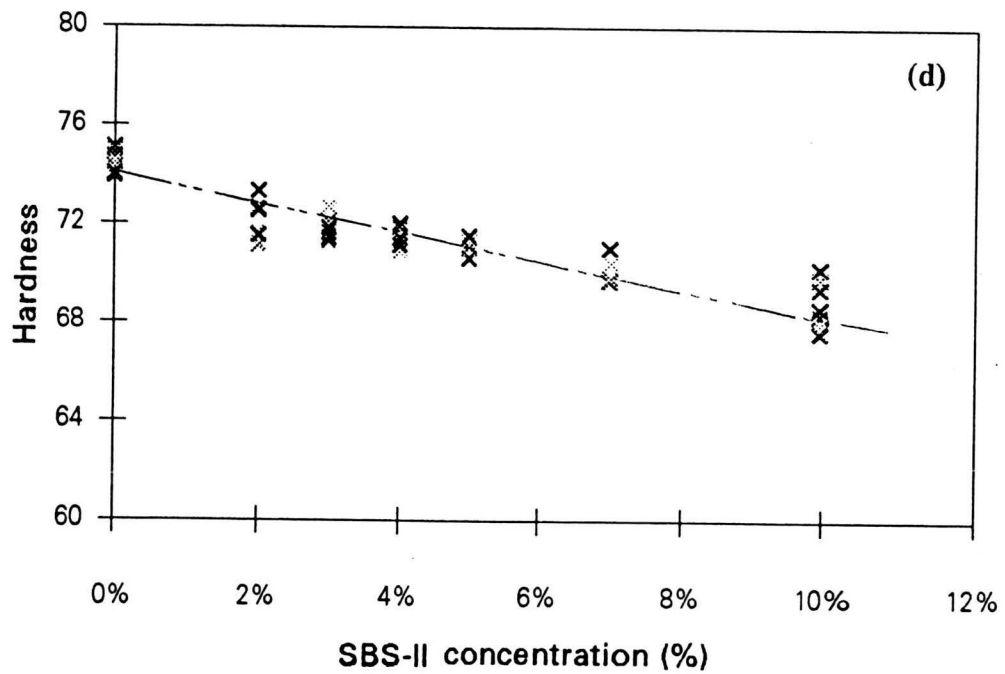
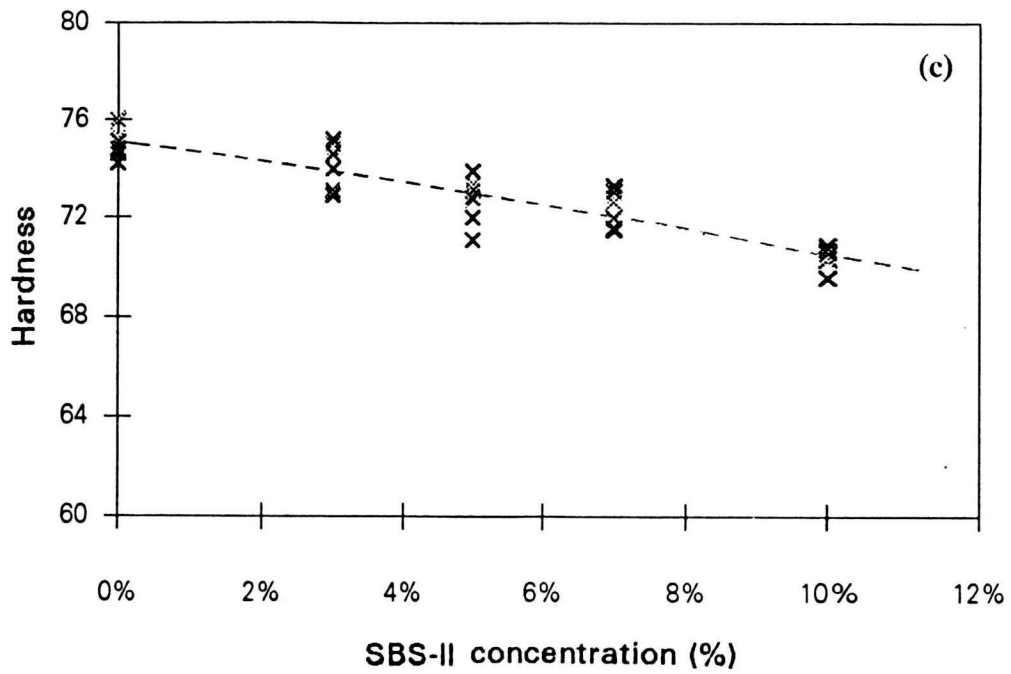


