

CHAPTER 3 : RESULTS AND DISCUSSION

3.1 FTIR Analysis

Results of FTIR-Transmission analysis are shown in Figures 2 to 11 and results of FTIR-ATR analysis are shown in Figures 12 to 21.

The spectra obtained from FTIR-Transmission on plastic wrapper of Kosyn 1502 (Figure 5), Kosyn 1712 (Figure 6), Ubepol 150 (Figure 7) and plastic bag of curative (Figure 10) and small tyre ingredients (Figure 11) were found differ in shape and intensity of the band as compared to those obtained from FTIR-ATR (Figures 15, 16, 17, 20 and 21) even though FTIR-Transmission and FTIR-ATR were performed on the same sample. However, for plastics wrapper of SDR 20CV (Figures 2 and 12), SDR 10 (Figures 3 and 13), SDR 10 CV (Figures 4 and 14) and plastics bag of reclaimed rubber (Figures 8 and 18), crumbs (Figures 9 and 19), the spectrum obtained from FTIR-Transmission is about similar to FTIR-ATR in term of shape but not in term of band intensity. This is similar to a study conducted by R.T. Graf et. al.¹⁸ on polymethyl methacrylate. In that study, R.T. Graf et.al explained that the differences were the effects of optical distortion.

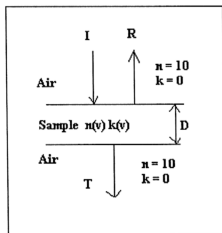


Figure 22 : Schematic diagram of FTIR Transmission¹⁸

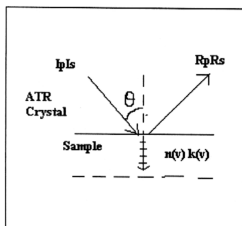


Figure 23 : Schematic diagram of FTIR-ATR¹⁸

(Note : n = refractive index; k = adsorption index)

Based on the relative intensity of the peak at about 1464 cm^{-1} to the peaks at about 720 cm^{-1} , the FTIR-ATR spectrum of plastics give a higher band intensity at longer wavelengths compared to FTIR-Transmission spectrum. This is because the effective depth to which the radiation penetrates the surface of the sample increases at longer wavelength for FTIR-ATR.¹⁹

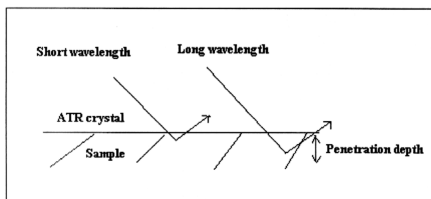


Figure 24 : Penetration depth¹⁹

The depth of penetration is the distance from the crystal sample interface where the intensity of the evanescent wave decays to $1/e$ ($\approx 37\%$) of its original value.²⁰ It is defined as :

$$d_p = \lambda / (2\pi n_1 (\sin^2 \theta - n_{21}^2)^{1/2})$$

where λ is the wavelength of infrared radiation, n_1 is the refractive index of the ATR crystal, θ is the angle of incidence, and n_{21} is the ratio of the refractive indices of the sample and the ATR crystal.²⁰

Interference fringes observed in the sealed cell pathlength calibration were detected present in the FTIR transmission spectrum especially for the plastic bag of curative (Figure 10) and plastic wrappers of SDR10 (Figure 3) and SDR10 CV (Figure 4). The above observation confirms interference fringes in the spectrum can be present in an empty or partly filled cell; or within a polymer film which has highly polished surface.¹⁹ For sealed cell, fringes are caused by interference between radiation which is transmitted through the cell and radiation which is reflected from the inner surfaces of the cell.²¹ For FTIR transmission spectrum of plastics, interference fringes in the spectrum are due to reflections occurring within the plastic film.

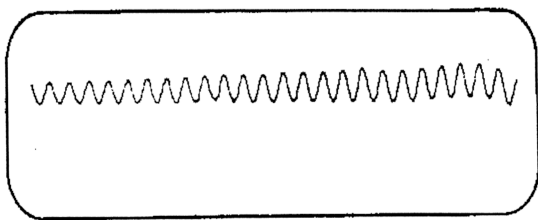


Figure 25 : Interference fringes²¹

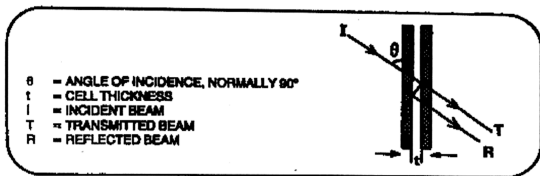


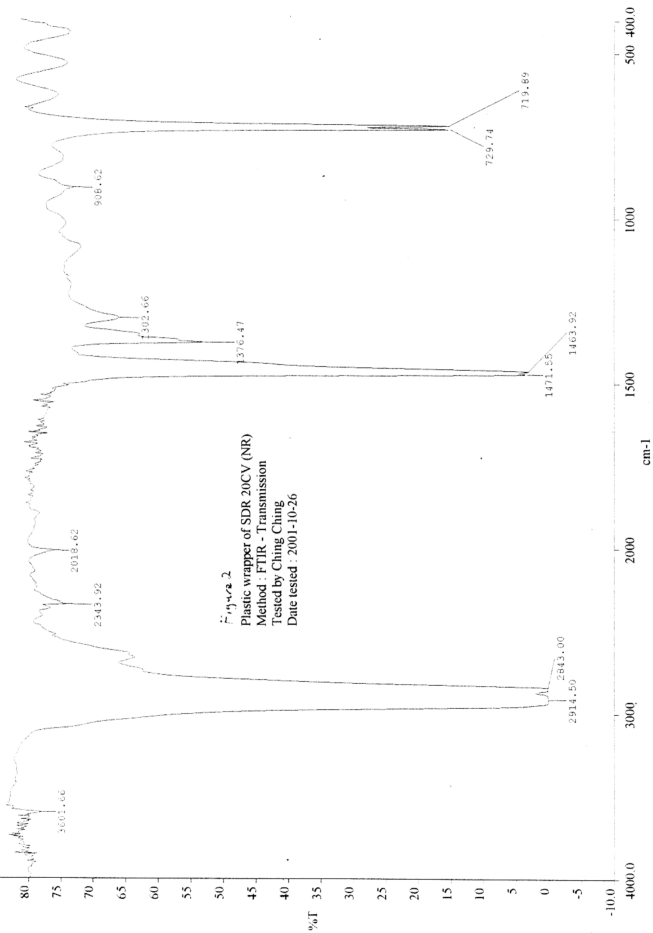
Figure 26 : The cause of interference fringes²¹

Figures 27 to 32 are the FTIR spectrum of polyethylenes.²² The FTIR transmission spectrum of all the analysed plastics are resemble that of polyethene. Thus, it can concluded that the analysed plastics are polyethene based.

Figures 33 and 34 are the correlation of IR vibration with absorption.²³ For FTIR transmission spectrum of all the analysed plastics, the absorption peaks are attributed by :-

Absorption	Vibration
2700 to 3000 cm^{-1}	C-H stretch
1370 to 1470 cm^{-1}	C-H bend
730 to 670 cm^{-1}	C-H bend

