CHAPTER IV
RESULTS AND DISCUSSIONS

4.1 Thermal Properties

Thermal stability was determined by DSC. Melting temperature and heat of fusion were investigated by operated under the temperature program which was repeated 5 cycles continuously. Each cycle was heat up from 30°C to 160°C at a rate of 10°C per minute and contained at isothermal temperature for five minutes. After that, the samples were cooled down to 30°C at the same rate. There were 3 levels of % ink removal from surfaces in this work which were 0, 50 and 100%. In each level composed of 2 type of samples which were the virgin plastic, the portion of the bottle that contain no print ink on, and the printed plastic, the portion of the bottle that cover with printed ink.

4.1.1 Melting Temperature

Melting temperature of both virgin and printed HDPE at 0, 50 and 100% ink removal from surfaces are shown in Figure 4.1 From this figure, the first cycle of temperature program represents the original melting temperature of sample. All melting temperatures vary in a range of 131.5-132.166°C which is a small deviation. This range of melting temperature is less than the unprocessed HDPE 's melting temperature, 134°C. That might be a result of the history treated of materials

For unremoval ink from surfaces condition, the printed HDPE shows a similar melting temperature as the virgin HDPE. Three conditions of percentage of ink removal from surfaces which were 0, 50 and 100% exhibit the uniform values of melting temperature for both virgin and printed types of samples Since the second cycle of temperature program represent melting temperature of plastic without its history. From Figure 4.1, all samples do not show the significant changes of melting temperature after treated with 5 times of the experimental procedure.

Melting temperature of both virgin and printed without deinking after 5 times of re-extrusion are observed in Figure 4.2. The first cycle of temperature program indicate the increasing of melting temperature in both virgin and printed plastic after 5 times of reprocessing. From the second to the fifth cycle, there is no significant observed in changing of the virgin and the printed HDPE after the samples were treated with 5 times of re-extrusions.

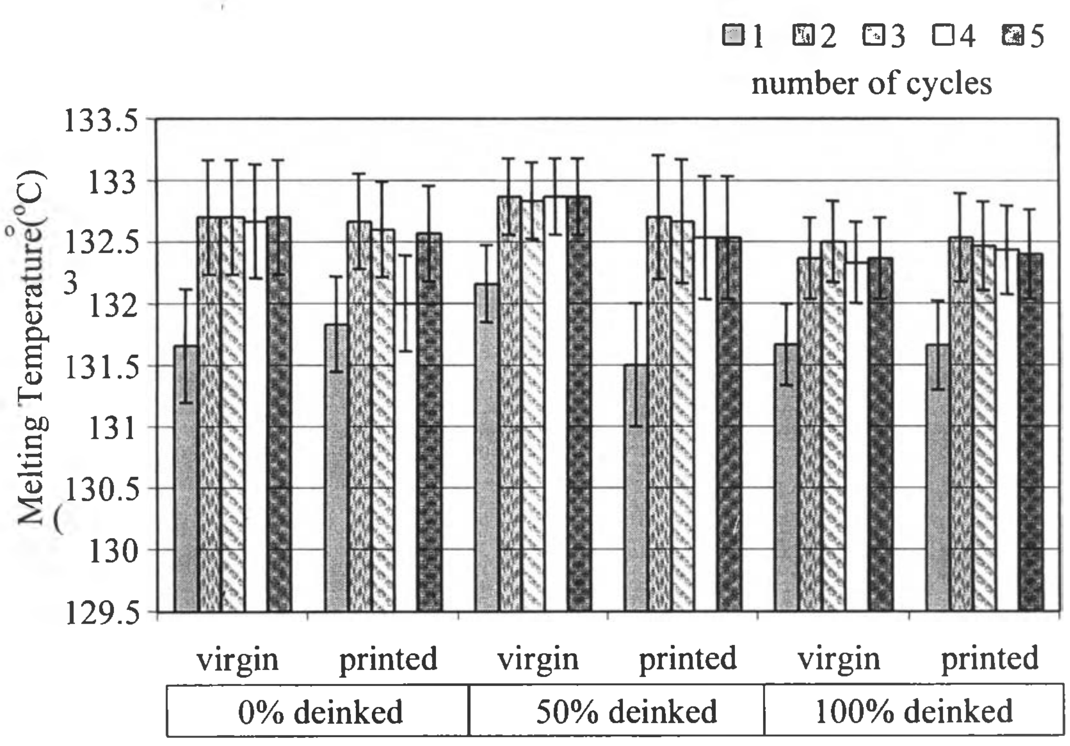

Figure 4.1 Melting temperature of re-extruded HDPE at 0, 50 and 100% ink removal from surfaces.