Figure 4.28 : The hardness of the scraps with SBS block copolymer plotted against the SBS block copolymer concentration.

(a) Scrap A with SBS-I

(b) Scrap B with SBS-I

(c) Scrap A with SBS-II

(d) Scrap B with SBS-II

Hardness test is a procedure for determining the indentation hardness of a material. It is usually defined as the resistance of a material to penetration on its surface.

For SBS-I, adding 3, 5, 7 and 10% of SBS-I results in a decrease in the hardness by 0.93, 2.66, 3.86 and 5.32% for Scrap A and 2.41, 4.97, 5.50 and 6.58 for Scrap B. For SBS-II, adding 3, 5, 7 and 10% of SBS-II results in a decrease in the hardness by 1.2, 3.2, 3.46 and 6.12% for Scrap A and 3.62, 4.43, 5.77 and 7.65% for Scrap B.

Hence, it is apparent that the addition of SBS block copolymers in HIPS scraps decreases the hardness of the mixture.

The SBS block copolymer, with its butadiene content is considered rubbery. It is tough and soft. The hardness of the SBS block copolymers themselves are quite low. The SBS-I has a shore A hardness of 47 while that of SBS-II is 71. These are much lower than that of the HIPS. The higher the amount of SBS block copolymer added, the lower is the hardness found in the mixture.

#### **4.3.3.3 Specific Gravity**

The specific gravity of the mixture of HIPS scrap with SBS block copolymer decreases with the increase of SBS block copolymer additive as shown in Figure 4.29. The change of the specific gravity is a gradual decrease with the amount of the SBS block copolymer.

