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Effect of recycled plastic and compound additives on the properties of an injection-moulded polypropylene co-polymer

Part 3 *Impact properties*

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Micromorphology studies and a falling-dart impact test have been used to investigate the effect of recycled material and pigments on the properties of an injection-moulded polypropylene co-polymer. The use of some pigments have been shown to have a more deleterious effect upon impact properties than that which occurs when recycled material is used as feedstock. The results have been partly explained in terms of changes in micromorphology which accompany the addition of pigments and recycled material to the feedstock.

1. Introduction

The main aim of the work reported in this paper was to assess the effect of incorporating recycled material and pigments on the micromorphology, impact and weathering properties of an injection-moulded polypropylene co-polymer. The moulds used in this work, the moulding procedures and the characterization techniques have been described in Part 1 [1].

2. Experimental method

The set processing conditions used in the moulding of all test specimens prepared for the experiments reported in this paper are given in Table I. It will be noted that these conditions are the same as those given in Part 1, Table I [1] except that the injection temperature was raised by 20° C. This increase in temperature was used to eliminate the previously reported orientation effects in the injection-mouldings. The previously described moulding procedures [1, 2] ensured that contamination and the reproducability of properties within batches of mouldings were kept to a minimum and maximum, respectively. The results presented in this paper are all based on 3 mm thick, 8 cm square plaques. The full range of feedstocks studied is given in Table II where the following notation applies. The type of pigmentation is represented by the letters V, A, B and C which corresponds to virgin unpigmented polymer, phthalocyanine blue, ultramarine blue and carbon black, respectively. The two blues were used in powder form and the carbon black in the form of masterbatch. The pigments were tumble-mixed with the virgin polymer prior to moulding. The second half of the notation represents the concentration and type of reground material used in the compound. For example 0.5B–25Gl represents feedstock containing 0.5 wt% ultramarine blue pigment and containing 25 wt% reground material in granulate form which had been recycled once prior to the final injection-moulding cycle.

TABLE I Set processing conditions used in the moulding of all test plaques used in the work reported in this paper which were prepared on a Stubbe SKM 76.110 injection-moulding machine

Condition	Value
Nozzle heating (° C)	225
Heating 1 (° C)	215
Heating 2 (° C)	195
Heating 3 (° C)	180
Mould temperature (° C)	60
Cooling time (sec)	30
Injection pressure stage 1 ($MN\,m^{-2}$)	5.5
Injection pressure stage 2 ($MN\,m^{-2}$)	5.2
Injection time (sec)	30

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TABLE II Tabulation of compounds from which the results presented in Part 3 were obtained. The notation used to identify the range of compounds is described in the text

General description of feedstock	Virgin no pigment	Virgin material with 0.1% pigment increasing percentage of recycled material	Virgin material with 0.5% pigment increasing percentage of recycled material	Virgin material with 2.0% pigment increasing percentage of recycled material
Phthalocyanine blue	V	0.1A–0Gl	0.5A–0Gl	2.0A–0Gl
		0.1A–10Gl	0.5A–10Gl	2.0A–10Gl
		0.1A–25Gl	0.5A–25Gl	2.0A–25Gl
		0.1A–100Gl	0.5A–100Gl	2.0A–100Gl
Ultramarine blue	V	0.1B–0Gl	0.5B–0Gl	2.0B–0Gl
		0.1B–10Gl	0.5B–10Gl	2.0B–10Gl
		0.1B–25Gl	0.5B–25Gl	2.0B–25Gl
		0.1B–100Gl	0.5B–100Gl	2.0B–100Gl
Carbon black	V	0.1C–0Gl	0.5C–0Gl	2.0C–0Gl
		0.1C–10Gl	0.5C–10Gl	2.0C–10Gl
		0.1C–25Gl	0.5C–25Gl	2.0C–25Gl
		0.1C–100Gl	0.5C–100Gl	2.0C–100Gl

3. Impact test results

The impact test results gained from the range of compounds identified in Table I before and after weathering are summarized in Figs 1 to 4. The first column in each figure shows the impact strength of plaques prepared from virgin feedstock containing no pigment, which is similar to the result presented in Part 2 [2]. The difference in impact values for the virgin compounds used in the two parts of the investigations is attributed to the difference in processing conditions used for the injection-moulding of the impact test specimens.

3.1. The effect of pigment at 0.1% concentration

The histograms shown in Fig. 1 represent the effect of incorporating pigment at the 0.1% level and recycled material at the 0%, 10%, 25% and 100% level upon the impact strength of 3 mm thick plaque mouldings at test temperatures of + 23 and – 10° C.

At + 23° C the virgin plaques containing 0.1% phthalocyanine blue showed a slight decrease in impact strength compared to that of the virgin plaques containing no pigment. The virgin plaques containing 0.1% ultramarine blue and 0.1% carbon black, however, showed no fall-off in performance due to the pigment and, indeed, a slight improvement was noted.

