

The Effects of Copper Contamination on the Properties of High Density Polyethylene

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ABSTRACT

It is a widely held belief that contamination of recycled thermoplastics presents a major barrier to their use for many applications. Loss of material performance and high costs associated with contamination removal are often cited as reasons against using recyclates. Common contaminants include paint flakes, immiscible polymers, oil, dirt and metal fragments picked up during the service life of a plastic part. This report presents results obtained from mechanical tests on high density polyethylene doped with known concentrations of metallic fragments, in this case copper; a common contaminant found in plastics recovered from applications in the electronic and automotive industries. Results show that properties such as Young's modulus, strain to failure, melt flow index, and impact energies are largely unaffected by copper contamination up to concentrations of 5 wt%, except at very low temperatures. This work highlights the possibility that recycled thermoplastics could be suited to a variety of applications without having to undergo costly cleaning processes, thus increasing profitability through informed use of these materials compared to virgin plastics.

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Approved on behalf of Managing Director, NPL, by Dr C Lea,
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CONTENTS

1. INTRODUCTION 1

2. MATERIALS AND TEST METHODS..... 2

 2.1 YOUNG’S MODULUS AND STRAIN TO FAILURE 2

 2.2 VISCOSITY AS INDICATED BY MFI..... 2

 2.3 IMPACT ENERGIES..... 2

 2.3.1 Charpy impact 2

 2.3.2 Falling weight impact..... 2

 2.3.3 Tensile impact 2

3. RESULTS..... 3

 3.1 YOUNG’S MODULUS AND STRAIN TO FAILURE 3

 3.2 VISCOSITY AS INDICATED BY MFI..... 3

 3.3 IMPACT ENERGIES..... 3

 3.3.1 Charpy impact 3

 3.3.2 Falling Weight impact..... 3

 3.3.3 Tensile impact 4

4. DISCUSSION..... 4

5. ACKNOWLEDGEMENTS 5

6. REFERENCES..... 5

FIGURES

1. INTRODUCTION

The results of a survey conducted by the NPL⁽¹⁾ highlighted feedstock contamination as the principal concern held by the UK plastics industry when using recycled thermoplastics. Contamination can be defined as any substance picked up by a plastic product during its service life. This can include 'foreign bodies', paint flakes, metal particles, chemical residues or other polymers used in e.g. labels or bottle caps that can form miscible or immiscible blends with the main component of the feedstock. Growth in the market for post-consumer recycled plastics is being restrained by lack of confidence in the performance of these materials in more demanding applications coupled with uncertain profit margins. The costs of recycling can be broken down into collection, sorting and cleaning the materials^(2,3,4). Any savings that can be made in these areas will enhance profitability. The work described in this report is concerned with the cleanliness of recyclate, as it is widely believed that post-consumer plastic must be extensively cleaned before reuse.

Other investigations have tended to focus on how chemical contamination affects the performance of recycled plastics. Bielinski and Sikora's investigation into the effects of fertiliser residues on the properties of recycled agricultural film^(5,6,7) showed that they are affected by the presence of such contaminants, but simple washing techniques can reduce the presence of chemicals to tolerable levels. A similar investigation by Baierwick et. al.⁽⁸⁾ into the effects of ethylene glycol residues on the recycling of glass fibre reinforced polyamide automotive coolant tanks produced recyclates which "can reach a considerable level of short-term properties....without modifying the material". Some work has been done investigating the effects of physical contaminants on recycled thermoplastics by various sector specific groups. However because of their commercial sensitivity these results are not available in the public domain.

This report presents the results of work conducted on a high density polyethylene (HDPE) artificially doped with different concentrations of copper fragments. Metallic fragments are common contaminants present in polymers that have been recovered from post-consumer waste⁽⁹⁾. Whilst most of this metallic material can be recovered there are cases where this is not economic. Copper fragments in particular have been found in plastics recovered from automotive waste where copper braid is used to aid welding of plastic parts, and waste electrical and electronic equipment where copper is widely used as a conductive material.