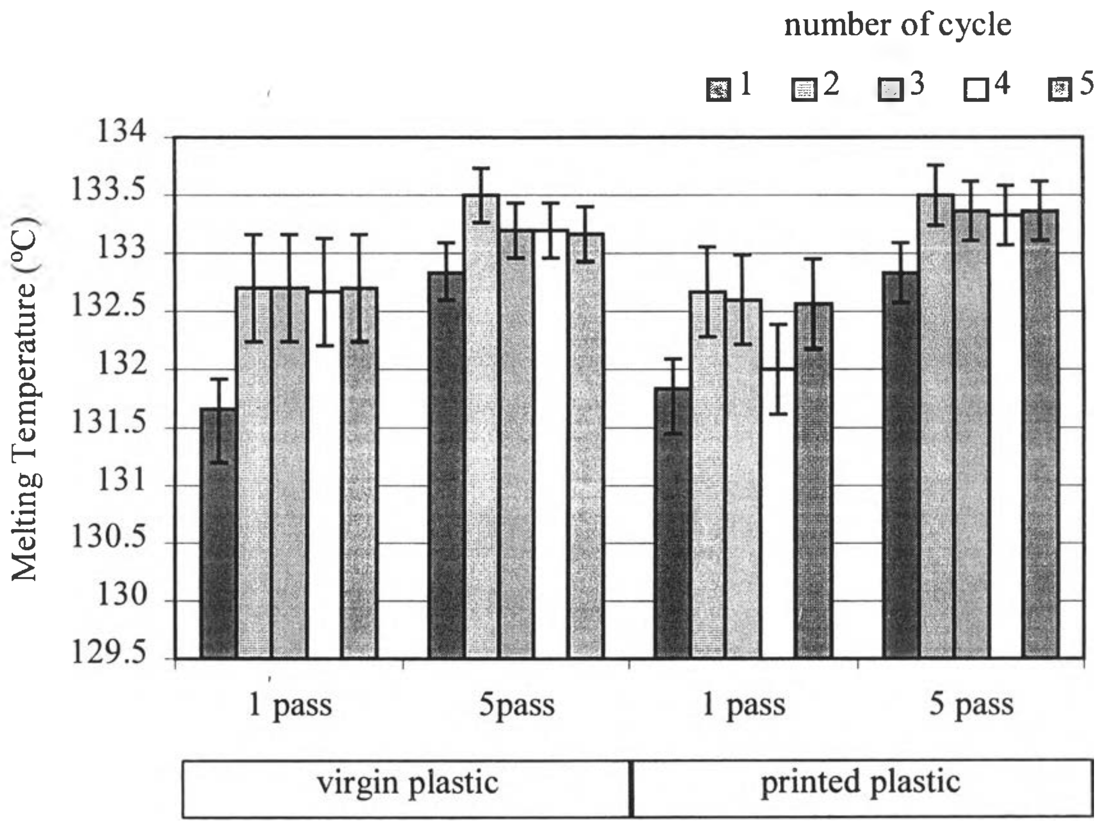

Figure 4.2 Melting temperature of the virgin and the printed HDPE after 5 times of re-extrusions.

4.1.2 Percent of Crystallinity

Percent of crystallinity of the virgin and the printed HDPE at 0, 50 and 100% removal ink from surfaces are shown in Figure 4.3. The results show that after the first cycle of every samples exhibit the original %crystallinity of materials. At 0% deinked from surfaces condition, the printed HDPE exposes the lower % crystallinity than the virgin. This might be a result from ink contamination caused the imperfection of crystal structure of HDPE. The results of the virgin samples at 0, 50 and 100% ink removed from surfaces show almost the similar values in a range of 66.27-67.27% which is a very small deviation. The printed samples at 0, 50 and 100% deinked from surfaces indicate the increasing % crystallinity of 63.81, 65.26 and 66.79%

respectivell. These level of crystallinity correspond to the amount of residual ink on HDPE surfaces, the less amount of contaminate ink, the higher of % crystallinity. There is no significant changes in % crystallinity of samples from the experiment which start from the second cycle of temperature program. From % crystallinity and melting temperature results since the second cycle of the temperature program mean all samples did not exposed the significant changes in thermal degradation.

Figure 4.4 presents % crystallinity of 5 passes re-extruded virgin and the printed HDPE without deinking. It indicates the % crystallinity of both virgin and printed HDPE increase 1.65 and 5.70% respectively after 5 times of reprocessing. Doyan *et al.* (1994) observed that crystallinity is higher after 10 cycles than 1 cycle of re-extrusion. They also concluded that both chain scission and crosslinking occurred simultaneously during extrusion. Chan scission was the dominant factor for the first cycle and crosslinking take over after a while because the accumulation of free radical during extrusion.