Table 8 : The correlation of IR vibration with absorption



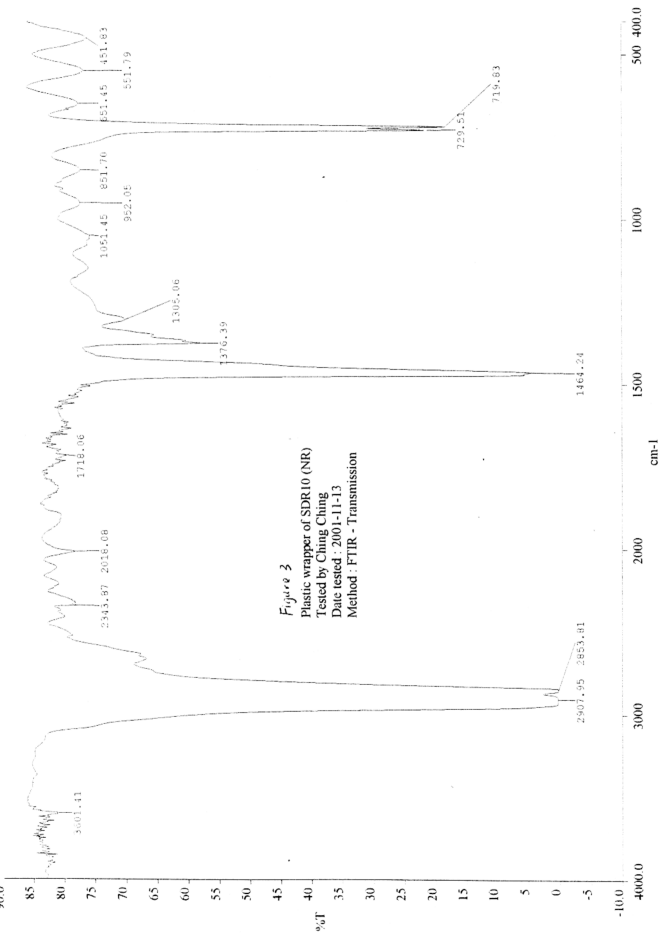
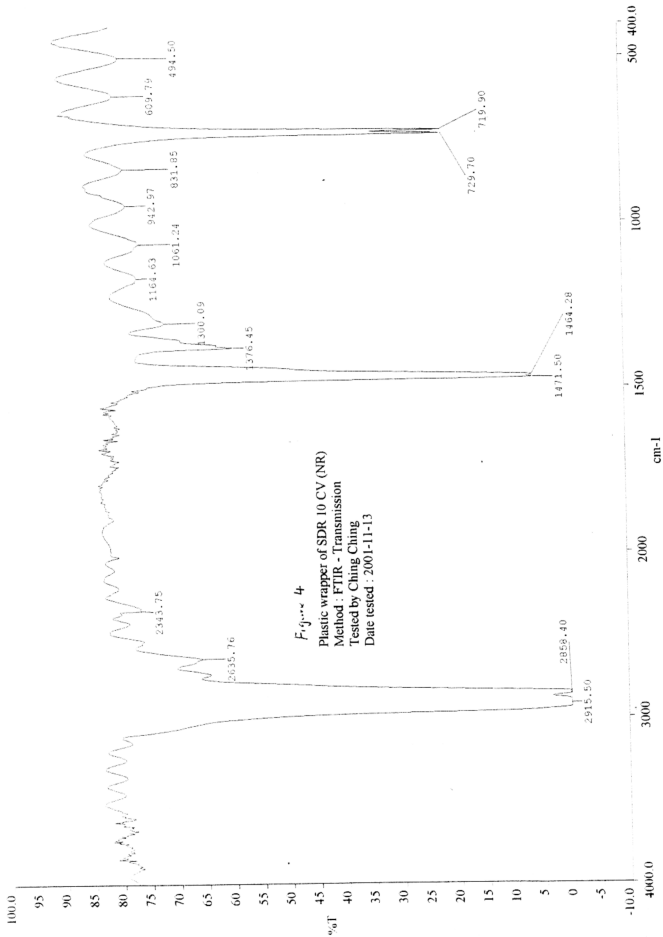
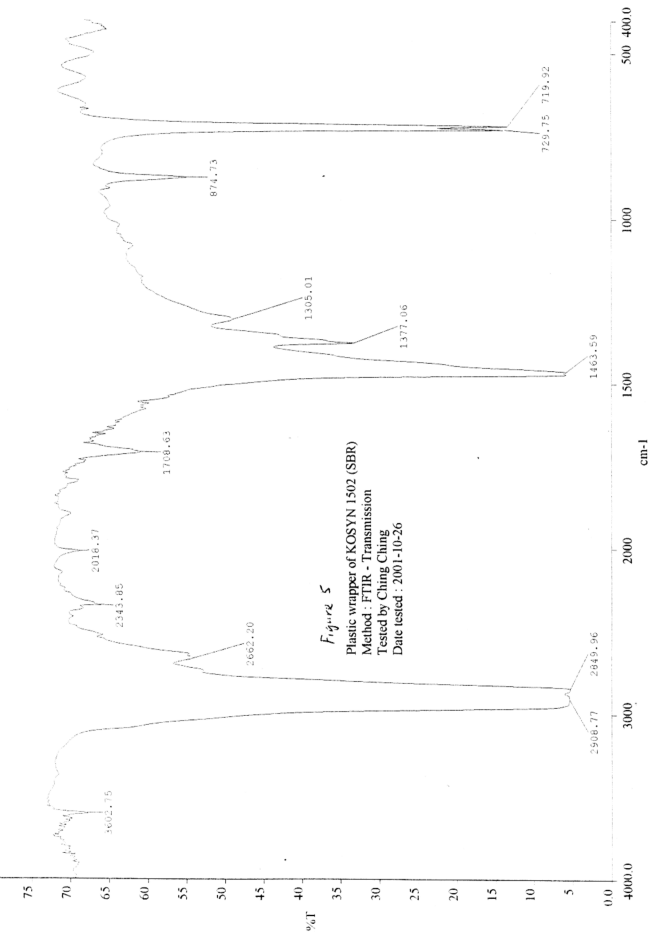
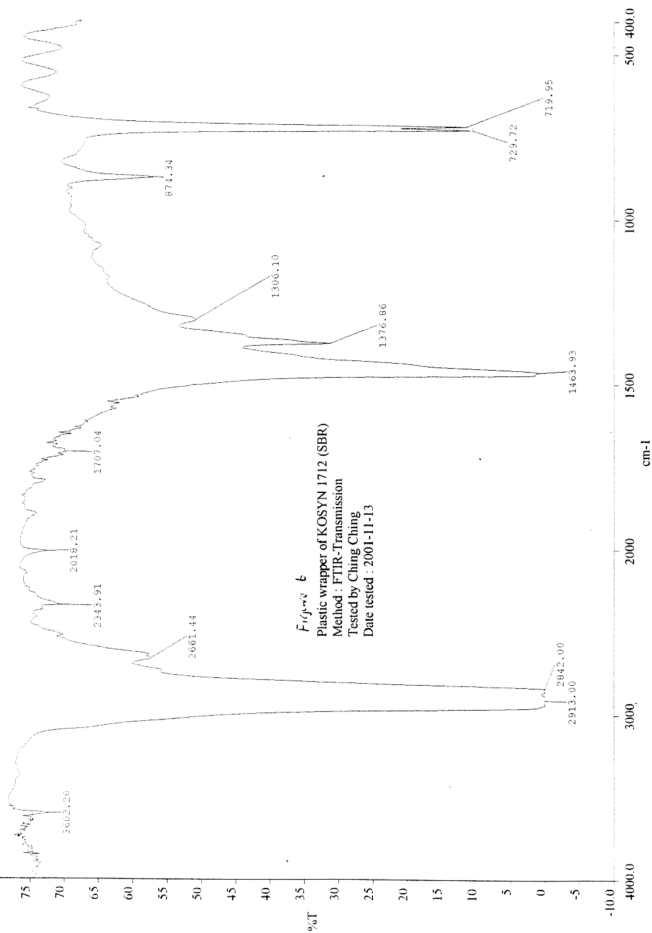


Figure 3
Plastic wrapper of SDR10 (NR)
Tested by Ching Ching
Date tested : 2001-11-13
Method : FTIR - Transmission





A510693619



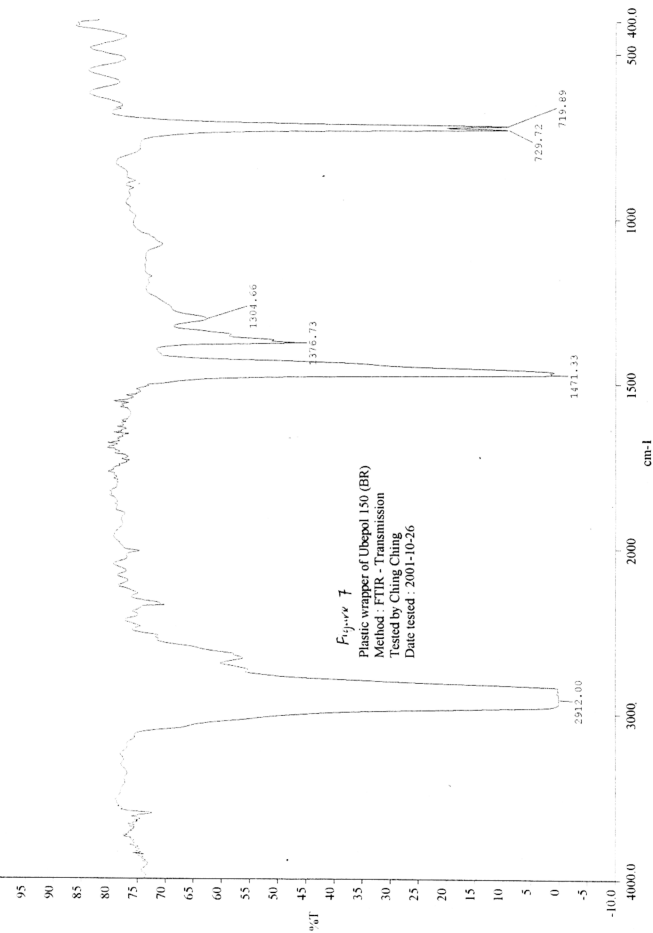


Figure 7

Plastic wrapper of Ubepol 150 (BR)

Method : FTIR - Transmission

Tested by Ching Ching

Date tested : 2001-10-26

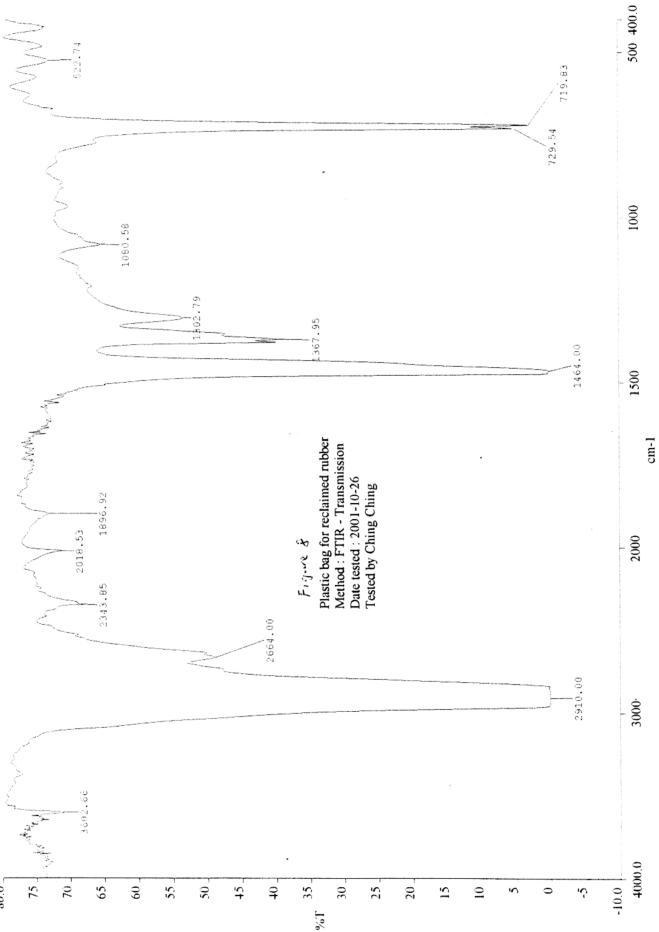


Figure 8
Plastic bag for reclaimed rubber
Method : FTIR - Transmission
Date tested : 2001-10-26
Tested by Ching Ching