The following properties, commonly used within industry to characterise polymers, were measured in order to assess their sensitivity to this particular contaminant, with respect to virgin materials:

- Young's modulus
- Strain to failure
- Viscosity as indicated by Melt Flow Index (MFI) measurements
- Impact energy as indicated by Charpy, tensile and falling weight impact (FWI) tests

2. MATERIALS AND TEST METHODS

Specimens were produced from an 8621 grade HDPE (Stamylan® supplied by DSM). Batches of HDPE were doped with 1, 2.5 and 5 wt% copper turnings, tumbled by hand, fed through a twin screw extruder and pelletised. These feedstocks were then injection moulded into 150×150×4 mm flat plates (see Figure 1) using a Demag D150 moulding machine. All test-pieces were machined from these plates in the orientations shown in Figure 2, apart from MFI tests which were conducted on samples of pellets.

2. YOUNG'S MODULUS AND STRAIN TO FAILURE

Young's modulus values at 0.5% strain were derived from stress/strain measurements conducted at 25°C using standard tensile test-pieces, at a crosshead speed of 1.0 mm.min⁻¹. Specimen elongation was measured using linear variable displacement transducer extensometers. After five such measurements the failure strain for the specimen was determined with the crosshead speed set at 10.0 mm.min⁻¹. A video extensometer was used to record elongation of the test-piece at these higher speeds.

2.2 VISCOSITY AS INDICATED BY MFI

Measurements were conducted in accordance with ASTM 1238-90⁽¹⁰⁾ using a Davenport model 3/80 machine, with a test temperature of 190°C and an applied load of 5.0 kg. Five measurements were made for each level of copper contamination, the MFI being calculated in g.10min⁻¹ from;

$$MFI = \frac{10W}{T}$$

where W is the average weight of the extrudate and T the extrusion time.

2.3 IMPACT ENERGIES

2.3.1 Charpy impact

Charpy impact energy measurements were conducted at 25°C on rectangular specimens of dimensions 50×4×4 mm using a small Hounsfield plastic impact machine fitted with an 0.113 kg pendulum. Prior to testing each specimen was given a sharp 1 mm deep notch using a fly-cutting tool. An accelerometer embedded in the pendulum head was used to monitor its retardation during impact. The retardation data were used to calculate the fracture energy of the specimen^(11,12).

2.3.2 Falling weight impact

FWI energy measurements were carried out in accordance with ISO 6603-2:1989⁽¹³⁾, on a Rosand FWI machine. The test-piece consisted of a 60 mm diameter disc, impacted in the centre by a 10 mm hemispherical striker mounted on a 5 kg mass. Tests were conducted at 25, 0 and -70°C. To ensure complete penetration of the HDPE the velocity of the striker on impact was increased from the standard 4.4 ms⁻¹ to 6.1 ms⁻¹ by increasing the drop height to 2 m. A transducer located directly behind the striker was used to monitor the force changes during impact. These data were used to generate graphs of force and deflection against time, and subsequently to calculate the fracture energy of the specimen.

2.3.3 Tensile impact

Tensile impact energy measurements were conducted on a Rosand FWI machine. The test geometry is shown in Figure 3. A dumbbell shaped test-piece of dimensions 90×5×4 mm was inserted between a fixed clamp and a freely suspended steel anvil. The specimen was broken by a 12 kg striker impacting the anvil at a speed of 6.1 ms⁻¹. The stress history of the sample was monitored using a transducer mounted in between the fixed clamp and its supports. Measurements were made at 25°C on both specimens with milled edges and those where the edges had been smoothed (using 400 grit emery paper) to alleviate concerns that the milling marks might act as stress concentrators.

3. RESULTS

3 YOUNG’S MODULUS AND STRAIN TO FAILURE

The Young’s moduli for virgin HDPE and material containing three levels of copper contamination are shown in Figure 4. The two small black marks on each of the bars give an indication of the scatter of results. The mean Young’s modulus of the virgin HDPE was 1085 MPa. The presence of copper particles had no effect on the modulus until the 5 wt% level, when the modulus increased by 83 MPa. Necking of the test-pieces occurred at strains in excess of approximately 3%. Material within this region appeared to flow around the copper inclusions causing them to protrude from the edges of the polymer. This phenomenon did not appear to affect the maximum tensile stress, as can be seen from the traces shown in Figure 5. Drawn specimens containing copper typically failed in the region of 25 to 30% strain, in contrast to virgin material which failed at 125% strain. These results suggest that contamination of this type limits the ductility of HDPE. However it must be emphasised that this change occurs at strains well in excess of those likely to be encountered in practical applications.