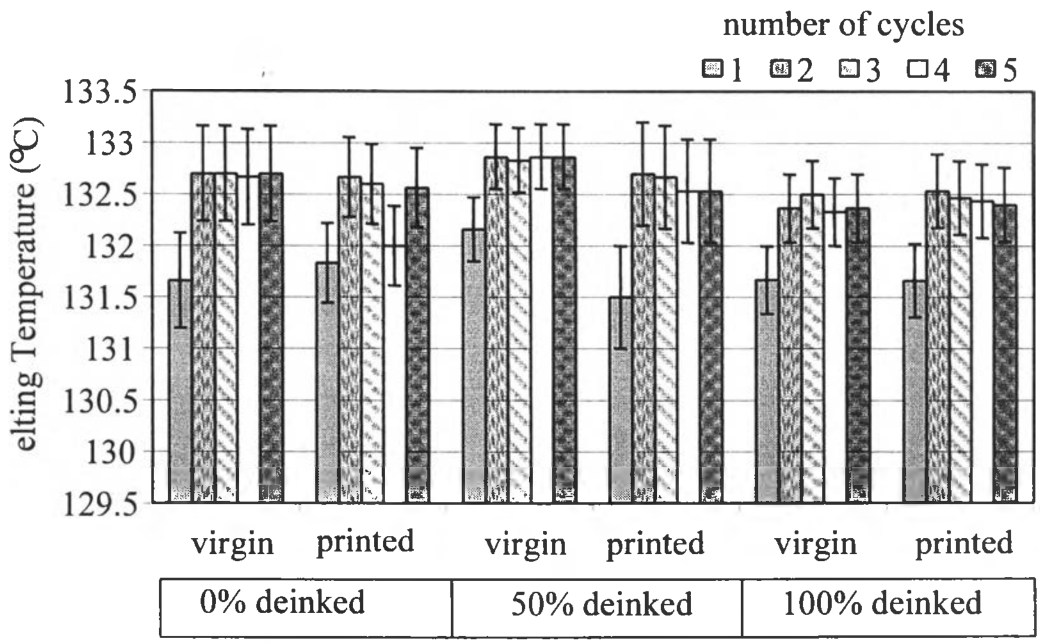

Figure 4.3 Percent of crystallinity of re-extruded HDPE at 0, 50 and 100% ink removed from surfaces.

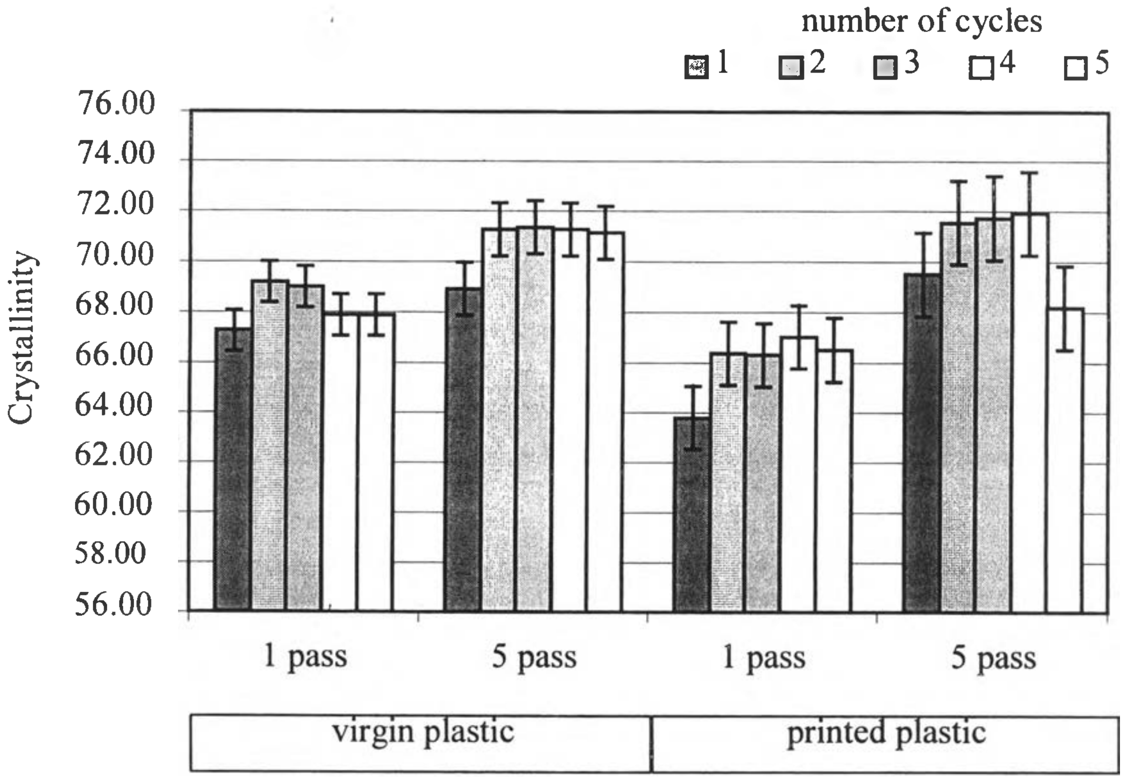

Figure 4.4 Percent of crystallinity of the virgin and the printed HDPE after 5 times of re-extrusions.