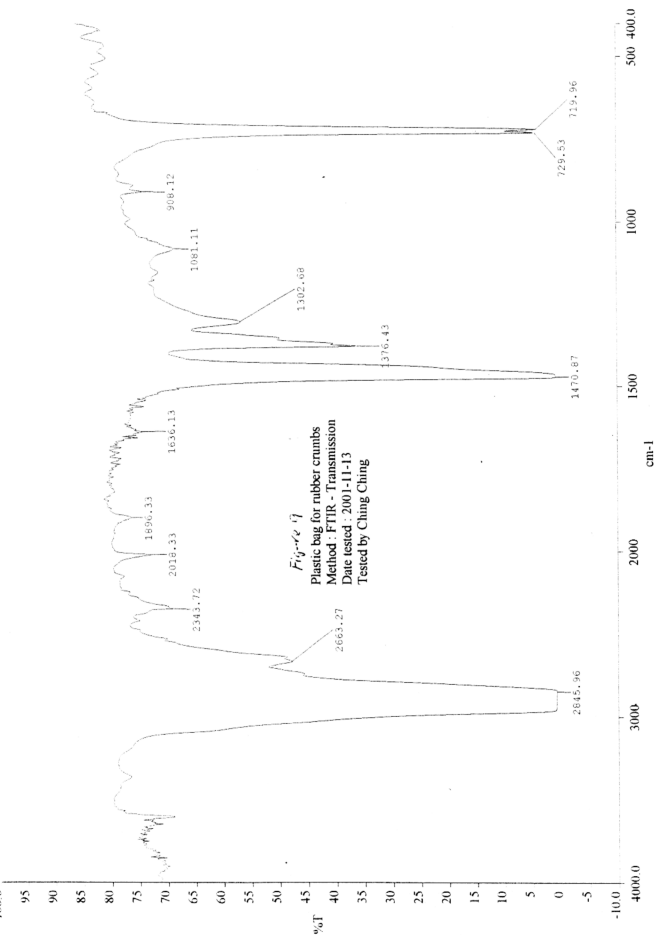


Figure 7

Plastic bag for rubber crumbs
Method : FTIR - Transmission
Date tested : 2001-11-13
Tested by Chung Ching

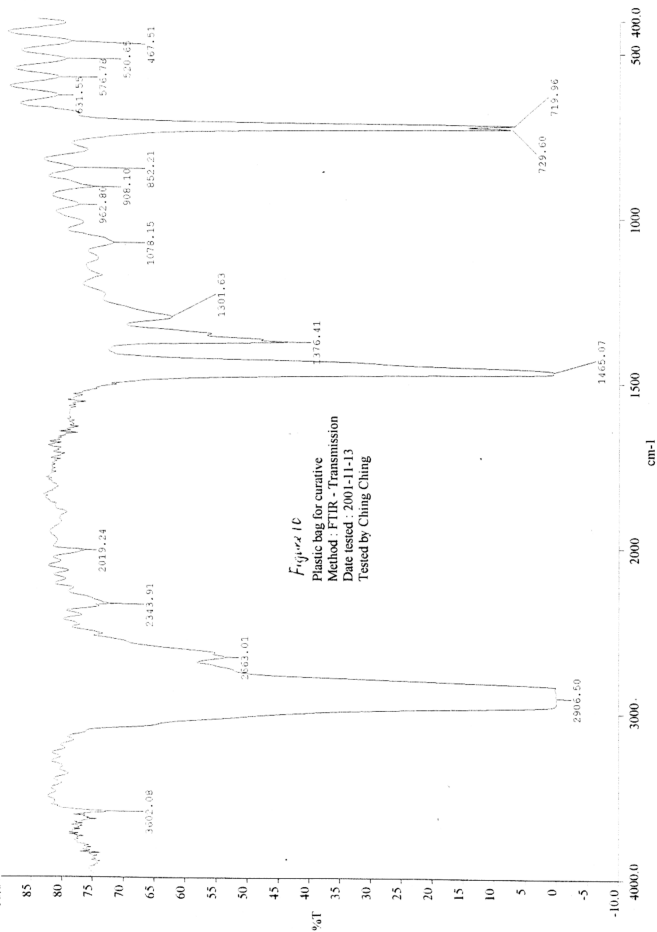


Figure 10

Plastic bag for curative
Method : FTIR - Transmission
Date tested : 2001-11-13
Tested by Ching Ching

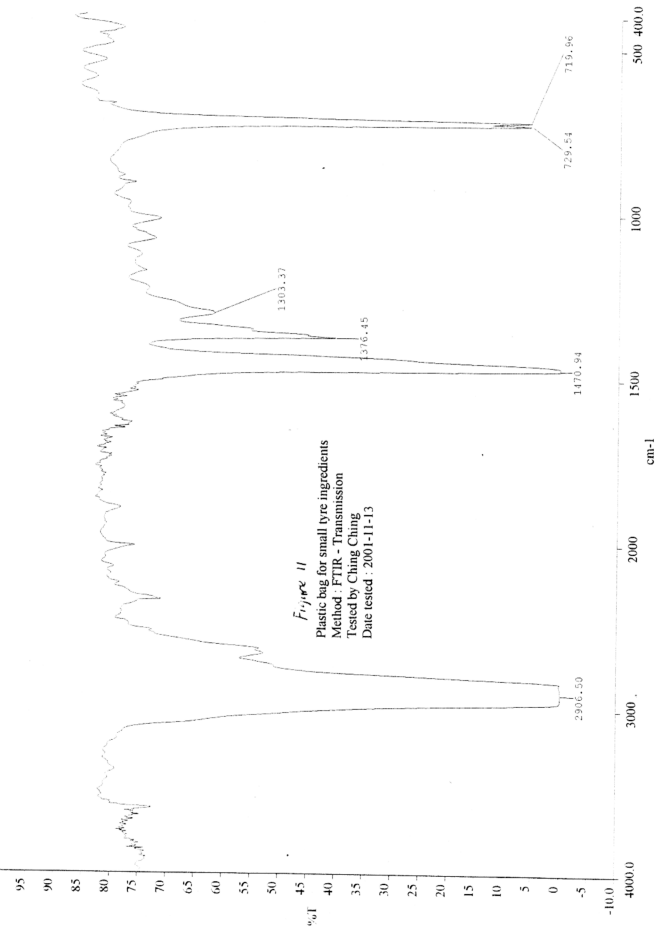
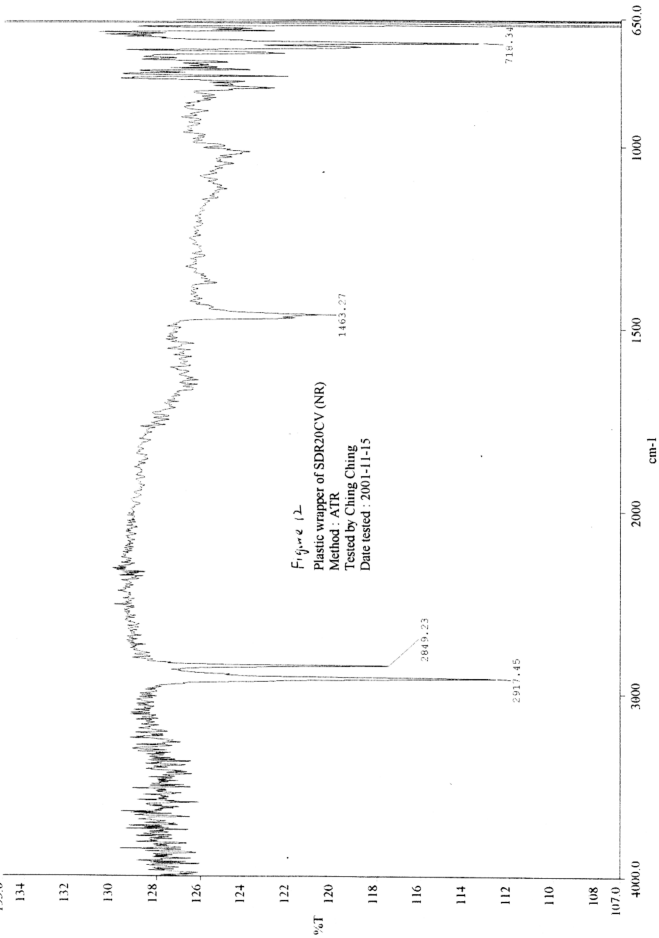
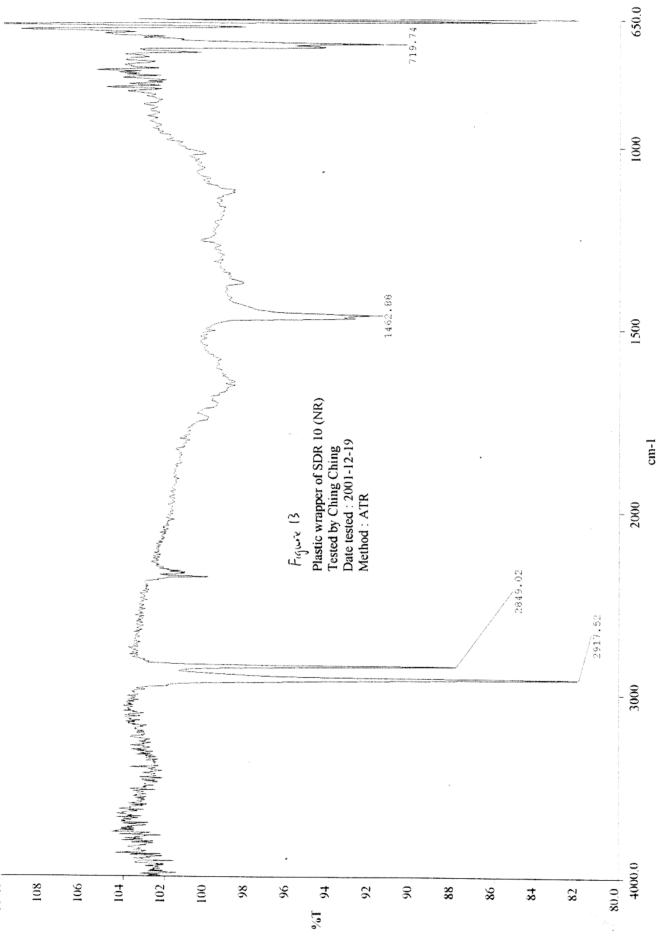