3.2 VISCOSITY AS INDICATED BY MFI

The MFI results are given in Table 1. The presence of the copper contamination has little effect on the viscosity of the HDPE. Although care was taken in preparing the MFI samples to ensure that no copper fragments large enough to block the die were present, the slight increase in the MFI with higher copper content can be attributed to the presence of small copper particles increasing the weight of the extrudate.

wt% copper turnings	MFI (g.10min ⁻¹)
0	0.83
1	0.90
2.5	0.97
5	1.03

Table 1: Melt Flow Indices of HDPE with copper turnings

3.3 IMPACT ENERGIES

3.3 Charpy impact

The Charpy impact energies are shown in Figure 6. Within experimental error the level of contamination had no effect on the impact energies. An examination of each fractured specimen showed that the area directly behind the notch was free of copper inclusions. During the Charpy test the force of impact is localised within a very small area around the notch tip, so a particle would have to be located in this zone to affect the impact behaviour. Since the probability of this occurring is small, this test was deemed unsuitable for detecting most types of contaminant particles.

3.3.2 Falling Weight impact

Figures 7, 8 and 9 show the impact energies of virgin and copper contaminated HDPE obtained at different temperatures. Contamination has no significant effect on impact energy at 25 and 0°C. However there is some indication that high levels of contamination reduce impact energy at -70°C. Note that the impact energy of virgin HDPE progressively increases with reduction in temperature. This is particularly noticeable between 0 and -70°C. An examination of the specimens showed that

the lower impact energies were caused by the presence of one or more copper particles near the impact site, as the test-piece had split around these inclusions instead of the striker simply puncturing the specimen.

3.3.3 Tensile impact

The tensile impact energies (Figure 10) and deflection at failure (Figure 11) decrease with increasing concentration of contaminant. However the scatter of results in the less contaminated specimens shows the test is sensitive to specimen surface quality. A small nick or defect in the specimen edge can act as a stress concentrator when subject to tensile shock loads, causing premature failure of the specimen. Measurements made using specimens with smoothed edges did reduce the scatter of results but the time and effort involved in smoothing the specimens far outweigh the improvements gained. An examination of the fracture surfaces showed that specimens with less contamination exhibited classic ductile fracture. The copper particles did not appear to adhere to the HDPE matrix, but simply reduced the effective cross sectional area of the specimen causing premature failure, although still in a ductile mode. The surface sensitivity of the test makes it difficult to distinguish which of the results might be due to contamination or a specimen surface defect.

4. DISCUSSION

Table 2 summarises the results obtained from the various tests:

Property	wt% copper turnings		
	1	2.5	5
Young's modulus	x	x	x
Max. tensile stress	x	x	x
Melt flow index	x	x	x
Charpy impact energy	x	x	x
Tensile impact energy	x	✓	✓
FWI energy	x	*	*

- ✓ = contamination detected
- x = contamination not detected
- * = contamination only detected at low temperatures

Table 2: Sensitivity of tests to copper contamination in HDPE

As expected, these results show that properties such as Young's modulus, maximum tensile stress, MFI and Charpy impact energy are insensitive to copper contamination in HDPE at the levels considered. The falling weight and tensile impact energies are adversely affected by contamination at levels in excess of 2.5 wt%. However, the scatter of data in the tensile impact test makes it difficult to perform any reliable interpretation of the results. Smoothing the specimen edges did marginally reduce the scatter, but is very time consuming. An alternative to using machined test-pieces would be to injection mould them directly. This would produce a much smoother specimen surface, but will change the microstructure of the specimens making it almost impossible to compare results obtained from test-pieces derived from different sources, such as a moulded plastic part. The specimen preparation for the FWI test is much quicker and easier, as the test is not affected by the condition of the specimen edges.