4.1.3 Decomposition Temperature

The results of decomposition temperature of both virgin and printed HDPE at 0, 50 and 100 % ink removal from surfaces present in Figure 4.5.It is observed that decomposition temperature of all materials vary in the range of 432 to 445°C. This values are not significant different from the range of HDPE 's decomposition temperature which is 335-450°C (MarH,1986). Moreover, the results from TGA as shown in the appendix C also indicate that there is only HDPE component in each samples. It could be implied that the amount of ink is very small when compared to the amount of plastic.

Figure 4.6 shows decomposition temperature of 5 passes re-extruded virgin and printed HDPE without deinking. Both cases present the slightly higher decomposition temperature after 5 times of re-extrusion. But they are still in the range of 335-450°C.However, it could be implied that these materials can be processed at high temperature processing condition (300 °C) with small effect of thermal decomposition.

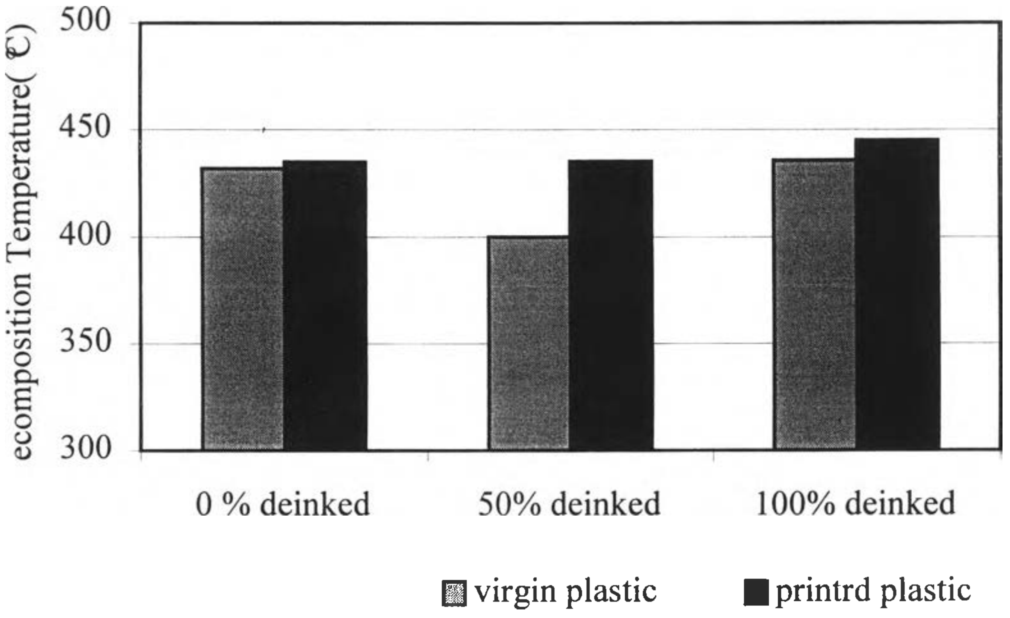

Figure 4.5 Decomposition temperature of re-extruded HDPE at 0, 50 and 100% ink removed from surfaces.

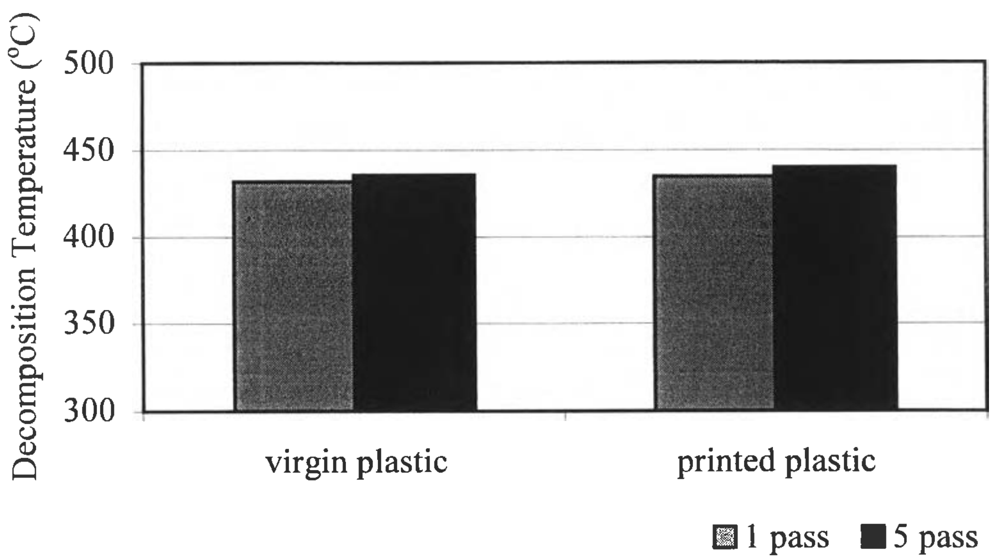

Figure 4.6 Decomposition temperature of the virgin and the printed HDPE after 5 times of re-extrusions.