Figure 11

Plastic bag for small tyre ingredients
Method : FTIR - Transmission
Tested by Ching Ching
Date tested : 2001-11-13





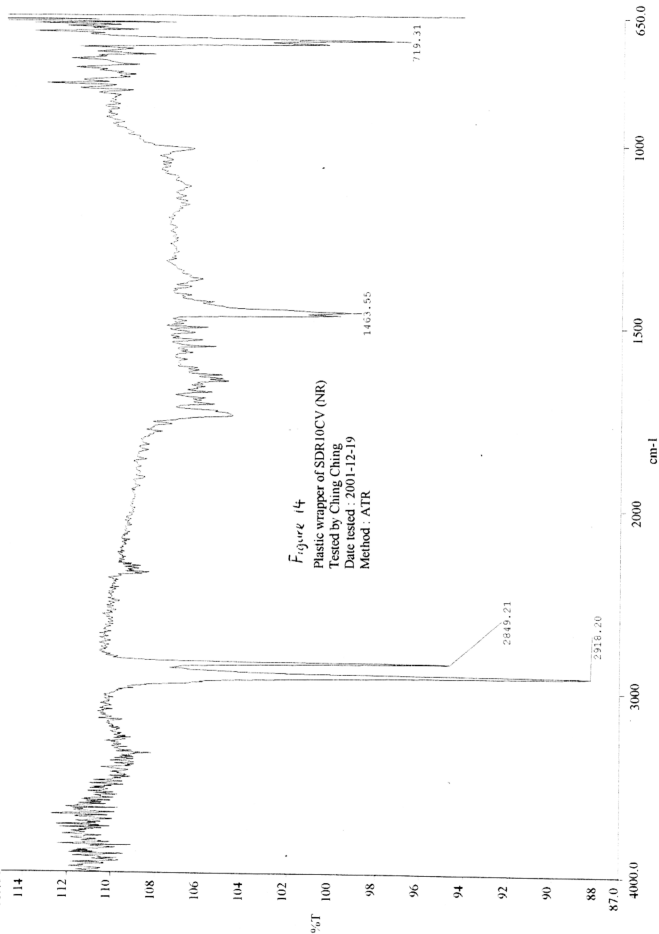
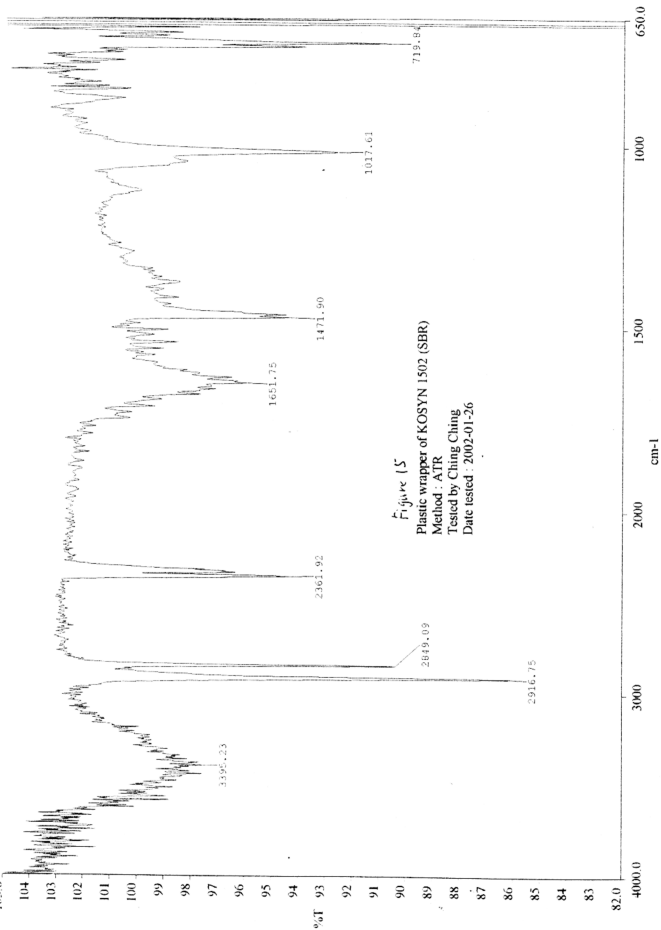


Figure 14
Plastic wrapper of SDR10CV (NR)
Tested by Ching Ching
Date tested : 2001-12-19
Method : ATR



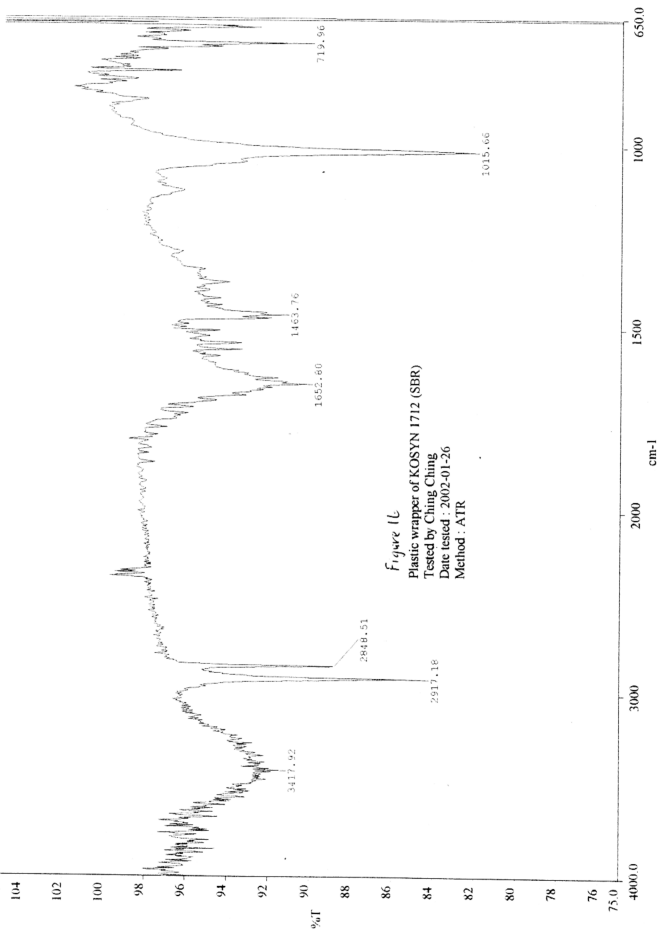
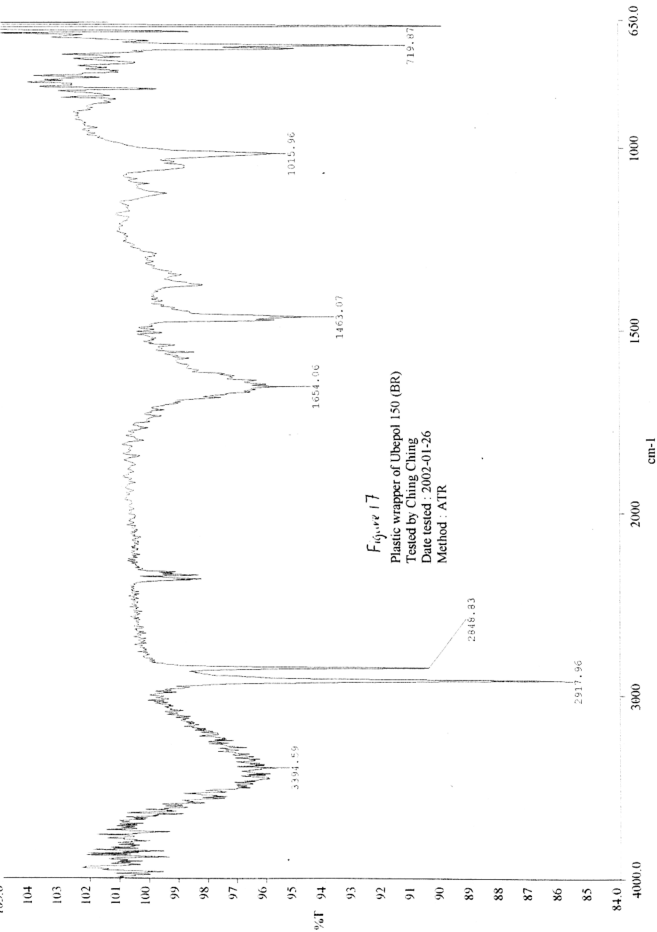
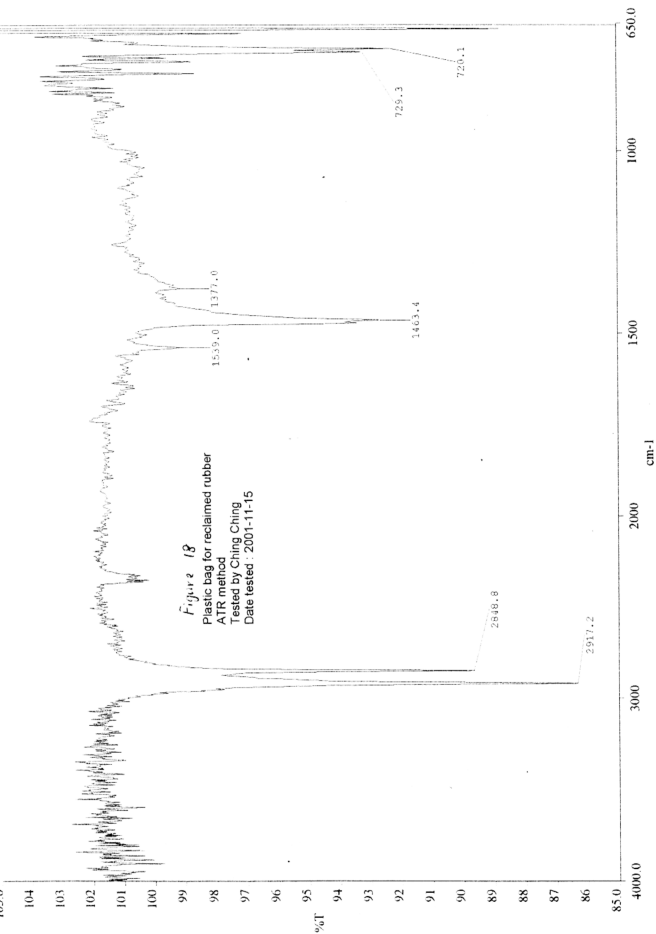