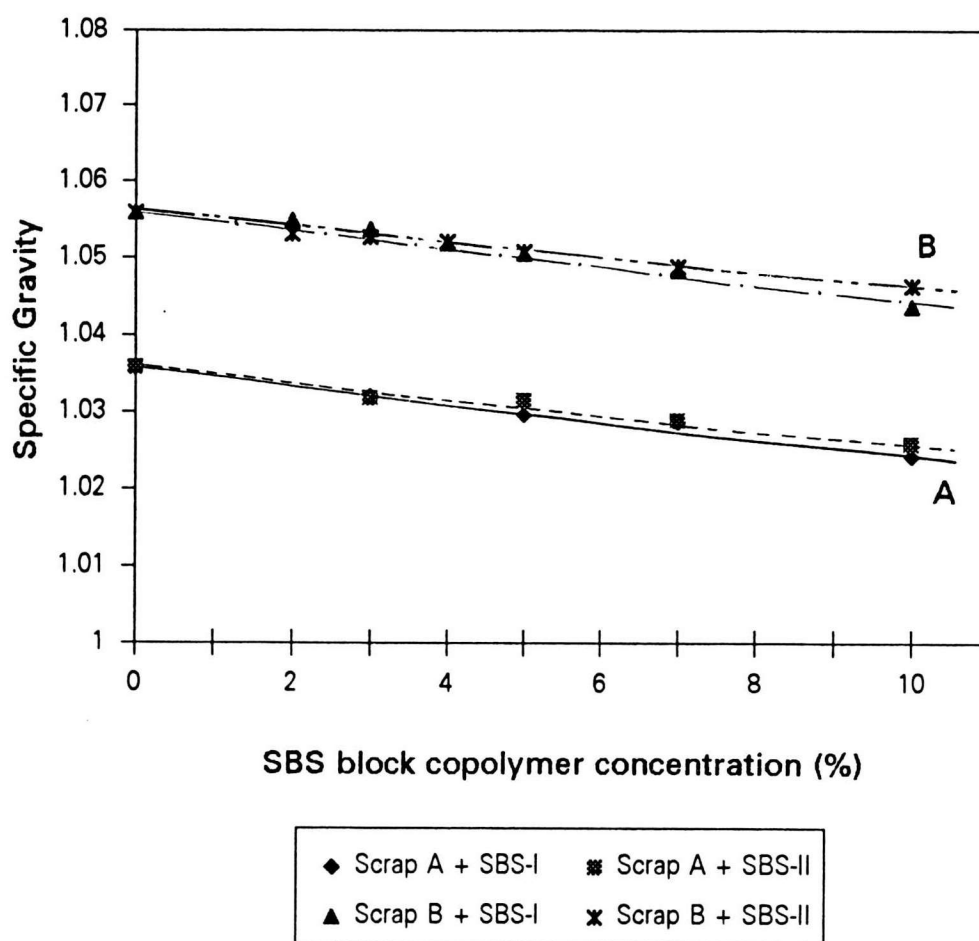


Figure 4.29 : The specific gravity of the scraps with SBS block copolymer plotted against the SBS block copolymer concentration.

For SBS-I, adding 3, 5, 7 and 10% of SBS-I decreases the specific gravity by 0.36, 0.59, 0.68 and 1.11% for Scrap A and by 0.21, 0.50, 0.71 and 1.15% for Scrap B. For SBS-II adding 3, 5, 7 and 10% of SBS-II decreases the specific gravity by 0.38, 0.48, 0.66 and 0.90% for Scrap B when compared with the HIPS scrap.

The specific gravity of Scraps A and B are different because of the additives in Scrap B. Titanium dioxide, the major additive in Scrap B, causes higher specific

gravity for pure Scrap B than that for pure Scrap A. The specific gravity of titanium dioxide is 4.06.

The specific gravity of both SBS block copolymers are lower than that of Scrap A and Scrap B. The specific gravity of Scrap A, Scrap B, SBS-I and SBS-II are 1.04, 1.06, 0.93 and 0.94 respectively. Thus, a higher percentage of SBS block copolymer can lead to a lower specific gravity in the mixture.

#### **4.4 Morphology**

The fracture surfaces of HIPS scraps, SBS block copolymer and HIPS scraps blended with SBS block copolymer were observed in this section.

##### **4.4.1 HIPS Scraps**

When article made from HIPS scrap fails, it tends to fail in a brittle to ductile manner. The overall fracture surface of HIPS scraps, is shown in Figures 4.30 and 4.31.



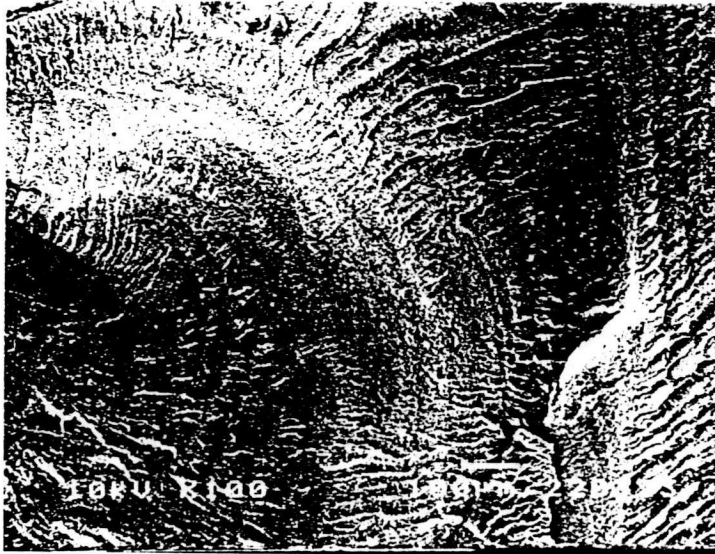


Figure 4.30 : The river pattern of HIPS scraps (x100).