At – 10° C the virgin plaques containing 0.1%' phthalocycanine blue showed a marked decrease in impact strength, falling from 24.3 J for the virgin plaques containing no pigment to 9.1 J for the virgin plaques containing 0.1% phthalocyanine blue. The virgin plaques containing 0.1% ultramarine blue showed no change in impact strength when compared with the corresponding unpigmented plaques. This was not, however, the case for the virgin plaques containing 0.1% carbon black which showed a fall-off in impact strength of ~ 8.8 J.

3.2. The effect of incorporating 10, 25 and 100% recycled material containing 0.1% pigment

At + 23° C test temperature an increase in the percentage of recycled material up to 100% had little, if any, effect upon the impact strength of the plaques when compared with the impact strength of plaques prepared from pigmented virgin feedstock. The plaques containing 10, 25 and 100% recycled 0.1% ultramarine blue and carbon black pigmented polypropylene all had very similar impact strengths, which were similar to the measured impact strength of the plaques prepared from unpigmented virgin feedstock. The slight fall-off in the performance of the virgin plaques containing 0.1% phthalocyanine blue when compared with unpigmented virgin material also occurs in the plaques containing recycled material, but no further decrease was associated with the incorporation of recycled material.

At – 10° C test temperature the incorporation of the recycled material had no effect upon the impact performance of the plaques containing 0.1% phthalocyanine blue. A similar result was

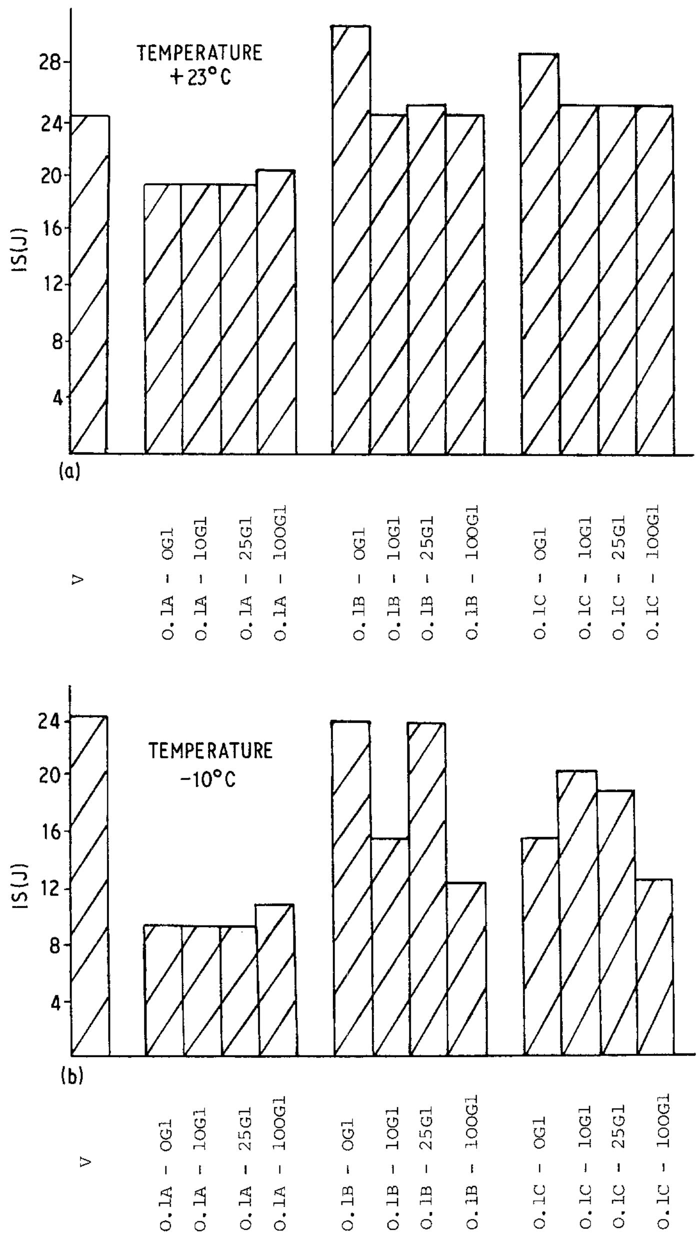


Figure 1 The impact strength (IS) in Joules of 3 mm thick plaque mouldings containing 0.1% pigment and 0, 10, 25 and 100% recycled material tested at (a) + 23° C and (b) — 10° C.

recorded for plaques containing 0.1% carbon black although in the latter case the plaques containing 10 and 25% recycled material showed a slight improvement in impact performance when compared with that of the corresponding virgin plaques. The effect of incorporating recycled material containing 0.1% ultramarine blue on impact strength is different from that recorded for the phthalocyanine pigment. A decrease in the impact performance from 23.7 to ~ 16 J on average is observed for the plaques containing 10 and 100% recycled material, whereas the impact strength of plaques containing 25% recycled material was similar to that recorded for plaques which were prepared from virgin feedstock.