Table 3 shows the FWI energy sensitivity to copper contamination at lower temperatures

Temperature °C	wt% copper turnings			
	0	1	2.5	5
25	x	x	x	x
0	x	x	x †	x †
-70	x	x	✓	✓

✓ = specimens exhibit brittle fracture
x = specimens exhibit ductile fracture
† = wide scatter of results (some specimens exhibiting brittle fracture)

Table 3: Temperature sensitivity of FWI test to copper contamination in HDPE

Comparing the two test methods which proved sensitive to copper contamination, the falling weight impact test is the technique which is easiest to use and produces the most repeatable results. Sample preparation is simple and the results are not dependent on the condition of the specimen edges. This would be advantageous for routine characterisation tests where identification of contaminated batches of material is required with minimum sample preparation.

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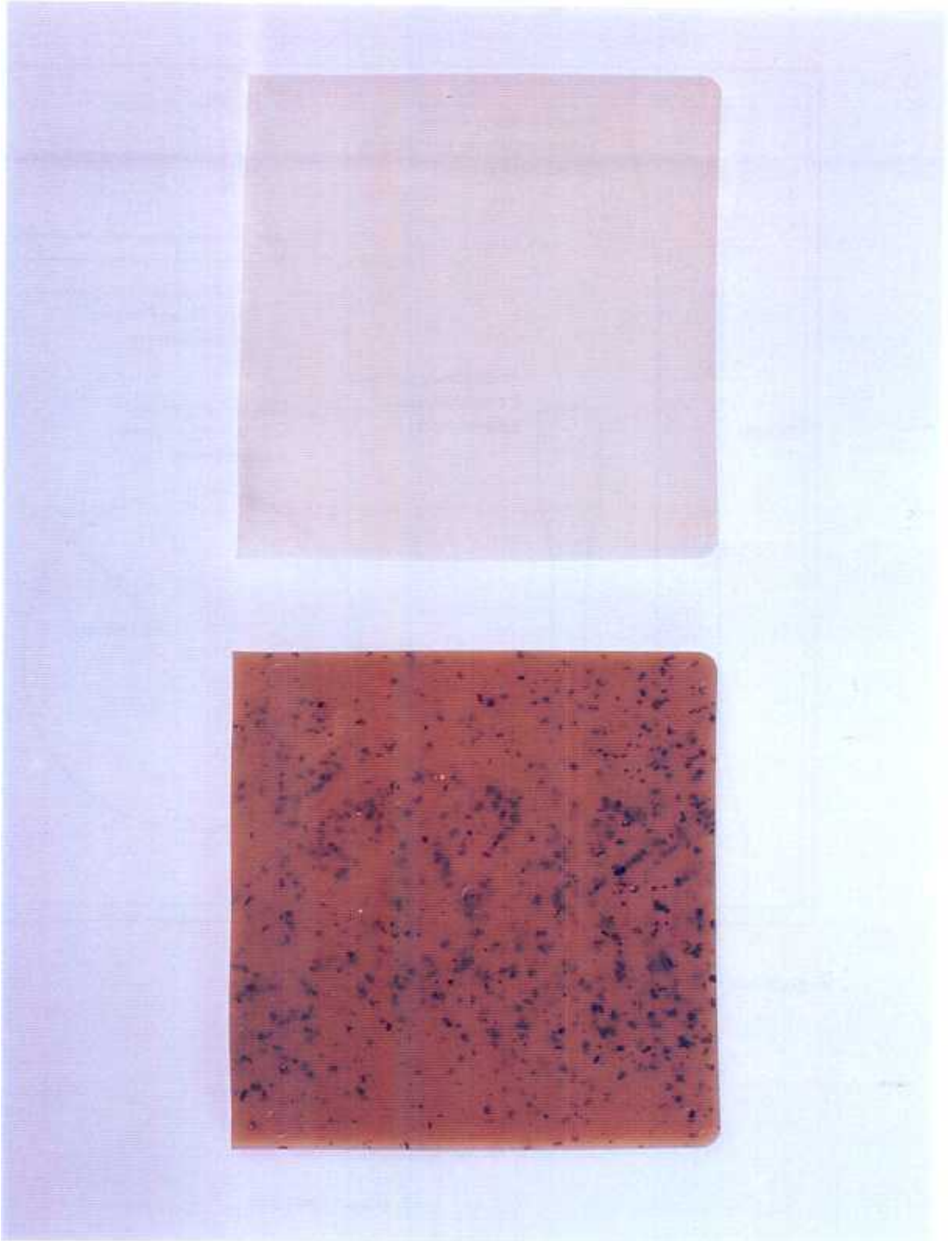


Figure 1: Injection moulded 150mm square plates. Upper plate is virgin material, lower plate contains 5 wt% copper fragments.