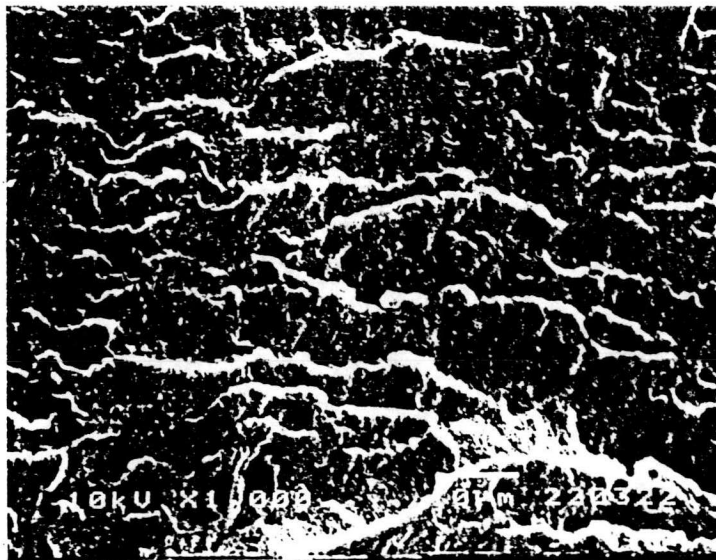


Figure 4.31 : The fracture surface of HIPS scraps (x1000).

Figure 4.30 shows the river pattern. As the fracture progresses, the fracture planes appear to further diverge by crack supersedence. Analogous to the flow in a

river, the direction of confluence of the tributaries indicates the direction of the local crack propagation [18-]. For the fracture micrograph shown in Figure 4.30, the crack propagates from the lower left corner.

Titanium dioxide, the additive initially added in Scrap B, was not observable by this model of SEM fractograph because of the inadequate magnification used. The titanium dioxide particles is quite fine, its diameter is about 180 nm. The micrographs from Tang's study provides information on the morphology of the matrix with titanium dioxide dispersed therein as shown in Figure 4.32.



Figure 4.32 : The fracture surface of polystyrene containing 20% by mass of titanium dioxide.

#### 4.4.2 SBS Block Copolymer

A typical surface of SBS-I is shown in Figure 4.33. A higher magnification is shown in Figure 4.34. For SBS-II, the typical surface is shown in Figure 4.35. A higher magnification is shown in Figure 4.36.

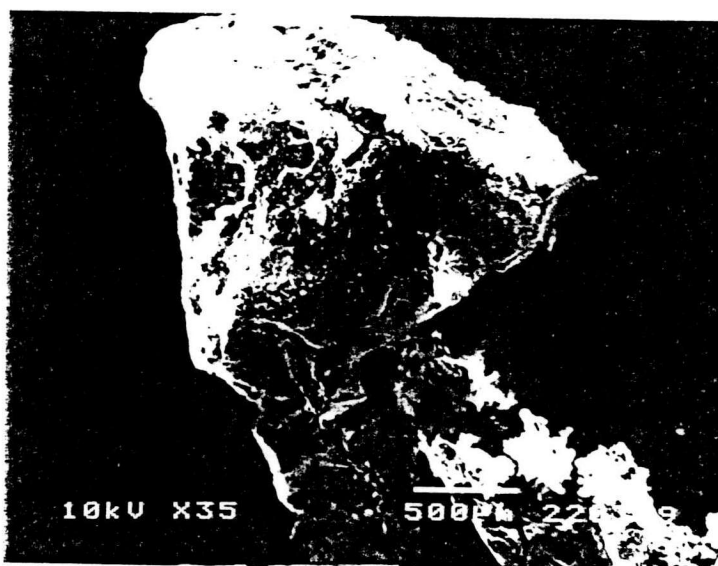


Figure 4.33 : General appearance of SBS-I (x35).



Figure 4.34 : Higher magnification of Figure 4.33 (x1000). The micrograph shows a porous surface characteristic of SBS-I.