3.3. The effect of compounding with pigment at 0.5% concentration

The histograms shown in Fig. 2 illustrate the effects of incorporating pigment at the 0.5% level and recycled material at the 0, 10, 25 and 100% levels upon the impact strength of 3 mm thick plaque mouldings measured at test temperatures of + 23 and — 10° C.

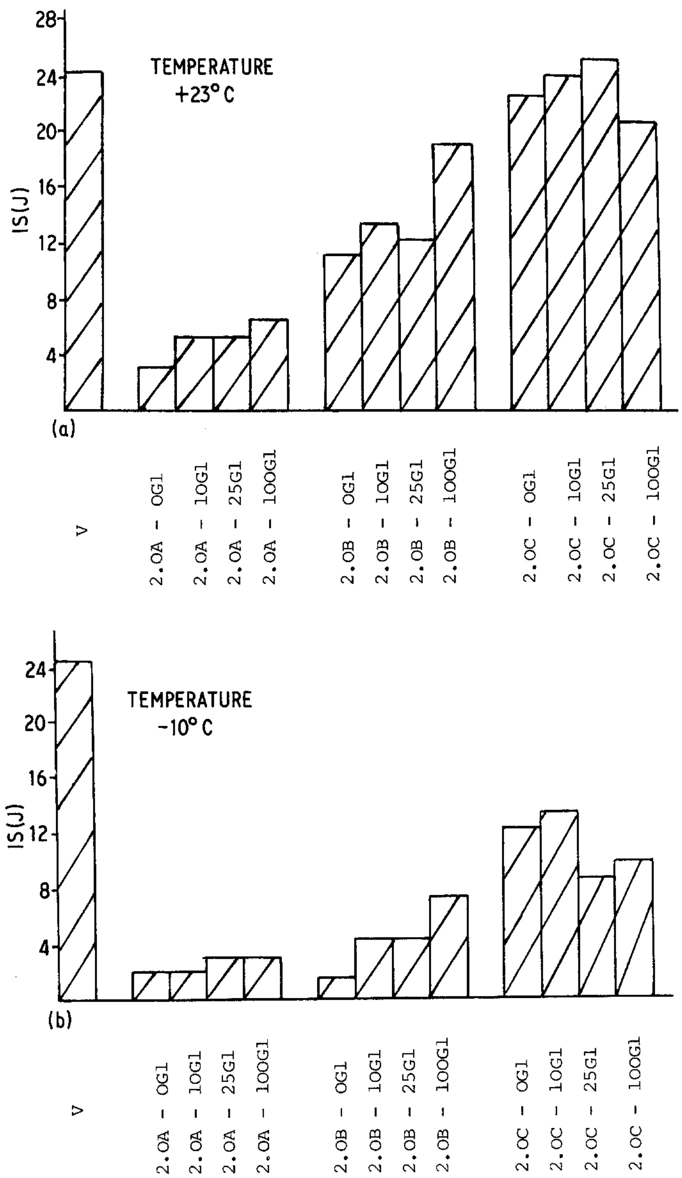


Figure 2 The impact strength (IS) in Joules of 3 mm thick plaque mouldings containing 0.5% pigment and 0, 10, 25 and 100% recycled material tested at (a) + 23° C and (b) — 10° C.

At an impact test temperature of + 23° C the incorporation of 0.5% phthalocyanine blue pigment in previously unpigmented virgin polymer caused the impact strength of the injection-moulded test plaques to be reduced from 24.3 to 11.2 J. The incorporation of 0.5% ultramarine blue and 0.5% carbon black had no deleterious effect upon the impact strength of the mouldings and some improvement was noted in the performance of the plaques containing 0.5% carbon black. At the test temperature of — 10° C the embrittling effect of the phthalocyanine blue upon the mouldings is quite marked, the impact strength falling from 24.3 to 5.2 J with the incorporation of the pigment, A smaller but none the less significant decrease in impact strength was also recorded following the incorporation of 0.5% ultramarine blue and 0.5% carbon black pigments, where the recorded impact strengths decreased by 6 and 11 J, respectively.

