Closed Loop Recycling Opportunities for PVC

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Abstract

This report considers how a continuing cycle of injection moulding, granulation and pelletising affects the processability and various physical properties of two dissimilar PVC-U materials. For each material, one a K50 suspension resin with a tin stabiliser and one a K57 suspension resin with a lead stabiliser , a full range of physical and thermal properties were evaluated. Virgin material, followed by 1st, 2nd 3rd and 4th generation regrinds (100%) were manufactured then tested. The evaluation confirms the closed-loop recycling potential of PVC albeit tested without physical ageing between cycles. This validation has subsequently been confirmed in the UK by commercial scale closed loop recycling of PVC business machine housings at our site at Aycliffe, Co Durham, via a joint venture between Hydro Polymers and Geon USA.

1. Introduction

The issue of plastics recycling is here to stay and the pressures to do more driven by public perception of their use in non-renewable resources are real. However, putting the issue of non-renewable resources into perspective is also important. For example, by far the vast majority of non-renewable petroleum resources go directly into one-trip applications such as heating and transport, with the total plastics industry representing only some 5% of petroleum resources (W Europe) for the actual materials used in manufacture with perhaps a 2-3% contribution for process energy, see Figure 1 for details (1). Furthermore, unlike other commodity thermoplastics, PVC is not derived entirely from oil and more than half the feedstock comes from salt, which although this is a non-renewable resource there is a plentiful supply to last thousands of years as opposed to perhaps hundreds of years for petroleum resources based on present usage. Nevertheless society should encourage sensible recycling, but both the economic and environmental consequences of end-of-life products need to be assessed in order to demonstrate their potential for new life applications. For example, it would seem nonsensical to attempt to separate, wash and reprocess used cling film from household waste and by far the most economical route would be disposal through energy recovery by incineration, whereas in contrast a much larger uncontaminated product such as a large automotive component at the end of its life should be seen as a resource for a secondary life and not as waste. It is often suggested that the preferred disposal technique must therefore depend both on the type and quantity of "waste" and where it is located (2).

One of the limiting factors in PVC recycling is its availability in a viable form. Indeed compared to other plastics, PVC represents only some 10% of all thermoplastics for use in food packaging applications i.e. short life applications, with the bulk of applications in longer term applications i.e. greater than 20 years, see Figure 2 for details (1). Nevertheless progress has been made where collection and return systems have been developed such as supermarket on-shelf trays which are reprocessed back into their original applications and post consumer bottles processed into other products (3). Waste packaging legislation recently introduced in the UK and more established in other European

Countries will influence the drive to significantly higher amount of returns. Perhaps an even greater limiting factor for unplasticised PVC is its use in very long-term applications such as the building markets. This essentially means that there is currently limited feedstock available in the UK. However, in other countries such as Germany where PVC-U window profiles originated, significant quantities of post consumer waste are becoming available for recycling and indeed commercial realisation of recycling such profile has been established by companies such as Veka, a leading German PVC window frame manufacturer (4), who have now established recycling of used PVC window frames extruded back into new applications, albeit with an exterior virgin skin for aesthetic appearance, such technology is known as "closed loop recycling". But what of injection moulding? known to be a far more demanding a process on the material compared to extrusion, due to the higher shear rates experienced during the moulding process. This paper sets out the technical viability of the continued recycling of two dissimilar PVC-U injection moulding compounds and thereby attempts to establish their limits. The work was originally examined since PVC has been successfully used in business machine housings and keyboards which have a relatively short life span compared to building applications. Consequently the availability of feedstock of such material is real, and last year as a result of a joint venture between Hydro and Geon, over 250 tonnes of regrind PVC mouldings were recompounded at our site in Aycliffe, Co Durham and sold to moulding companies who converted it back into business machine components. In this work, the processing and testing have been compressed into a relatively short space of time. Nevertheless the work does clearly demonstrate the technical merits of PVC-U as a reprocessable polymer.

2. Experimental

Two compounds were used in this research work. The first was based on a K50 resin formulation using tin stabiliser and a grey pigmentation, the second was based on a K57 resin formulation using a lead stabiliser and white pigmentation. Full formulation details are shown in Tables A & B. The initial virgin compounds were manufactured using large industrial scale compounding lines. Once the compounds were produced, the first injection moulding trials were evaluated by moulding physical test pieces from a family tool. The final stage of the initial process was to regrind the excess quantities of physical test pieces followed by re-compounding of the regrind back into pellets. In all cases reprocessing was based on 100% regrind without the addition of further stabilisers or process aids.