Figure 16
Plastic wrapper of KOSYN 1712 (SBR)
Tested by Ching Ching
Date tested : 2002-01-26
Method : ATR





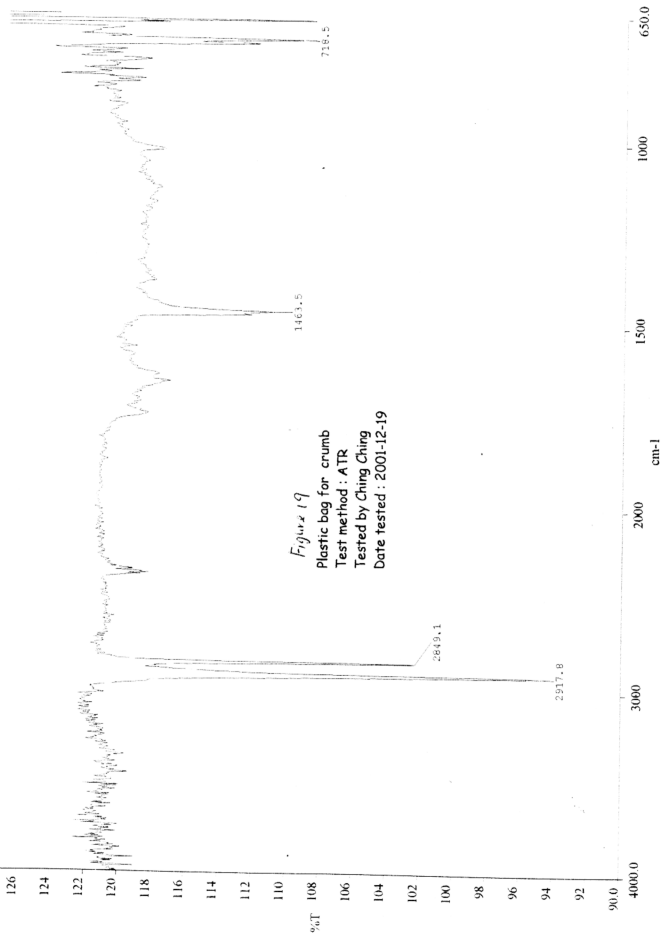


Figure 19
Plastic bag for crumb
Test method : ATR
Tested by Ching Ching
Date tested : 2001-12-19

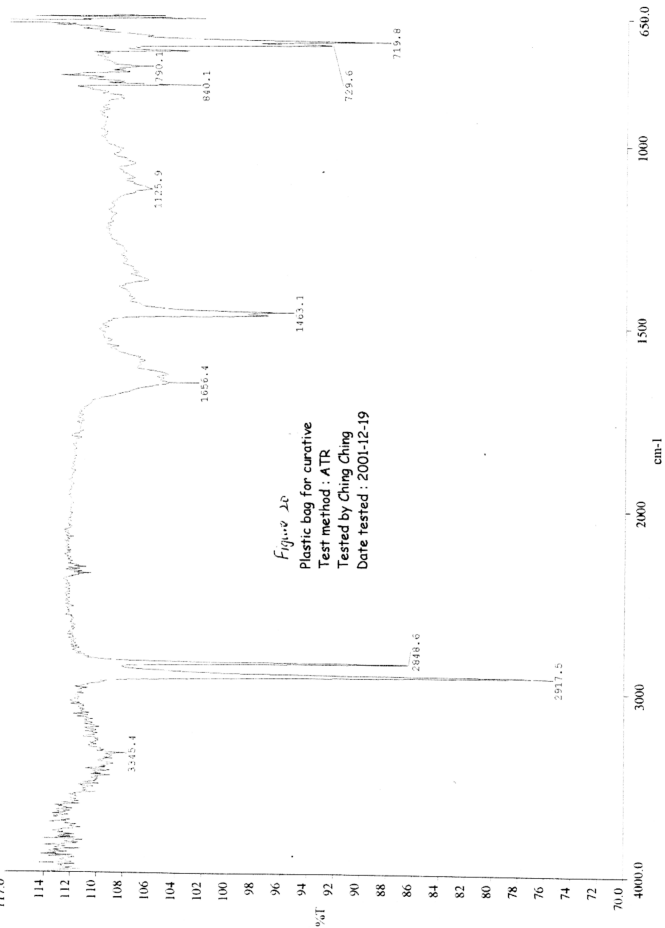


Figure 22
Plastic bag for curative
Test method : ATR
Tested by Ching Ching
Date tested : 2001-12-19