3.4. The effect of incorporating 10, 25 and 100% recycled material containing 0.5% pigment

In general, the effect of the incorporation of recycled material at the 10, 25 and 100% levels upon the impact performance of the plaques was negligible compared with the reduction in impact strength which occurred when 0.5% pigment was

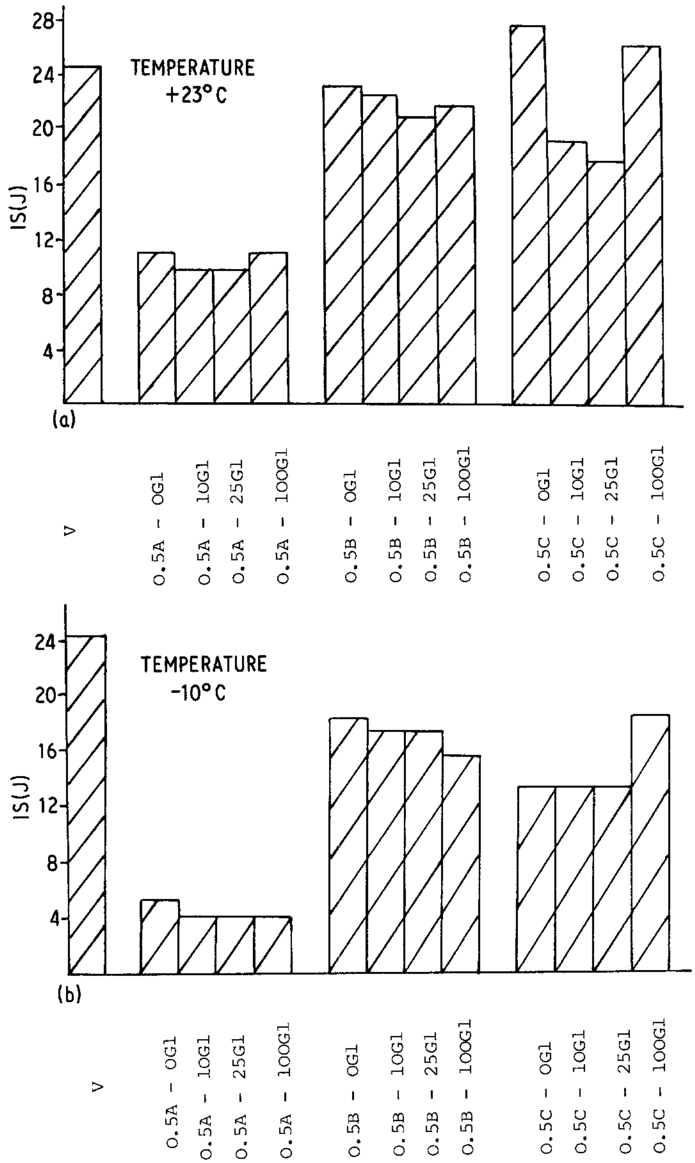


Figure 3 The impact strength (IS) in Joules of 3 mm thick plaque mouldings containing 2% pigment and 0, 10, 25 and 100% recycled material tested at (a) + 23° C and (b) − 10° C.

incorporated in virgin feedstock. The same result applied at impact test temperatures of + 23 and − 10° C.

3.5. The effect of compounding with pigment at 2% concentration

The histograms shown in Fig. 3 represent the effect of incorporating pigment at the 2% level and recycled material at the 0, 10, 25 and 100% levels upon the impact strength of 3 mm thick plaque mouldings measured at test temperatures of + 23 and − 10° C.

At a test temperature of + 23° C all of the plaques containing 2% phthalocyanine failed in a brittle manner, the impact strength falling to 3.3 J which represents a marked decrease in properties when compared with plaques prepared from virgin material containing no pigment and an impact strength of 21 J. A smaller reduction in impact strength but nevertheless still significant at 50% was recorded in the impact tests on plaques prepared from virgin material containing 2% ultramarine blue. The incorporation of carbon black, at the 2% level caused a very small change in the impact performance of the plaque mouldings when measured at + 23° C. At − 10° C all three pigments tested had an embrittling effect upon the plaque mouldings, the impact performance of the phthalocyanine blue, ultramarine blue and carbon black decreasing by 22.3, 22.8 and 12.1 J, respectively.

3.6. The effect of incorporating 10, 25 and 100% recycled material containing 2% pigment

At the test temperature of + 23° C the incorporation of recycled material up to 100% had no deleterious effect upon the impact properties of the mouldings when the recorded values were compared with those obtained from the plaques prepared from the corresponding virgin feedstock containing pigment. In general, an improvement in impact strength with the incorporation of recycled material was observed. The improvement in the impact properties of plaques prepared from 100% recycled material containing 2% ultramarine blue was quite marked, and increased from a value of 11.2 J for virgin plaques to 19.3 J for those prepared from 100% recycled material. At the test temperature of − 10° C the incorporation of recycled material again, in general, caused an improvement in the impact properties of the plaque mouldings when compared with the results gained from the corresponding virgin plaques. The exception at test temperatures of + 23 and − 10° C occurred with recycled carbon black pigment material which showed a slight decrease in impact strength. The marked improvement in the impact strength of mouldings prepared from 100% recycled material containing 2% ultramarine blue was also observed at − 10° C.