4.2 Mechanical Properties

The same series of samples in thermal stability were test in the mechanical properties testing.

4.2.1 Tensile Strength

Figure 4.7 shows tensile strength of both virgin and printed re-extruded HDPE at 0, 50, and 100% ink removal from surfaces conditions. It is founded that there is no trend shown in Figure4.7. Tensile strength values change in the narrow range of ca 27 to 31 MPa. All tensile strengths' materials are less than the original in the range of 8-20%. This small reducing may be due to the histories of materials. For unremoval of ink condition, the printed and the virgin plastic show very close values to each other. Tensile strength of the virgin plastic at 3 levels of ink removal from surfaces exhibited that tensile strength at unremoval of ink condition is slightly higher than the values of the virgin plastics which deinked from surfaces plastic by the cationic surfactant. Moreover, the printed plastics at 50 and 100% ink removal from surfaces exhibit the slightly lower tensile strengths than the printed plastic without deinking.

From Figure 4.8, tensile strength of both virgin and printed samples without deinking after 5 passes of extrusion are presented. The result of virgin HDPE from the first pass to the fifth pass changes only 0.13% while the values of the printed sample change only 0.87% at the same condition. This is correspond to Malloy et al. (1998) study. They indicated that both natural and white HDPE homopolymer exhibit small change (less than 6%) in the yield strength after 12 recycles histories.

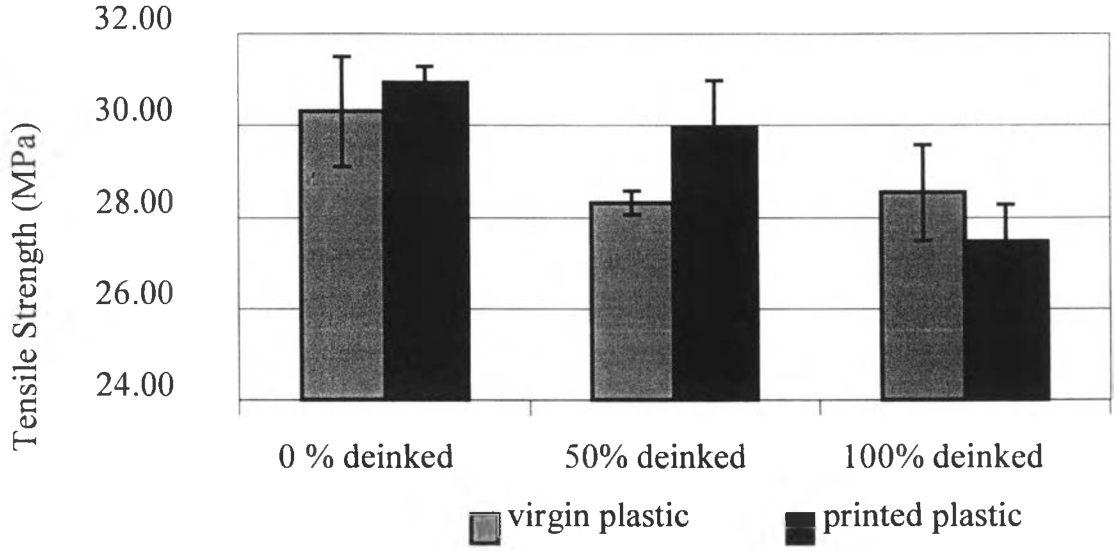

Figure 4.7 Tensile strength of re-extruded HDPE at 0, 50 and 100% ink removed from surfaces.