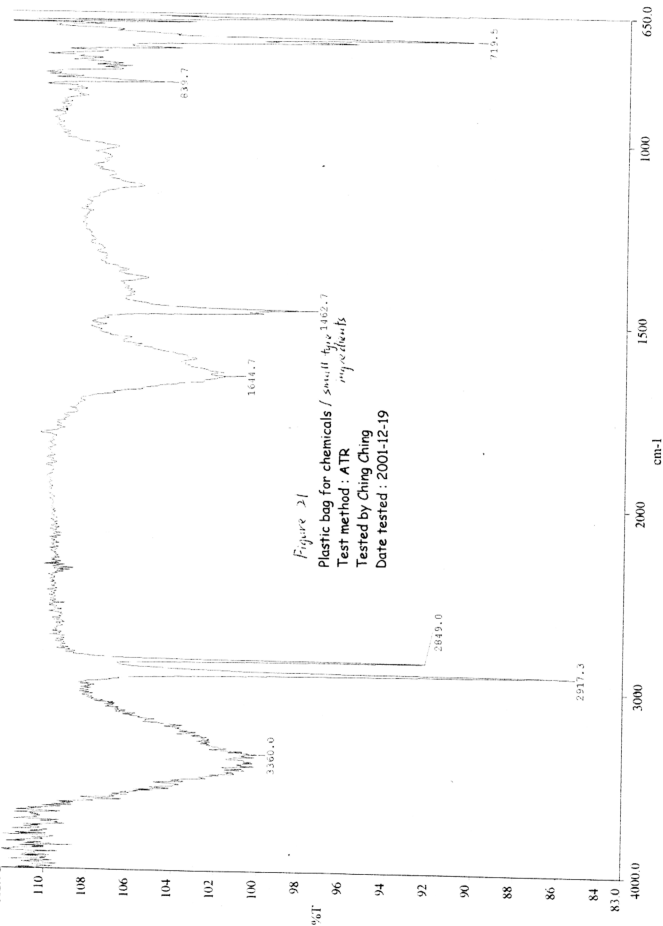


Figure 27

PT38.11903 Low Density Polyethylene

LDPE LUPOLEN 3020D.BASF.PRESS 120°C

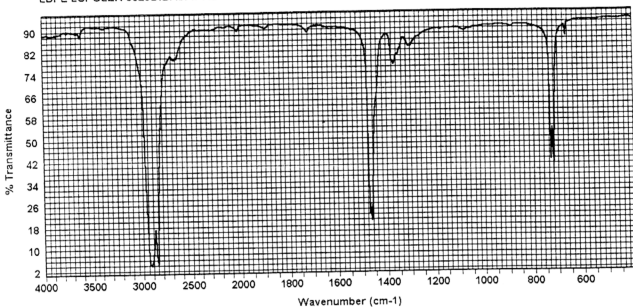


Figure 28

PT38.11904 Low Density Polyethylene + Butyl Acrylate

LDPE CARLONA.SHELL.PRESS 125°C

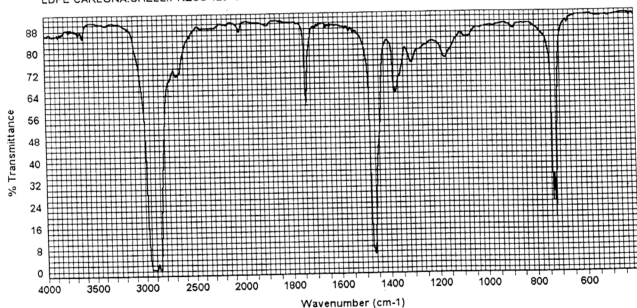


Figure 29

PT39.12101 Linear Low Density Polyethylene

LLDPE STAMYLEX 4046 MEDIUM DENSITY.DSM.PRESS 150°C

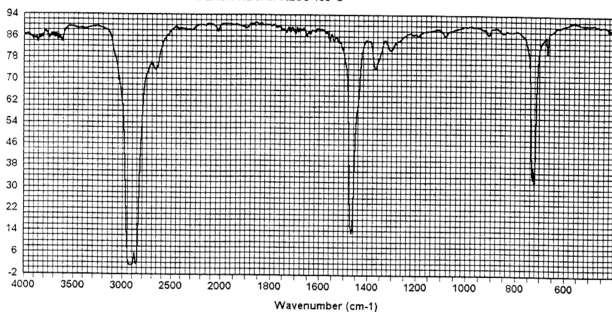


Figure 30

PT39.12102 Linear Low Density Polyethylene

LLDPE STAMYLEX 1026 LOW DENSITY.DSM.PRESS 150°C

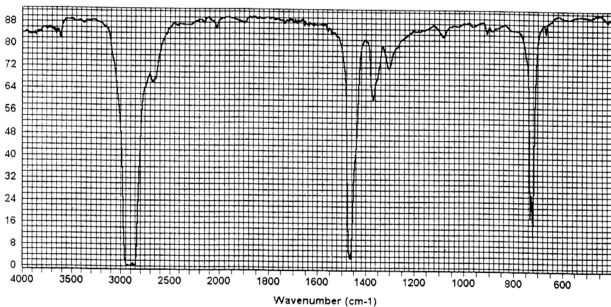


Figure 31

PT40.12301 High Density Polyethylene

HDPE RIGIDEX 94169.BP CHEM.PRESS 140°C

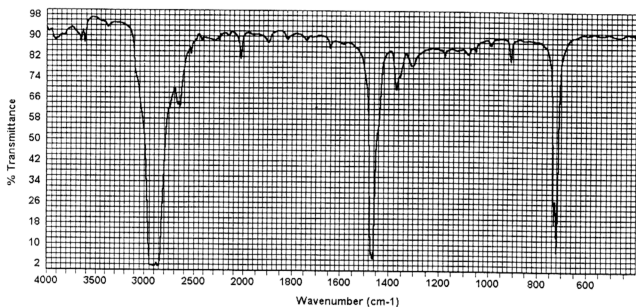
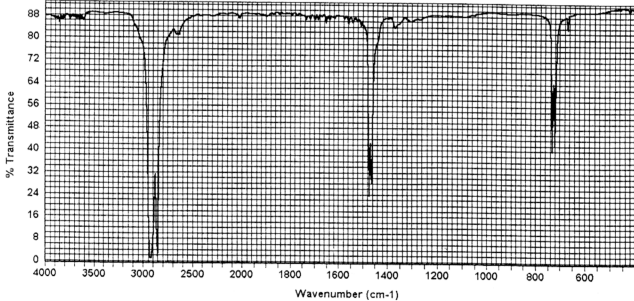


Figure 32

PT40.12302 High Density Polyethylene

HDPE ELTEX.SOLVAY.PRESS 140°C



Correlation of IR Vibration with Absorption. The absorptions shown are those to be expected for neat liquid films, melts or KBr wafers and are presented in decreasing order of absorption in cm⁻¹.

Vibration	Absorption	Intensity	Comments
O-H stretch	3525-3200	broad, S	H-bonded
	3400-2500	broad, M-S	H-bonded
N-H stretch	~3500, ~3400	W-M	two bands
	3500-3300	W	one band
	~3350, 3175-3150	M	two bands
	3325-3050	M	multiple bands as KBr wafer
C-H stretch	3325-3250	sharp, S	
	3100-3000	M-S	multiple bands
	3000-2800	M-S	multiple bands
	2850-2820, 2750-2700	sharp, W-M	two bands
S-H stretch	2600-2550	W	
	2270-2000	broad, S	
	2260-2240*	sharp, M	
	2260-2100*	W	often absent when symmetrical
C=O stretch	~1815*, ~1755*	S	two bands, first more intense
	~1800*	S	γ or smaller lactones higher
	~1745*	S	< α-X-substituted esters higher
	~1730*	S	(β-carbonyl esters absorb lower
	~1715*	S	
	~1695*	S	
C=N stretch	1690-1640	M	
	1670-1600*	W-M	weak or absent when symmetrical
C=C stretch	1600-1575, 1500-1450	M	often two bands in each range
	1655-1610	M	
	1650-1560	broad, M-S	
	1575-1510	W	
N-H bend	1515-1400	W	usually undetectable for secondary aliphatic amines
	~1560*, ~1375*	S	two bands
N-O stretch	1470-1370	W-M	
	1390-1380, 1370-1365	W	(two bands)
S=O stretch	1430-1310, 1225-1125	S	two bands
	~1410	M	
C-N	1250-1010	W-M	
	1370-1250	W-M	

Figure 34

TABLE V. Continued.

<u>Vibration</u>	<u>Absorption</u>	<u>Intensity</u>	<u>Comments</u>
C-F stretch	polyfluoroalkanes monofluoroaromatics monofluoroalkanes	1350-1110 -1225 1100-1000	S S S
	carboxylic acids	1320-1210	M
	esters	1290-1150, 1125-1000	S, M
C-O stretch	aryl alkyl ethers	1280-1200, 1080-1020	S
	alcohols, phenols	1255-1000	S
	dialkyl ethers	1150-1100	S
	CH ₂ -Cl	1300-1200	S
CH ₂ -X stretch	CH ₂ -Br	1250-1175	S
	CH ₂ -I	1200-1150	S
epoxide ring vibrations		-1250, -930, -800	S
asymmetric ferrocene ring breathing		-1100	M
	aromatic C-Cl	1100-1075	S
C-X stretch	aliphatic C-Cl	850-600	S
	aliphatic C-Br	700-510	S
	aliphatic C-I	600-475	S
S-O stretch	sulfoxides	1075-1025	S
ferrocene ring C-H bend		-1000	M
	trans-olefin	980-960	S
	terminal =CH ₂	900-880	S
C-H oop bend	aromatic	900-675	S
	cis-olefin	730-670	S
	amines	910-660	broad
N-H oop bend	amides	800-670	S
Si-C stretch	organosilanes	850-720	S
C-C oop bend	aromatic rings	720-670	S
ferrocene ring-Fe stretch		-475	broad, M
*conjugation shifts the absorption to lower energy			
S = strong, M = medium			

fatty acids have two bands
{methyl esters of fatty acids have
three bands: -1250, -1200, -1180
two bands
{phenols at high end and primary
alcohols at low end of range

this and the 1100 band denote
{that one ring is unsubstituted
generally reliable
generally reliable
{pattern helps establish
substitution (see TABLE VI)
not dependable

Si-CH₃ stretch at high end

3.2 DSC Analysis

Differential scanning calorimeters (DSC) use a method of heat flow measurement based on power compensation.²⁴ They are built of the following parts :

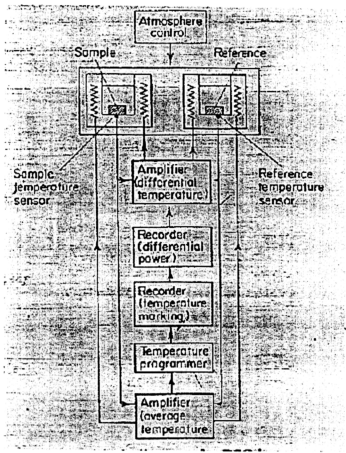


Figure 35 : The block diagram of DSC²⁴

The sample and reference are heated separately by individually controlled heat elements. The power to these heaters is adjusted continuously in response to any thermal effects in the sample. In this way sample and reference are at identical temperatures. The differential power required to achieve this condition is recorded as the ordinate on the recorder, with the programmed temperature of the system as the abscissa.

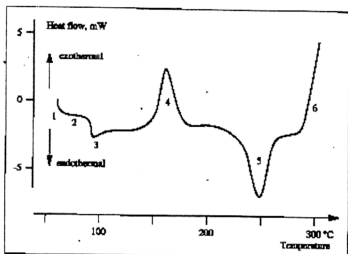


Figure 36 : DSC curve²⁵

(Notes : 1. Initial deflection that is proportional to the sample's heat capacity.

2. DSC curve with no thermal effect << baseline >>

3. Glass transition of amorphous fraction

4. Peak of cold crystallization (devitrification) ,

5. Melting peak of the crystalline fraction

6. Beginning oxidative degradation in air)

For DSC curve, the melting peak can be characterized by peak temperature,^{25, 27} Mettler Toledo has characterized PE and the test results obtained by Mettler Toledo are as follows ²⁵

:-

	PE-LD	PE-LLD	PE-HD
Peak temperature, °C	108.8	123.5	132.9

Table 9 : Test results of PE obtained by Mettler Toledo ²⁵

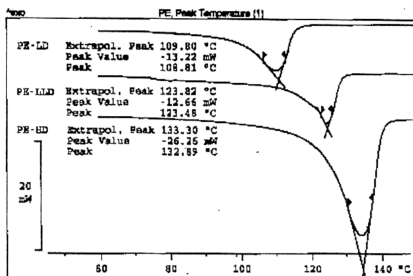


Figure 37 : DSC curve of PE obtained by Mettler Toledo ²⁵

For the project, figures 38 to 47 show the DSC melting curve of various plastics. The melting points of the plastics are as follows :-

	Peak temperature, °C
Plastic wrapper of SDR 20CV	108.96
Plastic wrapper of SDR 10	108.99
Plastic wrapper of SDR 10CV	109.08
Plastic wrapper of KOSYN 1712	108.74
Plastic wrapper of KOSYN 1502	109.46
Plastic bag of reclaimed rubber	124.43
Plastic wrapper of Ubepol 150	110.17
Plastic bag of crumbs	108.39
Plastic bag of curative	109.17
Plastic bag of small tyre ingredients	109.89

Table 10 : Test results of plastics

Based on the above, it was concluded that the various plastics consist of the following :-

	Polymer
Plastic wrapper of SDR 20CV	PE-LD
Plastic wrapper of SDR 10	PE-LD
Plastic wrapper of SDR 10CV	PE-LD
Plastic wrapper of KOSYN 1712	PE-LD
Plastic wrapper of KOSYN 1502	PE-LD
Plastic bag of reclaimed rubber	PE-LLD
Plastic wrapper of Ubepol 150	PE-LD
Plastic bag of crumbs	PE-LD
Plastic bag of curative	PE-LD
Plastic bag of small tyre ingredients	PE-LD

Table 11 : Test results of plastics

(Note : PE-LD is low density polyethylene, PE-LLD is linear low density polyethylene and PE-HD is high density polyethylene.)