In all, five passes of each material were made, Virgin through to 4th generation regrind, which in total meant that both materials underwent 10 thermal histories, see the enclosed process flow chart for details, Figure 3.

Processing Equipment

Injection Moulding

A Negri Bossi NB90 injection moulding machine was used, in combination with a family physical test piece mould. A check ring screw was used with the K50 formulation whilst the K57 formulation utilised a smear tip screw. Both screws were of conventional PVC type design.

With the exception of screw shot size which was altered to correspond with material viscosity, constant moulding conditions were used throughout the evaluation.

The samples produced included: Tensile bar, Izod and Charpy Impact Specimens, Vicat and relative density disks. Other physical tests were performed on the re-pelletised compounds including thermal stability based both on static and dynamic test methods.

Granulation

A Cumberland regrinding machine fitted with appropriate screen size to prevent bridging in the hopper of the compounding unit. The granulate required 3 passes through the machine in order to produce a nominal particle size of between 5-6 mm.

Recompounding (Pelletizing)

A Schloemann BT50 twin screw compounding extruder was used to transform the regrind into regular pellets. Constant processing conditions were maintained throughout.

Testing of Materials

The following physical and thermal test protocols were evaluated:

Specific Gravity	:	BS 2782 Part 6 Method 620A (1980)
50 N Vicat Softening Point	:	BS 2782 Part 1 Method 120
Notched Izod Impact Strength	:	BS 2782 Part 3 Method 350
Notched Charpy Impact Strength	:	BS 2782 Mart 3 Method 359 (1984)
Tensile Stress at Yield	:	BS 2782 Method 320B (1976)
Elongation at Break	:	BS 2782 Method 320 B (1976)
Flexural Strength	:	BS 2782 Part 3 Method 335A
Flexural Modulus	:	BS 2782 Part 3 Method 335A
Heat Distortion Temperature	:	BS 2782 Part 1 Method 121A
Static Heat Stability @ 180°C	:	BS 2782 Part 1 Method 130A
Dynamic Heat Stability		
Two Roll Mill method	:	ISO 1163/2, ISO 2898/2
Macklow Smith Finish/Gelation	:	HPL internal test method (CTM-006)
Melt Flow Index	:	BS 2782 Part 7 Method 720A

ICS L,a,b colour co-ordinates were also evaluated for each sample

3. Results

Table C shows the physical property and thermal stability data for the K50, tin stabilised formulation.

Table D shows the physical property and thermal stability data for the K57, lead stabilised formulation.

Table E shows the colour data for the K50, tin stabilised formulation

Table F shows the colour data for the K57, lead stabilised formulation

4. Discussion

In both formulations it was possible to process the materials through 4 generations, which meant that both materials had undergone a total of 10 thermal histories. No processing problems were encountered at any stage in the cycle for the tin stabilised formulation. However, poorer mouldings were noted from the 4th generation regrind based on the lead stabilised material, caused by increases in shot size and lubricant failure in the material. It was not until the 4th generation that a shift in thermal stability was noted for the tin stabilised system. An observable colour change was noted for the lead stabilised system. From the results the following trends were observed.

K50 Tin Stabilised Formulation

There was no visual change in colour between recycled samples even after the 4th generation regrind, minor changes were noted in colour measurements as shown in Table E. All materials processed satisfactorily with no decrease in processability throughout the evaluation

Several of the resulting series of data displayed a trend, whereas other results changed very little. An increase in the Izod and Charpy impact strength occurred between the virgin and 1st generation regrind. A plausible explanation for such an effect is better distribution of impact modifier throughout the matrix achieved by a higher degree of mixing via reprocessing. Most of the other physical properties remained the same. As anticipated the specific gravity was unchanged throughout, also the 50N Vicat, tensile stress and elongation at break remained fairly static. The thermal properties showed a marginally downward trend in static heat stability after the initial step change in virgin to 1st generation and only a step change upon the 4th generation regrind in dynamic heat stability. The recycling process increased the melt flow of the polymer as observed by the increasing index particularly for the change from virgin to 1st and 2nd generation regrind. A more consistent downward trend in heat distortion temperature was also noted from Virgin to 4th generation.