3.7. Summary of impact test results on unweathered plaques

It is evident from the results shown in Figs 1 to 3 that the incorporation of any of the three pigments studied can have a marked deleterious effect upon the impact properties of the injection-moulded parts. The impact strength of the injection-moulded plaques decreases with increasing pigment concentration in the range 0.1 to 2.0%. Carbon black had the least deleterious effect upon the impact strength of the plaques. Phthalocyanine blue caused the most marked change in measured values of impact strength and even at the 0.1% level the plaques which contained this pigment showed a marked fall-off in impact strength. The ultramarine blue had little effect at the 0.1% level, although at the higher loadings some embrittlement clearly occurs.

In general the effect of incorporating recycled material up to a 100% level is, if any, to improve the impact properties of the mouldings. The improvement in impact properties of plaques containing 2% ultramarine blue following the incorporation of recycled material is quite marked. However, the effect of incorporating recycled material on impact strength is negligible compared with the effect of incorporating pigments.

4. The effect of weathering on the impact strengths of moulded plaques

The histograms shown in Fig. 4 represent the effect of incorporating pigments at the 2% level and recycled material at the 0, 10, 25 and 100% levels upon the impact strength of 3 mm thick plaque mouldings. The impact test temperatures were chosen to be + 23 and − 10° C and the tests were carried out on specimens before and after being subjected to natural weathering.

4.1. The effect of compounding with pigment at 2% concentration upon the weathering characteristics of 3 mm plaque mouldings

At a test temperature of + 23° C the impact strength of the unpigmented virgin plaques was reduced after six months natural weathering to less than 0.3 J. All the mouldings were observed to fail in a brittle manner. A similar result was observed for plaques prepared from virgin feedstock containing 2% ultramarine blue. Some protection was afforded by 2% phthalocyanine blue pigment where the recorded impact strength was shown to decrease slightly from 3.3 to 3 J after weathering. The carbon black at 2% concentration afforded the best protection, where the measured impact strength of virgin plaques was recorded to increase from 22.9 to 27.1 J after weathering for one year.

The weathering resistance of the mouldings is improved by the addition of phthalocyanine blue pigment at the 2% level. This improvement is observed at test temperatures of + 23 and − 10° C and, indeed, after weathering a slight improvement in impact performance was noted.

When 2% ultramarine blue pigment is incorporated in weathered plaques, the effect of impact testing reverse sides for mouldings at − 10 and + 23° C is most clearly revealed. The impact strength of plaques tested at − 10° C, with the weathered side uppermost, being greater than those tested at + 23° C with the unweathered surface uppermost. The sensitivity of the plaques containing ultramarine blue to the position of the weathered surface compared with the lack