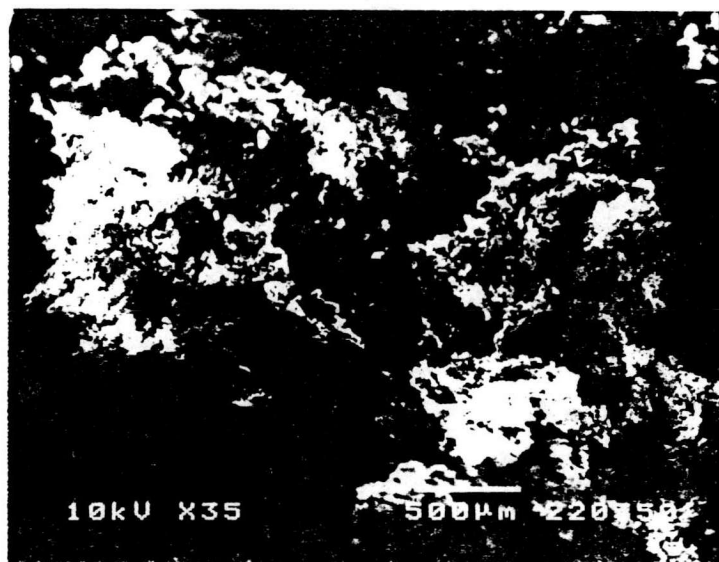


Figure 4.35 : General appearance of SBS-II (x35).

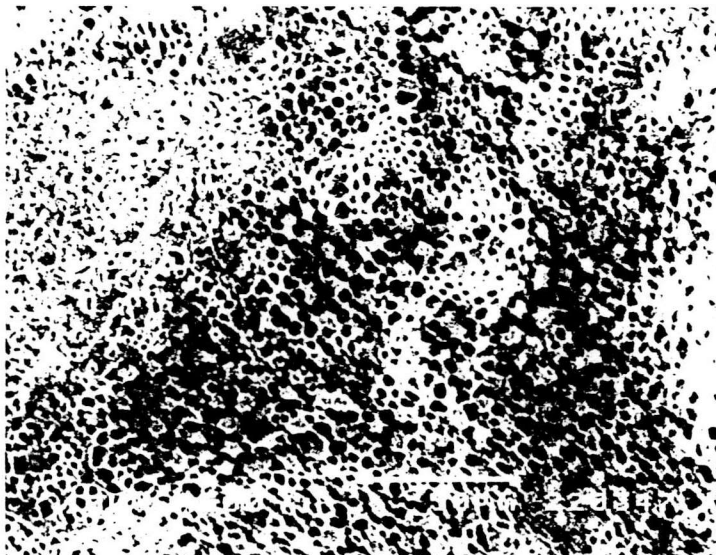


Figure 4.36 : Higher magnification of Figure 4.35 (x 500). The micrograph shows a porous surface characteristics of SBS-II.

From all of the above micrographs, it is apparent that the surface of SBS block copolymer is porous. The pores observed are of various size. In fact it looks as if one phase has been etched out from another phase which acts as the matrix. This surface characteristics may have been induced of the processing of the SBS block copolymer itself.

#### 4.4.3 HIPS Scraps Mixed with SBS Block Copolymer

Figure 4.37 shows the fracture surface of HIPS scrap with SBS-I and a higher magnification is shown in Figure 4.38.



Figure 4.37 : The fracture surface of HIPS scraps mixed with SBS block copolymer (x100).