K57 Lead Stabilised Compound

The same conclusions cannot be drawn for this material.

A larger shift in colour was apparent although this grade was white rather than grey, which progressively changed after reprocessing. A visible difference can be detected by visual inspection which is confirmed by increased yellowness using colour measurement. The 4th generation regrind gave some processing problems with increasing shot size and evidence of surging, suggesting lubrication failure in the material., although there was still a comfortable margin of thermal stability remaining as supported by the residual dynamic and static heat stabilities.

Significantly lower impact results were recorded for this grade which is not surprising since the formulation contained no impact modifier. Consequently there was no step change in performance in this test as noted for the impact modified grade after the 1st generation regrind, (confirming the plausible explanation of better distribution of impact modifier). The main consistent changes were again observed in thermal properties which as anticipated progressively decreased, although relatively safe margins of thermal stability still remained even after the 10th thermal history i.e. 4th generation regrind. Other physical properties remained more consistent such as Vicat Softening point, tensile stress at yield and melt flow index, suggesting that the base polymer is less susceptible to reprocessing than was the case for impact modified grade.

5. Conclusions

This study has demonstrated that two dissimilar PVC-U formulations can be successfully recycled (100%) several times without significant loss in physical properties. The process involved injection moulding these grades which is more liable to thermal degradation than extrusion. The process did not allow normal ageing between the cycles which according to some researchers may be expected to somewhat reduce the thermal stability of the material (5). However, no additional additives were incorporated between reprocessing. Clearly such modifications could be utilised in practice whereby the recycled material may not necessarily be 100% recycled but blended with virgin material. The study has confirmed that the physical properties of recycled PVC-U are very similar to virgin material even after several passes. Indeed the grade containing impact modifier may show moderately improved impact strength performance upon recycling due to better dispersion of the modifier.

In summary, this study has demonstrated the feasibility of 100% recycling in a worst case scenario. These conclusions have been supported from a successful ongoing commercial recycling operation.

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Figure 1 Uses of Petroleum Products in Europe