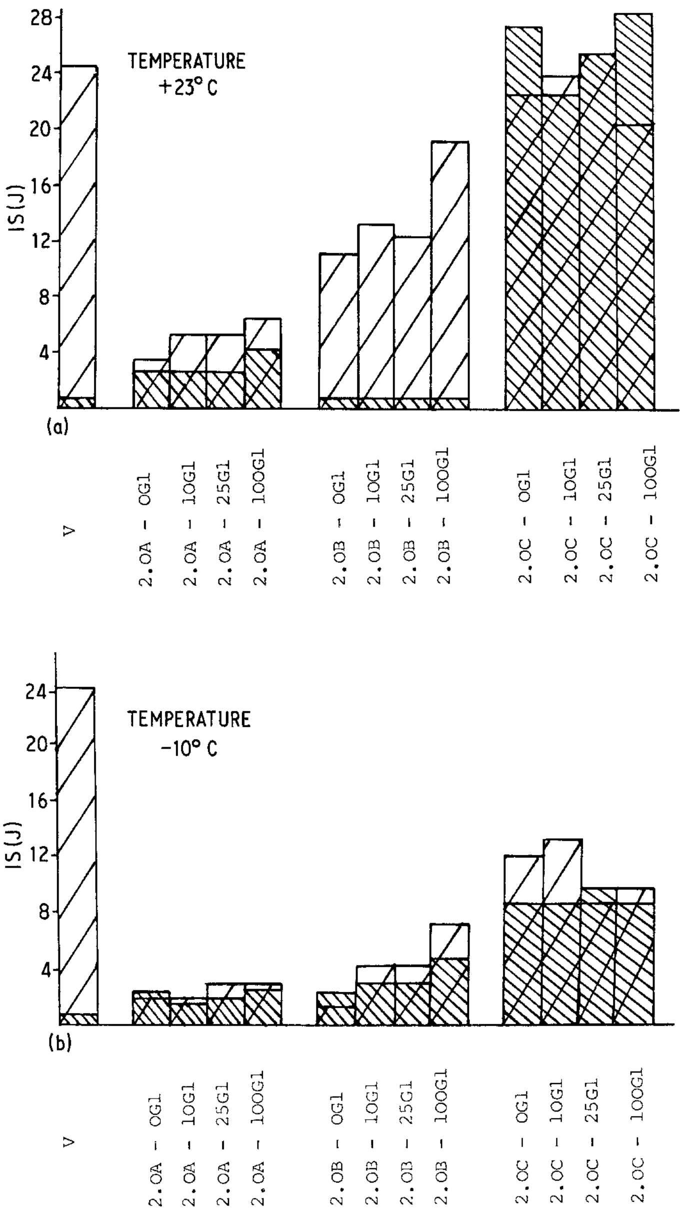


Figure 4 The impact strength (IS) in Joules of 3 mm thick plaque mouldings containing 2% pigment and 0, 10, 25 and 100% recycled material tested at (a) + 23° C and (b) — 10° C before and after natural weathering. The impact strength after natural weathering is shown in cross-hatching.

of sensitivity for the corresponding unpigmented plaques does indicate that the ultramarine blue reduces the extent of penetration of the ultraviolet degradation into the mouldings. This caused the degradation to be more confined to one surface than is the case for the unpigmented plaques. Carbon black afforded good protection although some reduction in impact strength at a test temperature of — 10° C was recorded when the impact strength decreased from 12.2 J for the unweathered plaques to 8.2 J after weathering for six months.

4.2. The effect of weathering on samples containing 0, 10, 25 and 100 % recycled material

The effect of incorporating 0, 10, 25 and 100% recycled material upon the impact strength of 3 mm thick plaque mouldings containing 2% pigment before and after six months natural weathering was negligible at both test temperatures. Any effect, if any, upon the weatherability of the plaques was shown to improve the performance of the plaques. This was especially true in the case of plaques prepared from 100% recycled material containing 2% carbon black which showed an increase, upon weathering and testing at + 23° C, of ~ 8 J in impact strength.

4.3. Summary of impact test results on weathered plaques

In general, the incorporation of 2% carbon black and 2% phthalocyanine blue afforded good protection against ultra-violet degradation. This is not the case, however, for 2% ultramarine blue which afforded little protection against photodegradation. The effect of incorporating recycled material upon the weathering characteristics of the injection-mouldings containing 2% pigment was negligible.

5. Microstructure of moulded plaques

Transmission light microscopy was used to examine thin sections from the injection-moulded plaques. In all cases the thin sections were prepared from the injection-mouldings by microtomy with a sledge microtome and in the orientations relative to the injection direction shown in Part 1 [1], Fig. 2. It was anticipated that the microstructural detail revealed by these sections would give an indication of the reasons why the impact properties of the mouldings are caused to change with changes in compound formulations.

5.1. Phthalocyanine blue

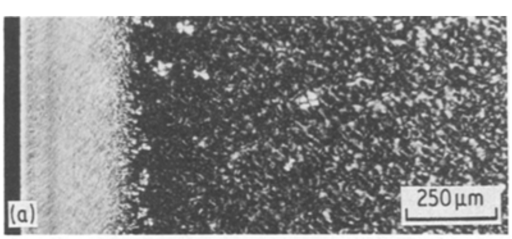
Light micrographs from mouldings containing the phthalocyanine blue pigment revealed that the pigment acts as a nucleating agent which causes a marked reduction in the size of the spherulites in the core of the mouldings compared with that observed in the pigment-free mouldings.

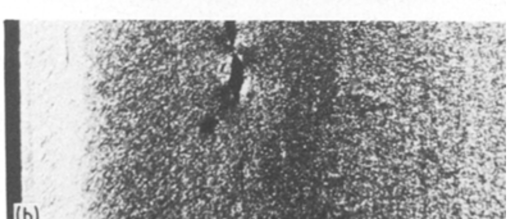
Fig. 5a and b illustrates the structure of the pigment-free and 2% phthalocyanine blue injection mouldings, respectively. The powerful nucleating effect of the phthalocyanine blue pigment is clearly illustrated and even at the lower loadings of 0.1 and 0.5% pigment a similar microstructure to that shown in Fig. 5b was observed. The dispersion of phthalocyanine blue pigment in polypropylene is relatively poor, a characteristic feature of this pigment, and even at low loadings and after recycling no significant change in the dispersion was observed. The marked reduction in the impact strength of injection-mouldings containing phthalocyanine blue pigment cannot simply be attributed to the nucleating effect of this pigment, because nucleation can also be accelerated by the presence of a good dispersion of carbon black pigment, as illustrated in Fig. 5c, without the attendant decrease in impact strength. This observation indicates that apart from pigment agglomerates the actual structure of the spherulites in the two materials and/or the degree of crystallization may differ.