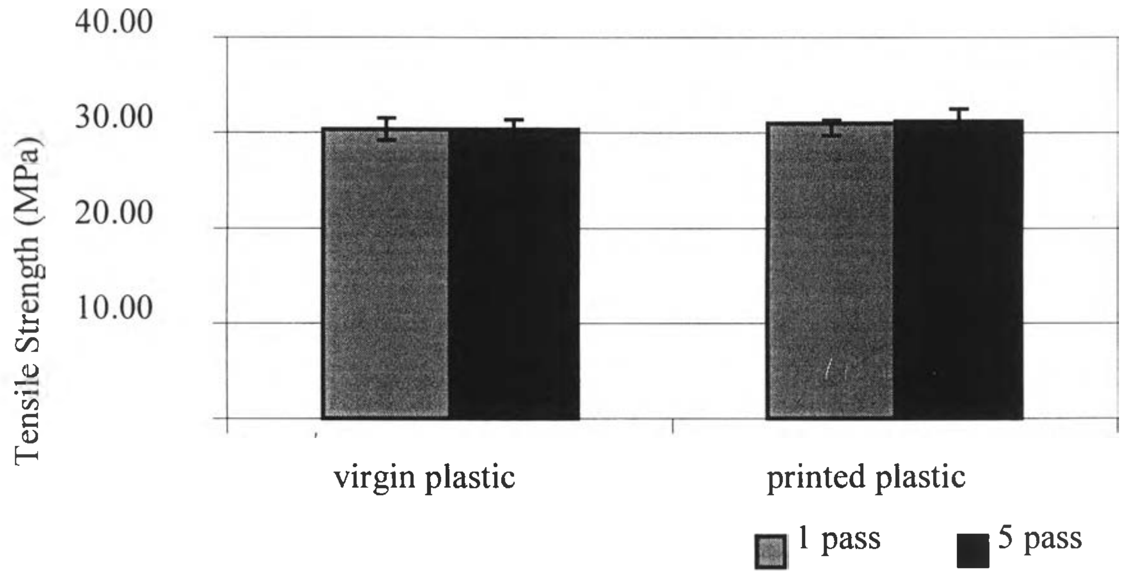

Figure 4.8 Tensile strength of the virgin and the printed samples after 5 times of re-extrusions.

4.2.2 Impact Resistance

Impact resistance of the virgin and the printed HDPE at various % deinked from surfaces are shown in Figure 4.9. The values of all impact resistance vary between 11.78 to 14.82 kJ/m^2 which is a small range. As exhibits in Figure 4.9, impact resistance of both virgin and printed plastic types without deinking show the lower values than the printed and the virgin samples which are treated with the cationic surfactant at 50 and 100% removal of ink from surfaces. Impact resistance of virgin sample corresponded to its degree of crystallinity result which is the highest one. At higher degree of crystallinity, impact strength decrease (Nelsen, 1994). On the other hand, the result of the printed HDPE without deinking from surfaces did not correspond to the above statement. It might be because there were some additives put in the plastics and ink formula that effect impact resistance of the sample.

Figure 4.10 exhibits impact resistance of both virgin and printed HDPE without deinking from surfaces which reprocessed for 5 passes of extrusion. It is founded that both virgin and printed samples show the higher impact resistance after 5 passes of extrusion. The virgin HDPE 's value presents the higher value than the printed HDPE 's value after 5 times of reprocessing.

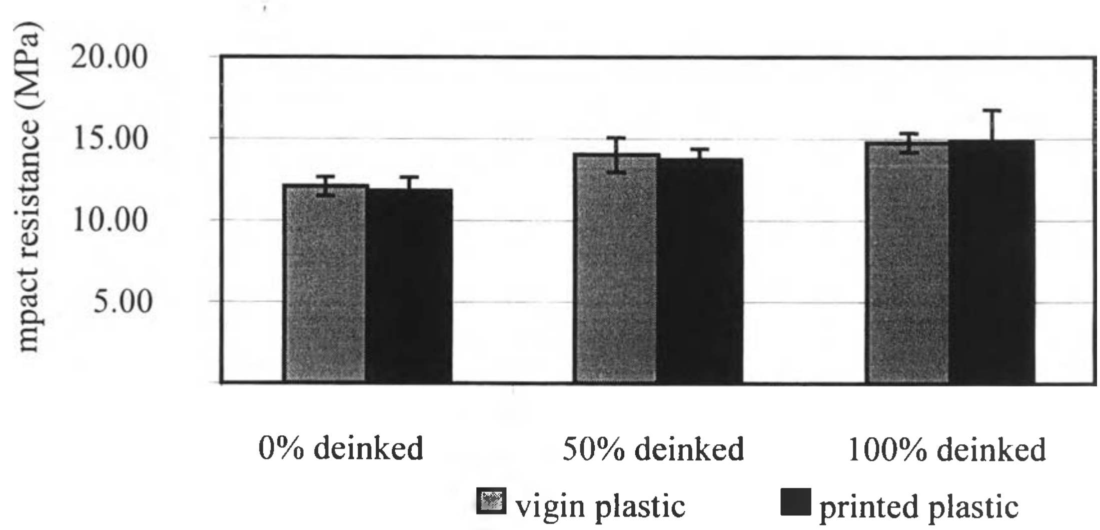

Figure 4.9 Impact resistance of re-extruded HDPE at 0, 50 and 100% ink removal from surfaces.