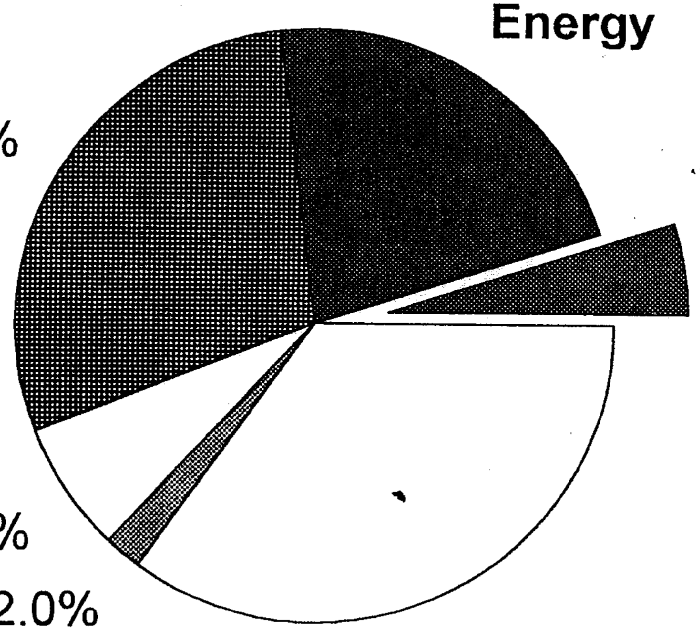
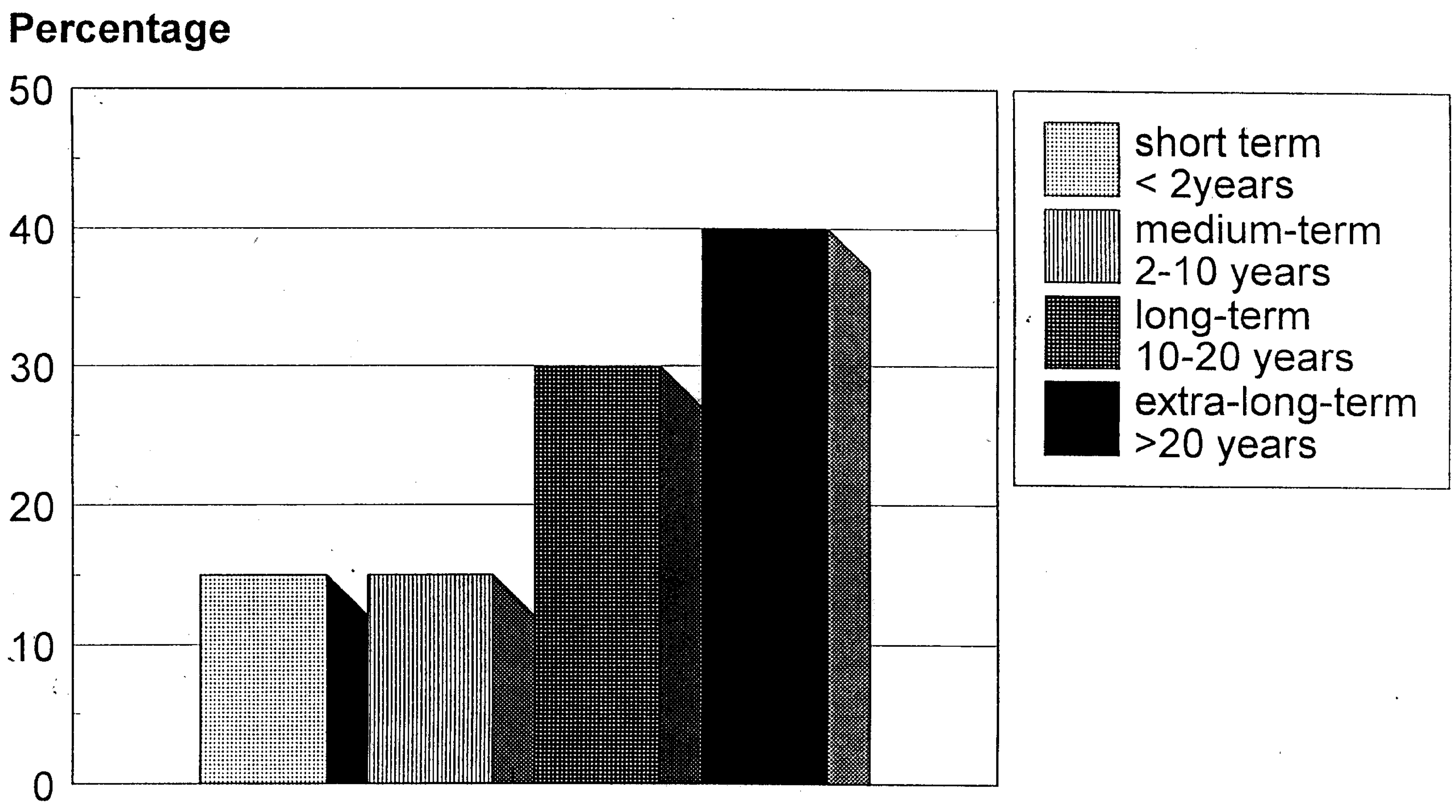