5.2. Ultramarine blue

The effect of increasing the concentration of ultramarine blue pigment on the microstructure of injection-mouldings is illustrated in Fig. 6. The micrographs show that an increase in the concentration of ultramarine blue pigment causes an increase in the proportion of Type III negatively bi-refringent spherulites in the skin-core region of the mouldings.

The structure of the core spherulites and the skin remains essentially the same and is independent of pigment concentration. The Type III spherulites appear as bright regions in Fig. 6.





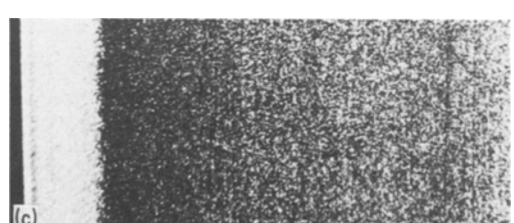


Figure 5 Micrographs taken parallel to the injection direction illustrating the structure of 3 mm thick plaque injection-mouldings manufactured from (a) virgin compound containing no pigment, (b) material recycled at the 100% level containing 2% phthalocyanine blue pigment and (c) material recycled at the 100% level containing 2% carbon black pigment.

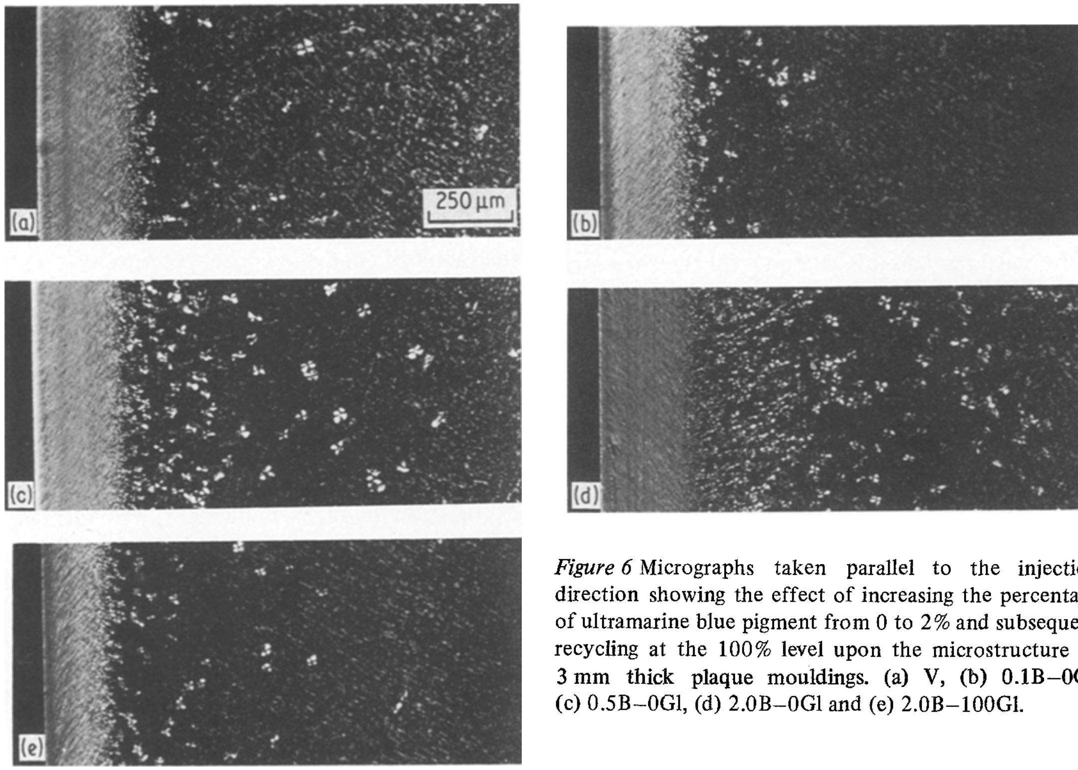


Figure 6 Micrographs taken parallel to the injection direction showing the effect of increasing the percentage of ultramarine blue pigment from 0 to 2% and subsequent recycling at the 100% level upon the microstructure of 3 mm thick plaque mouldings. (a) V, (b) 0.1B–0Gl, (c) 0.5B–0Gl, (d) 2.0B–0Gl and (e) 2.0B–100Gl.

This specific nucleating characteristic of certain compounds has been reported previously [3] although a search of the literature revealed that this effect has not been observed for a commercially used pigment.

At the 0.1% pigment concentration the microstructure of the plaques is very similar to that observed in the unpigmented plaques as shown in Fig. 6a and is reflected in the similar impact properties of the two sets of mouldings.

An increase in the proportion of Type III spherulites was observed when the pigment concentration was increased to 0.5% and subsequent impact testing revealed a significant decrease in the impact strength of these mouldings.