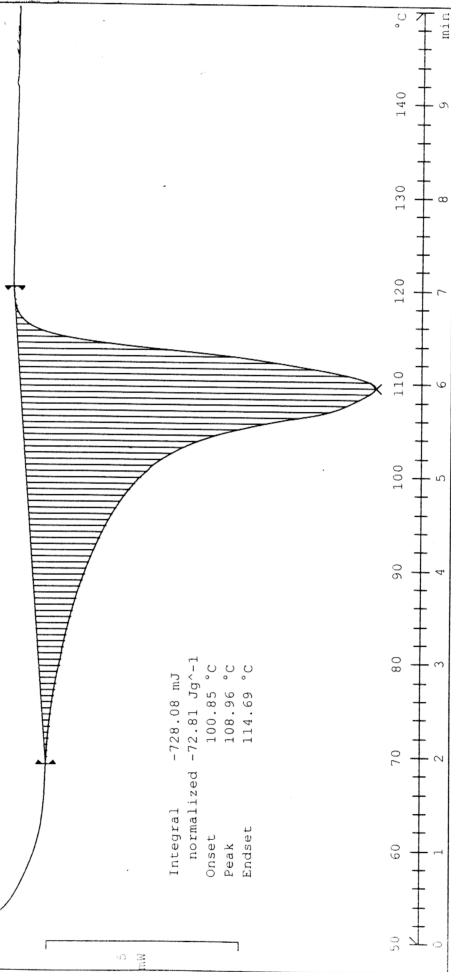
Referring to Figure 37, the DSC melting curves of PE obtained by Mettler Toledo consist of a single melting peak. However, not all the analysed plastics show a single melting peak. The plastic wrapper of KOSYN 1712 (Figure 37) and the plastic wrapper of KOSYN 1502 (Figure 39) have an additional small shoulder at about 80°C. This seems to indicate the presence of other additives beside PE in KOSYN 1712 and KOSYN 1502. This also explains the presence of additional peaks at 1708 cm⁻¹ and 874.73 cm⁻¹ in the FTIR-transmission spectrum of KOSYN 1712 (Figure 6) and KOSYN 1502 (Figure 5).

exo

t02047, 28.02.2002 18:57:47
t02047, 10.0000 mg

Figure 38

Sample D - Plastic wrapper of Ketorolac Tablets SDSC Co. Ltd.
Tested by Ching Ching
Date tested : 2002-02-28



Sime Darby Technology Centre: CTL

METTLER TOLEDO STAR^e System

^exo

et01160

04.03.2002 16:18:39

et01160, 04.02.2002 18:53:11

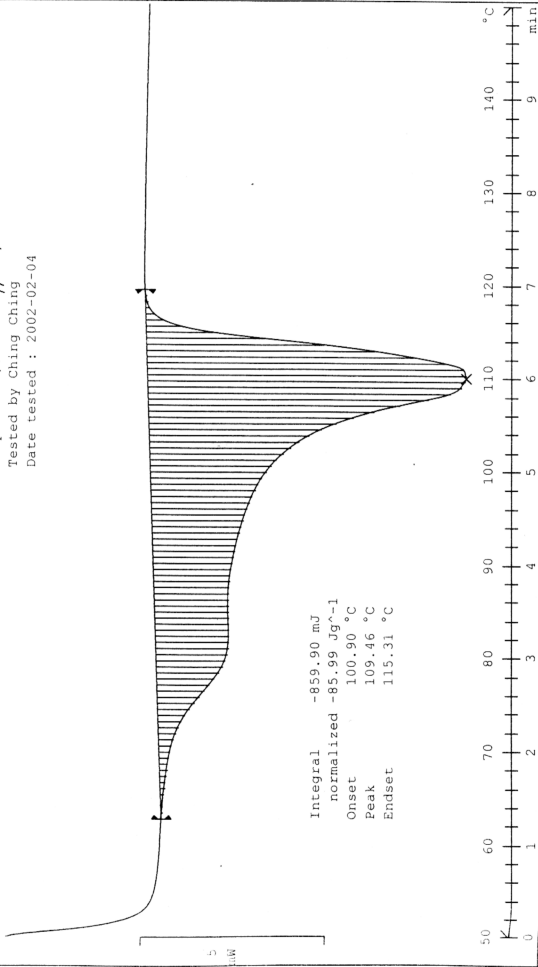
et01160, 10.0000 mg

Fig. 2.54

Sample E - Plastic wrapper of Resynol 150.2 (662)

Tested by Ching Ching

Date tested : 2002-02-04



Sime Darby Technology Centre: CTL

METTLER TOLEDO STAR[®] System

t02038, 25.02.2002 17:41:39

t02038, 10.4000 mg

Figure 4c

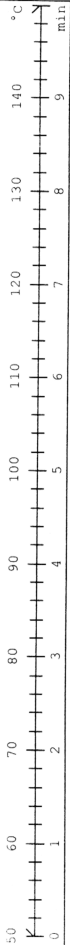
Sample G - flash sample of 40,000 mg (K2)

Tested by Ching Ching

Date tested : 2002-02-25

1.0
mW

Integral -933.79 mJ
Normalized -89.79 Jg⁻¹
Onset 100.51 °C
Peak 110.17 °C
Endset 115.03 °C



Sime Darby Technology Centre: CTL

METTLER TOLEDO STAR[®] System

exo

t02046, 28.02.2002 18:00:54

t02046, 10.0000 mg

Figure 41

6301

Sample J Plastic bag of ~~antistatic tape~~ ~~antistatic~~ SDZ 10

Tested by Ching Ching

Date tested : 2002-02-28

1.0
mW

Integral -908.28 mJ
normalized -90.83 Jg⁻¹
Onset 99.56 °C
Peak 108.99 °C
Endset 114.93 °C



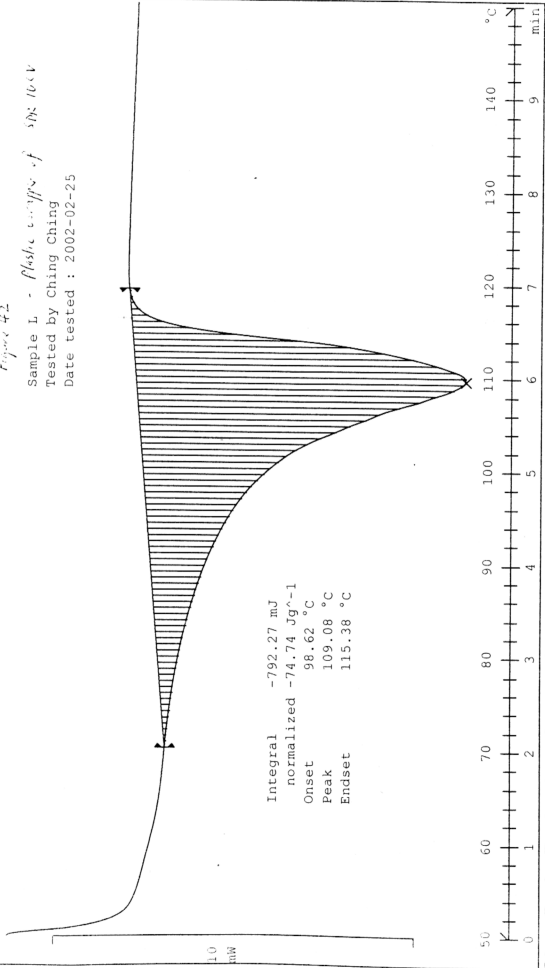
Sime Darby Technology Centre: CTL

METTLER TOLEDO STAR^e System

exo

t02042, 25.02.2002 18:25:01
t02042, 10.6000 mg

Figure 4.2
Sample L - Plastic wrap of 50g 160V
Tested by Ching Ching
Date tested : 2002-02-25