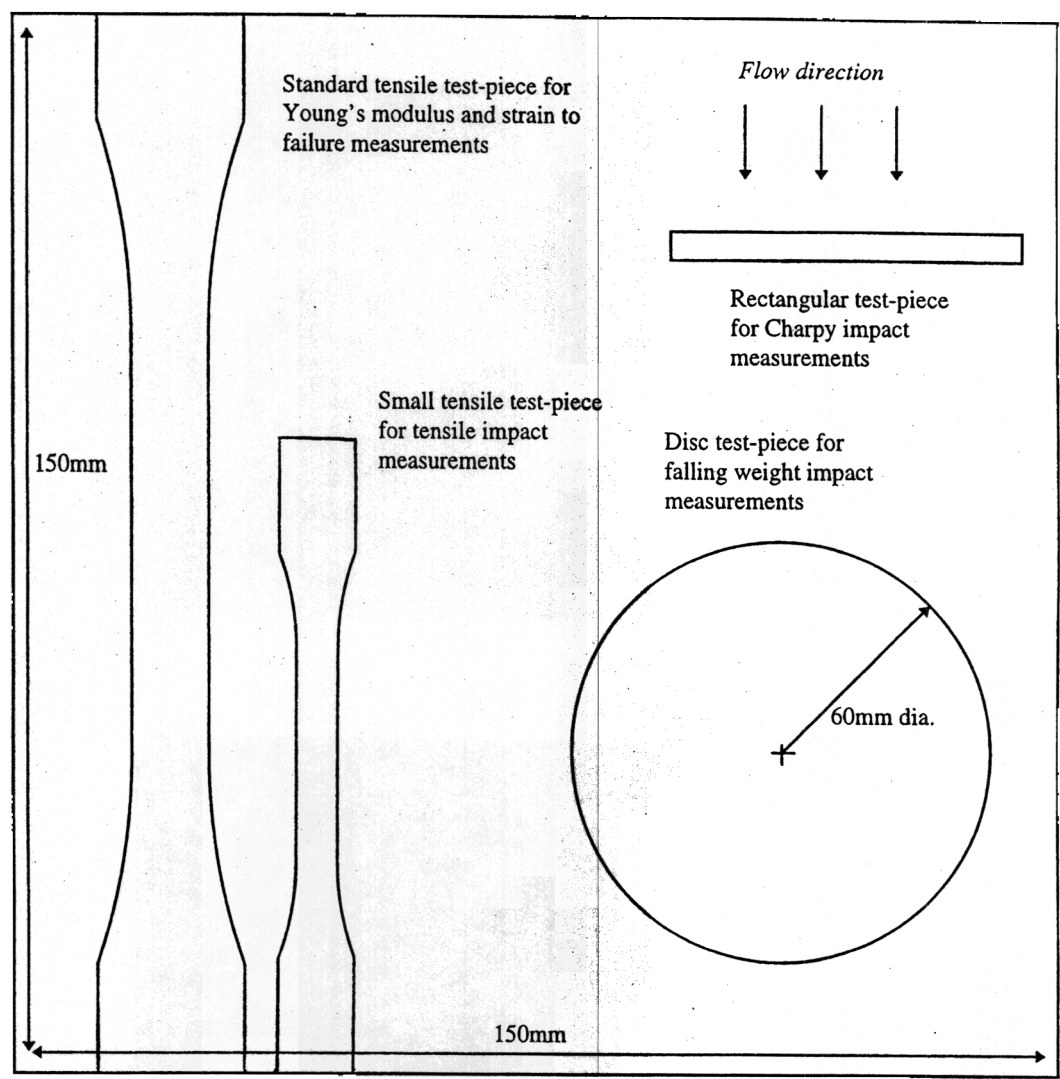


Figure 2: Orientation of test-pieces machined from flat plates.