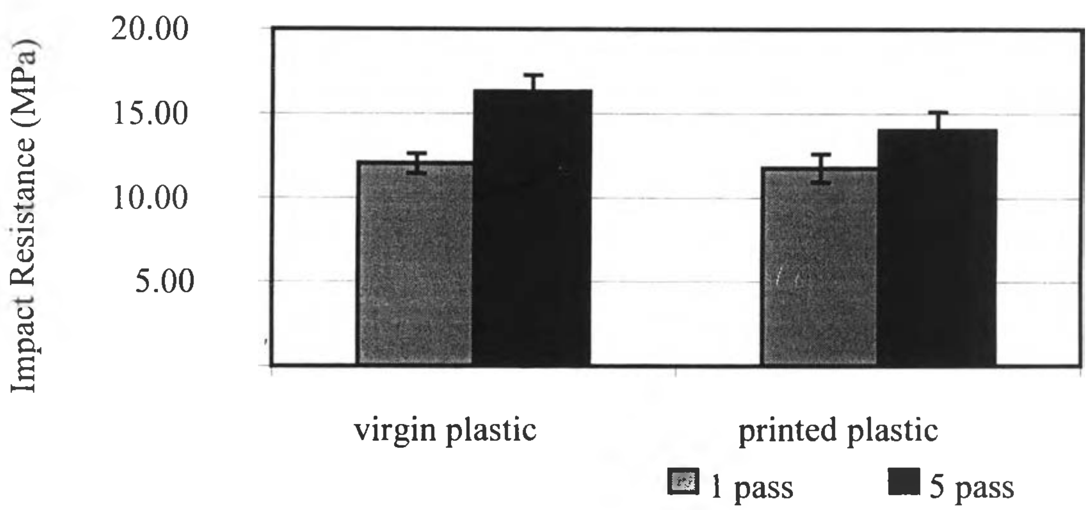

Figure 4.10 Impact resistance of the virgin and the printed samples after 5 times of re-extrusions.

4.2.3 Hardness

Hardness of the virgin and the printed HDPE at 0, 50, 100% ink removed from surfaces are shown in Figure 4.11. All sample exhibit the uniform values of shore D in a range of 69.45-71.75. Although after 5 times of re-extrusion, the hardness of the virgin and the printed HDPE also do not exhibit the significant changes in their hardness as shown in Figure 4.12.

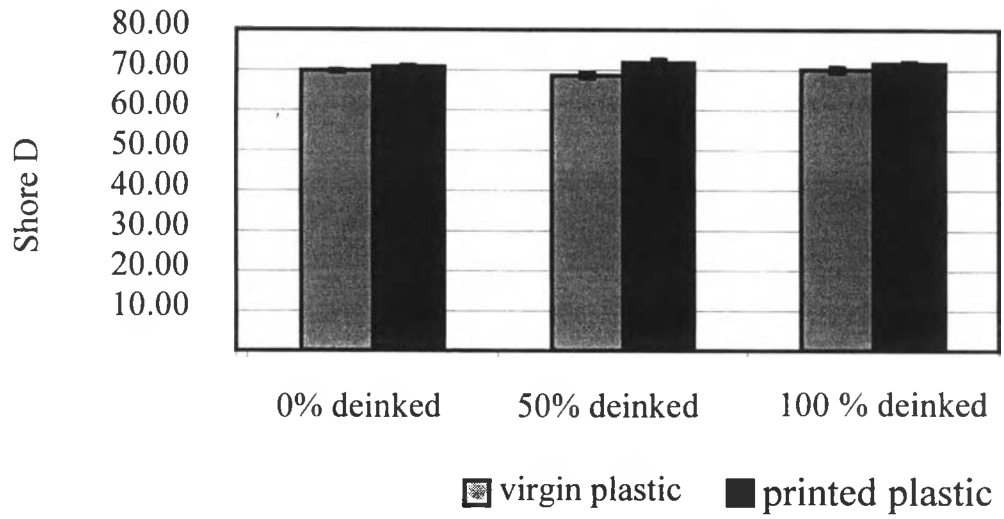

Figure 4.11 Hardness of re-extruded HDPE at 0, 50 and 100% ink removal from surfaces.

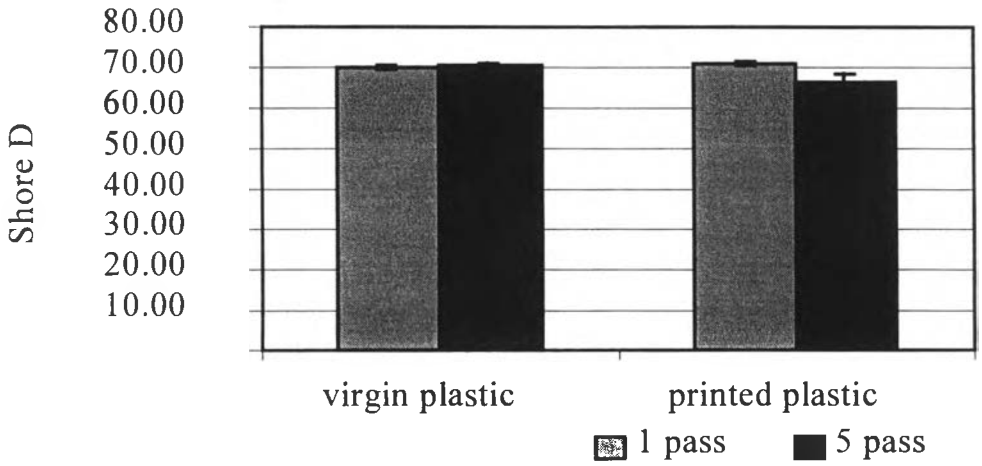

Figure 4.12 Hardness of the virgin and the printed samples after 5 times of re-extrusions.