Figure 2 PVC Product Lifetimes



MATERIAL FORMULATIONS

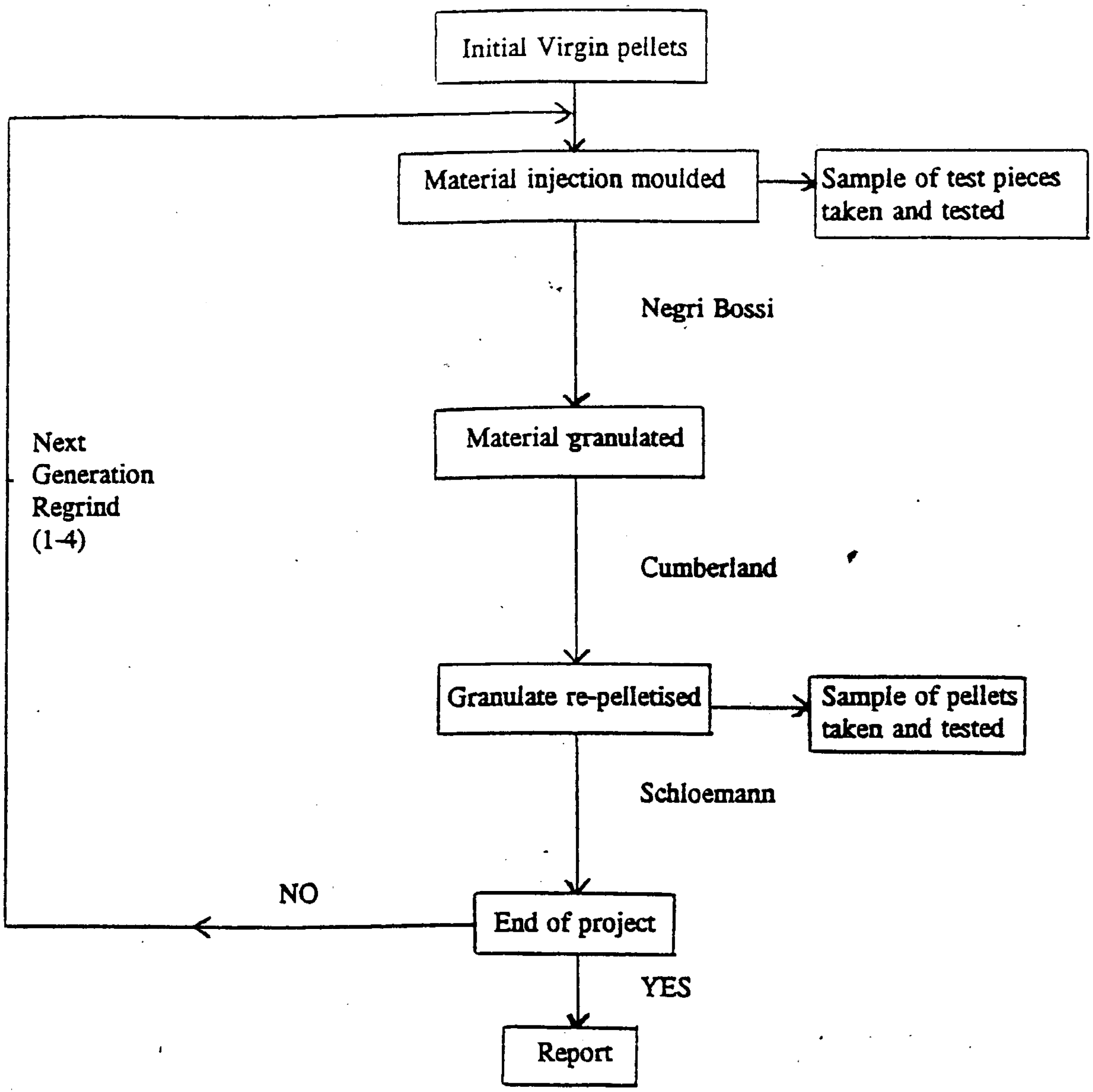
TABLE A

COMPOUND REFERENCE: 3360/84/1	
INGREDIENTS	**PARTS PER HUNDRED RESIN (PHR)**
PVC SUSPENSION RESIN (K50)	100.00
TIN STABILISER	2.00
IMPACT MODIFIER	14.00
LUBRICANTS - INTERNAL/EXTERNAL	4.00
PIGMENTATION	5.00

TABLE B

COMPOUND REFERENCE: 3360/84/2	
INGREDIENTS	**PARTS PER HUNDRED RESIN (PHR)**
PVC SUSPENSION RESIN (K57)	100.00
LEAD STABILISER/LUBRICATION	8.00
FILLER	5.00
PIGMENTATION	7.50

Figure 3 Process Flow Chart



1 pass of material = Injection moulding, granulation, compounding (pelletising).

TABLE C

Test	Units	3360/84/1 K50, TIN STABILISED				
		Virgin	1st Generation Regrind	2nd Generation Regrind	3rd Generation Regrind	4th Generation Regrind
Specific Gravity	g/cm³	1.372	1.370	1.370	1.370	1.370
50N Vicat Softening Point	°C	70.5	70.2	69.8	69.2	69.8
Izod Impact Strength	kJ/m²	45.99[D]	56.08[D]	55.29[D]	50.28[D]	50.71[D]
Standard Deviation	-	2.978	1.567	1.410	1.83	0.77
Charpy Impact Strength	kJ/m²	17.13[B]	30.33[D]	16.83[B]	16.27[B]	31.08[D]
Standard Deviation	-	0.943	1.175	0.80	0.34	0.81
Tensile Strength	MPa	42.21	43.21	43.25	44.43	42.39
Standard Deviation	-	0.26	0.20	0.15	0.30	0.43
Elongation at Break	%	41.20	41.80	42.40	38.20	54.60
Standard Deviation	-	8.11	3.56	2.88	3.56	9.74
Flexural Strength	MPa	56.91	53.74	57.83	55.77	56.30
Standard Deviation	-	0.77	0.95	0.52	0.51	0.38
Flexural Modulus	GPa	2.223	2.070	2.166	2.123	2.135
Standard Deviation	-	0.035	0.021	0.082	0.06	0.068
Heat Distortion Temperature	°C	57.0	56.0	54.0	53.0	49.5
Static Heat Stability @ 180°C	mins	102	83	83	83	77
Dynamic Heat Stability	mins	46	46	51	47	36
Macklow Smith Finish	-	C/D	C	B	A/B	A/B
Macklow Smith Pressure	kg/cm³	152	163	149	137	130
Melt Flow Index	g/10 min	44.57	65.58	71.93	75.07	74.65
Standard Deviation	-	1.23	0.85	0.94	1.27	2.04