Sime Darby Technology Centre: CTL

METTLER TOLEDO STAR^e System

t02039, 25.02.2002 17:57:25

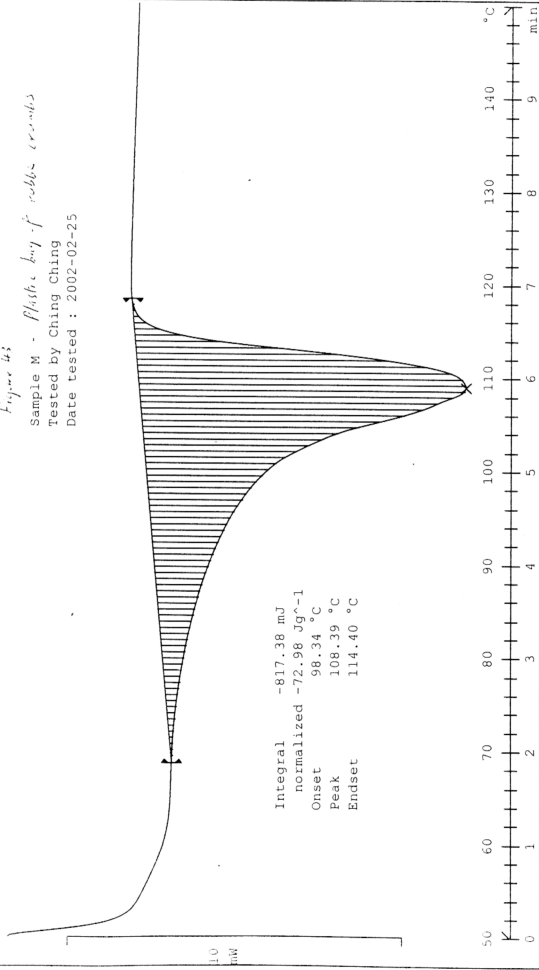
t02039, 11.2000 mg

Figure 43

Sample M - Plastic bag - 1st robbery events

Tested by Ching Ching

Date tested : 2002-02-25



t02044, 28.02.2002 17:29:01

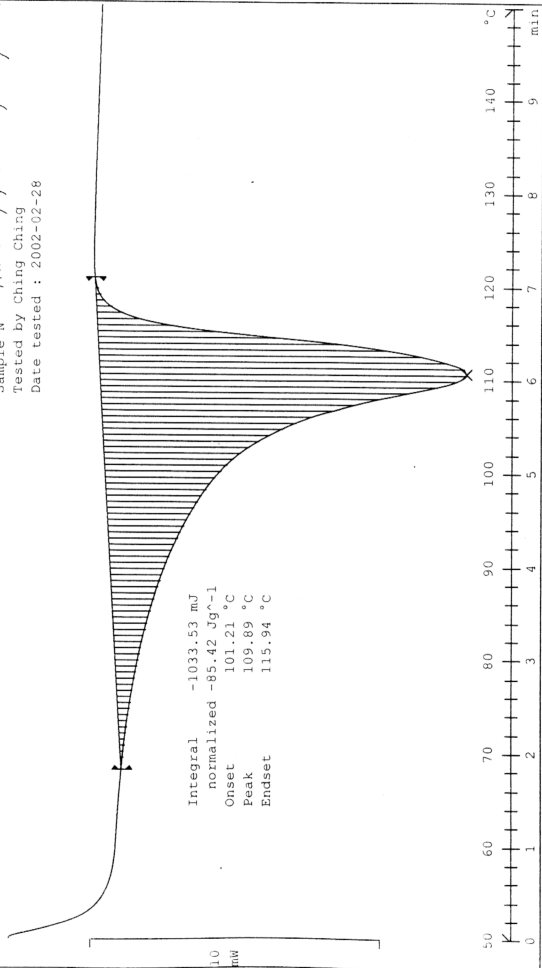
t02044, 12.1000 mg

Figure 44

Sample N - Plastic bag of small type vegetables

Tested by Ching Ching

Date tested : 2002-02-28



t02043, 28.02.2002 17:12:22

t02043, 10.6000 mg

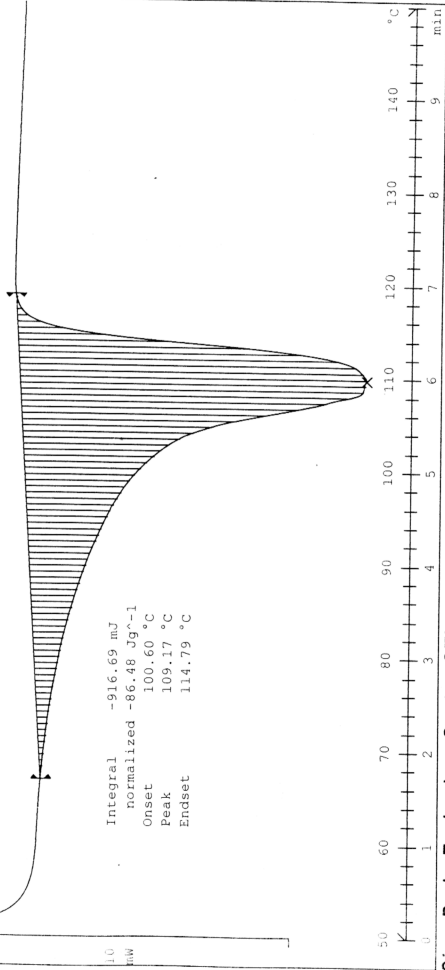
Figure 45

Sample 0 - Plastic bag of carbonate

Tested by Ching Ching

Date tested : 2002-02-28

Integral -916.69 mJ
normalized -86.48 Jg⁻¹
Onset 100.60 °C
Peak 109.17 °C
Endset 114.79 °C



exo

102046, 28.02.2002 18:34:59

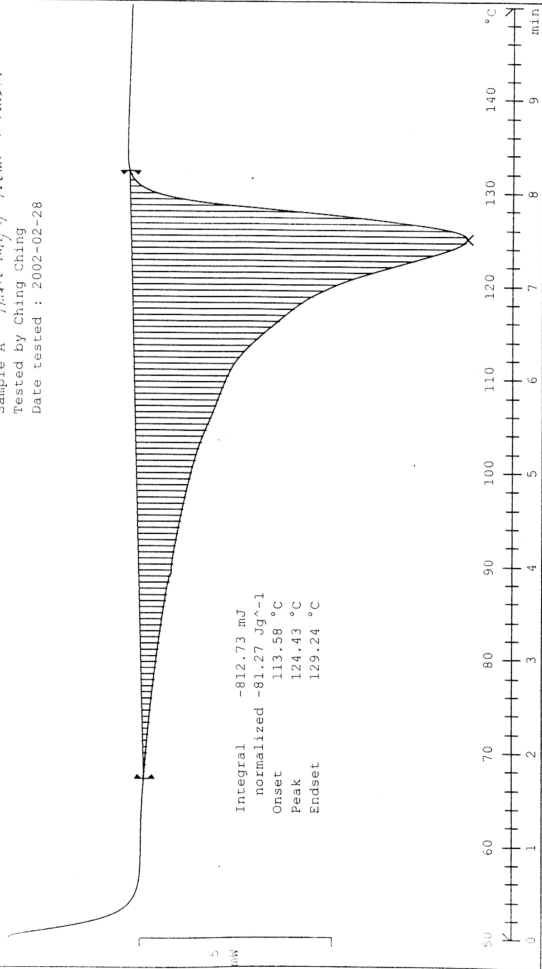
102046, 10.0000 mg

Figure 4i

Sample A - Plastic bag of polystyrene

Tested by Ching Ching

Date tested : 2002-02-28



Sime Darby Technology Centre: CTL

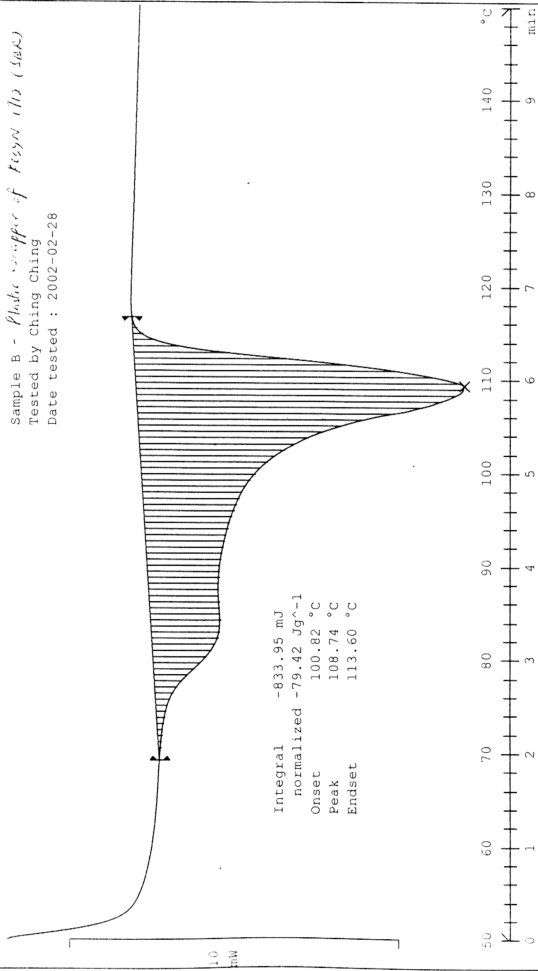
METTLER TOLEDO STAR^e System

exo

102045, 28.02.2002 17:45:55
102045, 10.5000 mg

Fig. 47

Sample B - Plastic wrapper of Kevlar 110 (100L)
Tested by Ching Ching
Date tested : 2002-02-28



3.3 Softening Point Analysis By the Ring And Ball tester technique

The ring and ball tester is one of the few equipment available to determine the softening point of the ointments, synthetic and natural resins, edible fats, lubrication greases, waxes, fatty polymers, bitumen and tars.²⁶ These materials do not have a well defined melting point. They soften with increasing temperature and gradually become liquid over a wide temperature range. The softening point obtained is defined as the temperature at which the substance becomes sufficiently liquid for a drop to fall out of the sample tube that is open at the lower end.²⁵ In the other words, the softening point is reported as the mean of the temperatures at which the samples soften enough to allow each ball to fall a distance of 25 mm to the bottom of ring supporter.^{15, 16}

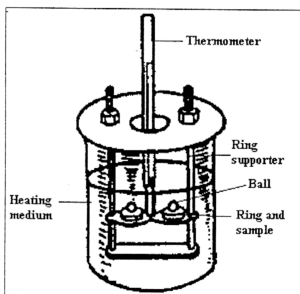


Figure 48 : Ring and Ball Assembly

For ointments, synthetic and natural resins, edible fats, lubrication greases, waxes, fatty polymers, bitumen and tars, the samples are melted and then cast in rings for testing. In this study, the plastic samples are clamped between two rings for testing.

The results obtained are reported below.

	Determination I, °C	Determination II , °C	Average, °C
Plastic wrapper of SDR 20CV	106.0	107.4	106.7
Plastic wrapper of SDR 10	111.8	110.6	111.2
Plastic wrapper of SDR 10 CV	112.4	112.9	112.7
Plastic wrapper of KOSYN 1712	111.0	111.3	111.2
Plastic wrapper of KOSYN 1502	107.1	112.7	109.9
Plastic bag of reclaimed rubber	124.5	123.7	124.1
Plastic wrapper of Ubepol 150	115.2	117.1	116.2
Plastic bag of rubber crumbs	108.2	112.0	110.1
Plastic bag of curative	112.4	111.6	112.0
Plastic bag of small tyre ingredients	112.2	108.1	110.2

Table 12 : Test results of softening point analysis

In general, most of the test results of softening point are higher than those obtained by the DSC technique. An average for duplicate determinations is obtained to indicate the softening point since some of the test results do not show very good repeatability.