Gecol *et al.* (1998) pointed out that ink contamination makes the plastic less stiffness and weaker. But there are some different point s between her work and this work. The plastic film was used as material in their work and this plastic film composed of HDPE and LDPE while this work used rigid blow mold HDPE bottles as materials. However, the important point is the amount of residual ink when compared to whole amount of plastic film is dramatically greater than the amount of residual ink in HDPE bottles. In HDPE bottles case, residual ink act as only small contamination when compare to the plastic film. Hence it does not give the observe results as the plastic film case.

In polymer field, the significant in mechanical properties changes is changing in ten times or one hundred times. The small deviations of mechanical properties show in the above figure could be a result from contamination of ink in plastic that causes the imperfection crystal structure. This imperfection crystallinity could act as the stress point and applied force cannot disperse well along the specimen. In addition, materials in this work were commercial HDPE bottles, quality of materials cannot be controlled hence it should be another considered factor that it might the reason of small deviation of the mechanical properties shown above. Moreover, there are many additives put in both bottles and print screen ink that could be show the very small deviation on thermal and mechanical properties of re-extruded HDPE above. However, sample preparation could be one point that cause the small deviation of mechanical properties present.

4.3 Color Difference

Color difference is difficult to obtain and describe universally. A spectrophotometer L*-a*b* color coordinate was used to evaluate the color difference in this work. The color difference, ΔE, obtained from

$$\Delta E \quad = \quad ((\Delta a^*)^2+(\Delta b^*)^2+(\Delta L^*)^2)^{1/2}$$

From Table 4.1, ΔE based on the color of the virgin HDPE without deinking. It is founded that the printed re-extruded HDPE at 0 and 50% ink removed from surfaces show dramatically increasing of ΔE which are 31.107 and 31.521 respectively. These two values of the color difference are very close to each other. This might be due to contaminate ink in plastic. The exactly component of this ink is unknown according to the commercial secret. This print screen ink is pigment concentration when compared to color used in polymer process which is polymer concentration. Hence only few amount of the printed screen ink give the visually color in re-extruded plastic. The color difference is affected by many factors. Although this print screen ink showed the blue color but the formula of this ink contain more than only blue pigment. Thus when some of inks are removed, the ratio of composition in ink also changed and the difference of color shade in plastic might be present. Moreover, the processing could be one factor of color deviation.

As shown in Table 4.1, the color difference of the virgin HDPE at 50 and 100% deinked from surfaces and the printed HDPE at 100% deinked from surfaces exhibit almost the similar values. This can be implied that deinking with cationic surfactant completely removed ink from surfaces. However, these 3 values are greater than the color reference, which was the virgin sample without deinking ,ca 2 while the commercial acceptation value is 1. This might be due to the raw materials which are commercial HDPE bottles. These commercial bottles compose of recycled and fresh materials together which is the save cost way in practicality. Hence there could be some impurity plastic that make these virgin HDPE at 50 and 100% ink removed from surfaces condition contain increasing of the color difference.

Table 4.1 The color difference of the virgin and the printed HDPE at 0, 50 and 100% ink removal from surfaces.

samples		L*	a*	b*	ΔE	Commend
0% ink removal from surfaces	virgin	72.09	-1.19	-8.06	-	-
	printed	43.25	5.02	-17.92	31.11	darker, more blue, redder
50% ink removal from surfaces	virgin	71.63	-0.70	-10.32	2.35	darker, less green, more blue
	printed	49.71	9.50	-27.52	31.52	darker, redder, more blue
100% ink removal from surfaces	virgin	71.37	-2.14	-10.04	2.49	darker, more green, more blue
	printed	71.69	-2.77	-10.30	2.76	darker, more green

As shown in Table 4.2, the virgin HDPE without deinking exhibits the shift of color equal to 5.99. Malloy *et al.* 1998 studied the color change of natural HDPE after 12 cycles of extrusion. They founded that ΔE of the natural HDPE increase with a number of passes. Hence this work is corresponding to their result. It could be observed the increasing of color difference from the printed HDPE without deinking. Its value increase from 31.107 to 35.793 when the number of passes increased from 1 to 5 passes. This could be indicated that the increasing of a number of passes, the increasing of color difference presents.

Table 4.2 The color difference of the virgin and the printed HDPE without deinking after 5 passes of re-extrusion.

Sample		*L	*a	*b	ΔE	Commend
virgin	1 passes	72.091	-1.193	-8.063	-	-
HDPE	5 passes	68.307	-2.859	-4.591	5.399	darker, more green, less blue
printed	1 passes	43.247	5.016	-17.919	31.107	darker, more blue, redder
HDPE	5 passes	38.513	4.185	-19.233	35.793	darker, more blue, redder