*N.B. Izod, Charpy Impact Strengths — B denotes Brittle fracture; D denotes Ductile fracture

TABLE D

Test	Units	3360/84/2 K57, LEAD STABILISED				
		Virgin	1st Generation Regrind	2nd Generation Regrind	3rd Generation Regrind	4th Generation Regrind
Specific Gravity	g/cm^3	1.510	1.509	1.510	1.510	1.508
50N Vicat Softening Point	°C	78.9	79.3	79.5	79.6	79.3
Izod Impact Strength	kJ/m^2	6.21[B]	6.23[B]	6.35[B]	4.97[B]	5.55[B]
Standard Deviation	-	0.626	0.640	0.798	0.40	0.99
Charpy Impact Strength	kJ/m^2	6.81[B]	6.22[B]	5.72[B]	5.81[B]	6.32[B]
Standard Deviation	-	0.668	0.891	0.31	0.52	1.20
Tensile Strength	MPa	50.28	51.09	50.14	50.98	48.06
Standard Deviation	-	0.87	0.25	0.35	0.61	0.54
Elongation at Break	%	90.00	53.80	45.60	68.6	92.40
Standard Deviation	-	42.08	6.53	5.03	19.19	20.88
Flexural Strength	MPa	67.54	64.47	70.06	68.33	63.40
Standard Deviation	-	0.53	0.45	0.30	0.53	1.95
Flexural Modulus	GPa	2.952	2.789	2.940	2.927	2.568
Standard Deviation	-	0.041	0.054	0.122	0.052	0.151
Heat Distortion Temperature	°C	57.5	57.0	56.5	54.5	51.0
Static Heat Stability @ 180°C	mins	367	269	259	249	280
Dynamic Heat Stability	mins	62	47	51	45	42
Macklow Smith Finish	-	E	B/C	B/C	C	B/C
Macklow Smith Pressure	kg/cm^3	254	245	239	231	226
Melt Flow Index	g/10 min	9.77	9.98	10.15	10.01	10.78
Standard Deviation	-	0.19	0.35	0.37	0.31	0.18

*N.B. Izod, Charpy impact strengths   B denotes Brittle fracture

3360/84/1 - K50, TIN

TABLE E

	L	a	b	dl	da	db	dE
Virgin	78.75	-0.85	7.55	0	0	0	0
1st Generation Regrind	78.16	-0.42	7.75	-0.59	0.43	0.20	0.76
2nd Generation Regrind	78.21	-0.86	7.49	-0.54	-0.01	-0.06	0.54
3rd Generation Regrind	78.42	-0.77	7.61	-0.33	0.08	0.06	0.34
4th Generation Regrind	77.20	-0.68	7.47	-1.55	0.17	-0.08	1.56

Notes:

1st generation regrind: Darker, less green, slightly yellower than Virgin.

2nd generation regrind: Slightly lighter, more green, less yellow than 1st generation regrind.

3rd generation regrind: Lighter, less green, yellower than 2nd generation regrind.

4th generation regrind: Darker, less green, less yellow than 3rd generation regrind.

3360/84/2 - K57, LEAD

TABLE F

	L	a	b	dl	da	db	dE
Virgin	91.94	-1.30	0.37	0	0	0	0
1st Generation Regrind	91.48	-1.32	1.48	-0.46	-0.02	1.11	1.20
2nd Generation Regrind	91.11	-1.32	2.58	-0.83	-0.02	2.21	2.36
3rd Generation Regrind	91.55	-1.39	2.62	-0.39	-0.09	2.25	2.29
4th Generation Regrind	91.08	-1.59	3.89	-0.86	-0.29	3.52	3.64

Notes:

1st generation regrind: Darker, slightly greener, more yellow than virgin.