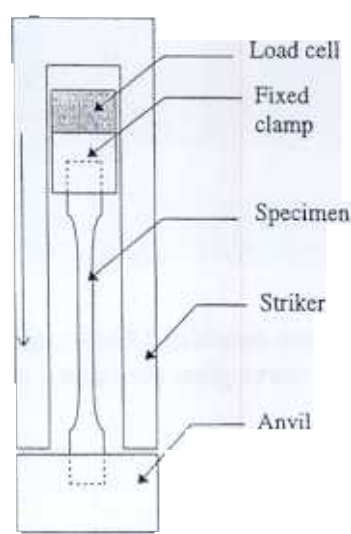
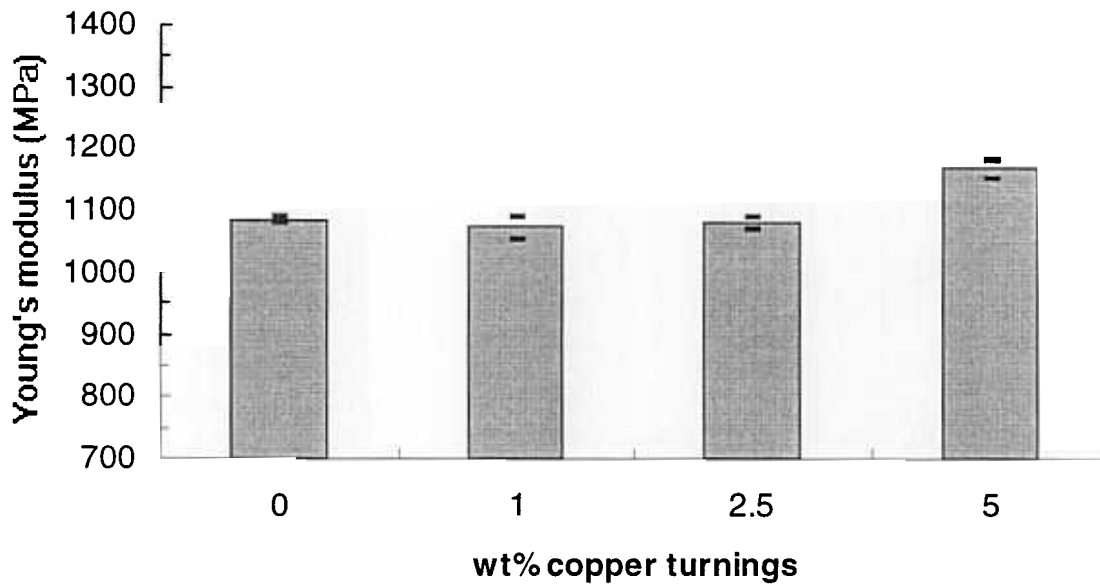
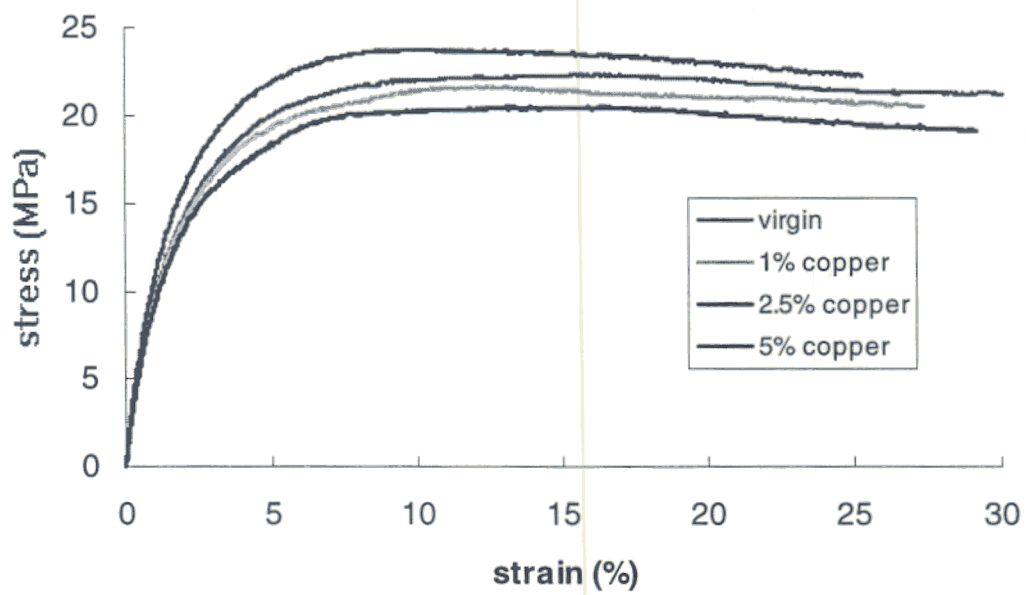