The nucleation of Type III spherulites is even more apparent in compounds containing 2% ultramarine blue pigment. Fig. 6d shows that the proportion of Type III spherulites in the skin-core region increases with percentage increase in pigment extending into the core of the moulding. The predominance of Type III spherulites in the skin-core region of the mouldings indicates the importance that shear forces in the melt play in their formation, as reported previously [4]. A reduction in these shear forces caused by a decrease in viscosity of the melt would therefore be expected to cause a decrease in the proportion of Type III spherulites. A comparison of micrographs of mouldings prepared from virgin (2.0B–0Gl) and 100% recycled material (2.0B–100Gl) both containing 2% ultramarine blue pigment supports this. The microstructure of mouldings prepared from recycled material (2.0B–100Gl) in terms of the proportion of Type III spherulites is more similar to that observed in pigment free plaques (V). This is attributed to the reduction in shear forces in the melt which accompanies the decrease in molecular weight caused by the recycling process. The decrease in molecular weight also accounts for the reduction in thickness of the skin region of the mouldings prepared from 100% recycled material.

The impact test results show that a reduction in Type III spherulites with increasing percentage of recycled material at the 2% ultramarine pigment concentration results in an improvement in impact performance, and more than compensates for the reduction in molecular weight and skin thickness associated with recycling.

5.3. Carbon black

The microstructure of plaques produced from virgin (V) and 100% recycled material (2.0C–

100Gl) containing 2% carbon black pigment are illustrated in Fig. 5a and c, respectively. Recycling clearly results in a marked improvement in the dispersion of the pigment which reduces the likelihood of premature failure initiation at large pigment agglomerates. The ability of the carbon black particles to act as heterogeneous nuclei is increased with an improvement in the dispersion of the particles and this accounts for the decreases in the size of the core spherulites in mouldings prepared from recycled material. A combination of this nucleating effect and agglomerates providing premature failure initiation sites leads to a small reduction in the impact strength of mouldings (at low temperature) containing a relatively high concentration of carbon black.

6. Concluding remarks

The main aim of the work described above was to investigate the influence of recycled material and pigments on the impact properties of one grade of an injection-moulded polypropylene co-polymer. The incorporation of recycled material and pigments into the polypropylene feedstock used for injection-moulding caused marked changes in micromorphology, which could be used in part to explain some of the reported changes in impact properties of the moulded plaques with changes in compound formulation.

The impact properties of the mouldings, which were all produced under the same injection-moulding conditions were not significantly altered by increasing the concentration of recycled material, whereas an increase in the concentration of blue pigments caused a decrease in impact strength. A combination of increasing concentrations of pigment and recycled material in the case of ultramarine blue pigment caused the impact strength of the moulded plaques to be maintained to a relatively high level, as featured in Fig. 6. This example illustrates the complexity of the factors which influence the micromorphology and impact properties of injection-moulded polypropylene co-polymer.

In this one example the incorporation of lower molecular weight recycled material caused a reduction in the nucleation of Type III spherulites in the shear-zone layer structure, a banded structure whose presence is associated with brittle impact behaviour. Similar changes in micromorphology could have been produced by using virgin feedstock material with a different molecular weight distribution in the first place. Hence, it would be unwise to extrapolate the reported results to different grades of polypropylene co-polymer. Furthermore the injection-moulding process conditions used to produce the test specimens represent one set in a large window of process conditions which could be used to produce mouldings of acceptable appearance. The micromorphology of the moulded thermoplastic and the impact properties, including temperature dependence of impact strength and the dispersion of pigments will all vary with processing conditions and will in turn be modified to different extents by additions of pigments and recycled material to the feedstock compound.

The addition of carbon black pigment at 2 wt% provides excellent protection against degradation by ultra-violet light, and the impact properties were not affected by the addition of recycled material. Some protection also results from the use of phthalocyanine blue pigment, while less protection is given by ultramarine blue pigment for the grade of polypropylene used as the base of the compound.

A more detailed assessment of the effects of weathering on the impact properties of injection-mouldings will be presented in a following paper, which deals primarily with the influence of pigments and recycled materials on the same grade of polypropylene, but with the further addition of an ultra-violet light stabilizer.

In the preparation of materials which were used as feedstock for the experiments referred to above extreme care was taken to exclude particulate impurities which can arise in the reclamation process, and whose presence in injection-moulded parts can cause a marked reduction in impact strength, as can poor dispersion of pigment. The recycled materials used in the tests reported to date therefore represent a practical situation where off-cuts and sprues and runners, for example, are regranulated and used as part of the feedstock. The following and final paper in this series of four papers will include some results on tests conducted with used polypropylene scrap and these will indicate the role of particulate impurities and other contaminants on the properties of recycled polypropylene.

Work is also in progress on similar studies on polypropylene co-polymers with higher molecular weights and in the near future these results will provide a useful comparison with the results presented above.

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