2nd generation regrind: Darker, same greenness, more yellow than 1st generation regrind.

3rd generation regrind: Lighter, slightly greener, slightly yellower than 2nd generation regrind.

4th generation regrind: Darker, greener, yellower than 3rd generation.

RECYCLING PROJECT - SUMMARY OF WEATHERING DATA

Natural Weathering - Aycliffe 45° South - 6 months

MATERIAL	INITIAL READING			FINAL READING			
K50, TIN	L	a	b	L	a	b	dE
Virgin	77.72	-0.85	7.77	77.86	-0.83	7.53	0.3
1st G.R.	77.51	-0.89	7.77	77.56	-0.86	7.37	0.4
2nd G.R.	77.3	-0.89	7.65	78.14	-0.9	7.08	1
3rd G.R.	77.02	-0.86	7.66	78.43	-0.89	6.56	1.8
K57, Lead							
Virgin	91.29	-1.52	1.16	90.58	-1.06	0.73	0.9
1st G.R.	90.77	-1.5	1.66	90.29	-1	1	1
2nd G.R.	90.46	-1.66	2.67	89.72	-1.01	1.66	1.4
3rd G.R.	90.18	-1.75	3.45	89.48	-1	1.98	1.8

Natural Weathering - Florida, 45° South - 6 Months

MATERIAL	INITIAL READING			FINAL READING			
K50, TIN	L	a	b	L	a	b	dE
Virgin	78.27	-0.97	8.04	79.47	-0.95	7.38	1.4
1st G.R.	77.96	-1.03	8.02	81.55	-0.88	6.21	4
2nd G.R.	77.64	-1.05	8.03	82.99	-0.81	5.37	6
3rd G.R.	77.28	-1.01	8	83.23	-0.8	5.38	6.5
K57, Lead							
Virgin	91.81	-1.66	1.36	90.02	-0.16	3.23	3
1st G.R.	91.4	-1.71	2.47	90.27	-0.27	2.98	1.9
2nd G.R.	90.99	-1.8	3.19	90.38	-0.39	2.75	1.6
3rd G.R.	90.68	-1.84	3.72	90.14	-0.39	2.88	1.8

RECYCLING PROJECT - SUMMARY OF WEATHERING DATA

Q.U.V. (2000 Hours)

MATERIAL	INITIAL READING			FINAL READING			
K50, TIN	L	a	b	L	a	b	dE
Virgin	77.72	-0.85	7.77	79.37	-0.73	8.5	1.8
1st G.R.	77.51	-0.89	7.77	81.98	-0.62	6.56	4.6
2nd G.R.	77.3	-0.89	7.65	79.62	-0.09	9.11	2.9
3rd G.R.	77.02	-0.86	7.66	81.19	-0.59	7.58	4.2
K57, Lead							
Virgin	91.29	-1.52	1.16	92.78	-1.14	1.14	1.5
1st G.R.	90.77	-1.5	1.66	92.24	-1.14	1.5	1.5
2nd G.R.	90.46	-1.66	2.67	92.26	-1.2	2.34	1.9
3rd G.R.	90.18	-1.75	3.45	92.41	-1.19	2.32	2.6

Heraeus (4000 Hours - Partially Complete @1500 Hours)

MATERIAL	INITIAL READING			FINAL READING			
K50, TIN	L	a	b	L	a	b	dE
Virgin	77.72	-0.88	7.77	77.94	-0.91	9.68	1.9
1st G.R.	77.51	-0.89	7.77	73.53	1.59	13.12	6.7
2nd G.R.	77.3	-0.89	7.65	77.16	0.53	10.97	3.6
3rd G.R.	77.02	-0.86	7.66	76.03	0.64	12.35	5
K57, Lead							
Virgin	91.29	-1.52	1.16	93.15	-0.98	-0.37	2.5
1st G.R.	90.77	-1.5	1.66	91.96	1.59	13.12	11.9
2nd G.R.	90.46	-1.66	2.67	91.8	-1.01	0.14	2.9
3rd G.R.	90.18	-1.75	3.45	92.46	-0.88	0.07	4.2