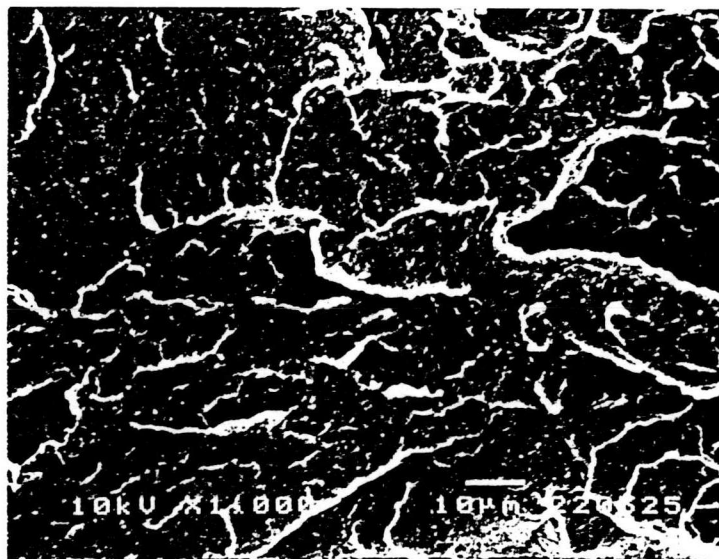


Figure 4.38 : The fracture surface of HIPS scraps mixed with SBS block copolymer at ten times the magnification of Figure 4.37 (x1000).

The typical surface of HIPS scraps shown in Figure 4.30 and 4.31 shows river pattern of crack. No phase separation was observed in the mixture, this is a clear indication of the compatibility and the miscibility of HIPS with SBS-I and SBS-II. Hence, it seems SBS block copolymer can be used as an interphase compatibilizer between the polystyrene and the polybutadiene in the HIPS formulations. Although the two micrographs in Figures 4.39 to 4.40 show residual lumps of SBS-I and SBS-II respectively in the mixture, these lumps of SBS block copolymer was hardly observed on most fracture surface.

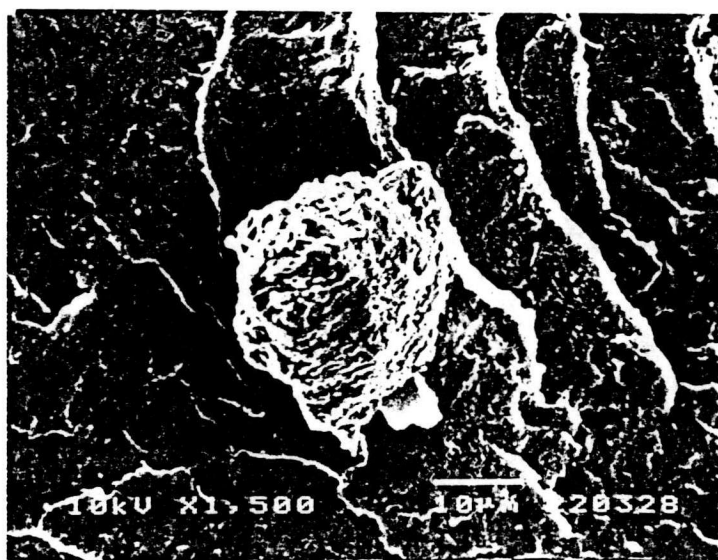


Figure 4.39 : The surface of SBS-I in the mixture (x1500).

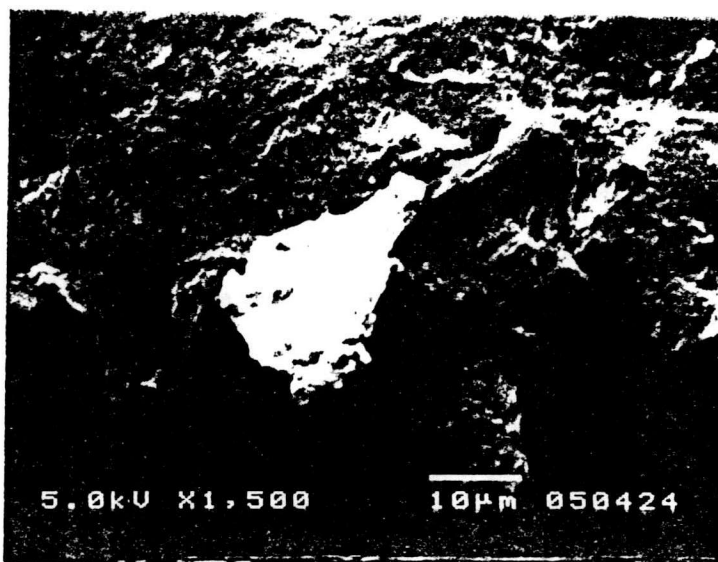


Figure 4.40 : The surface of SBS-II in the matrix (x1500).