Figure 3: Tensile impact rig (fixed clamp supports not shown for clarity)

Figure 4: Young's modulus**Figure 5: Tensile strain to failure**

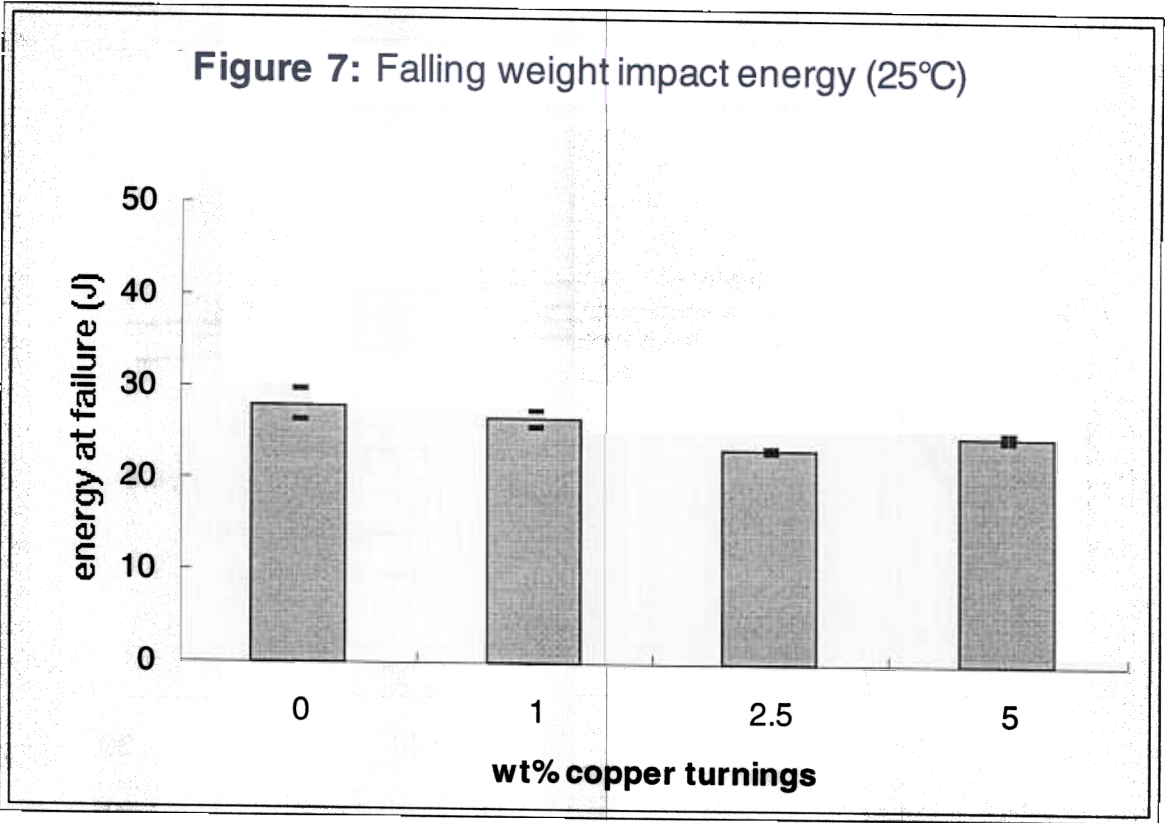
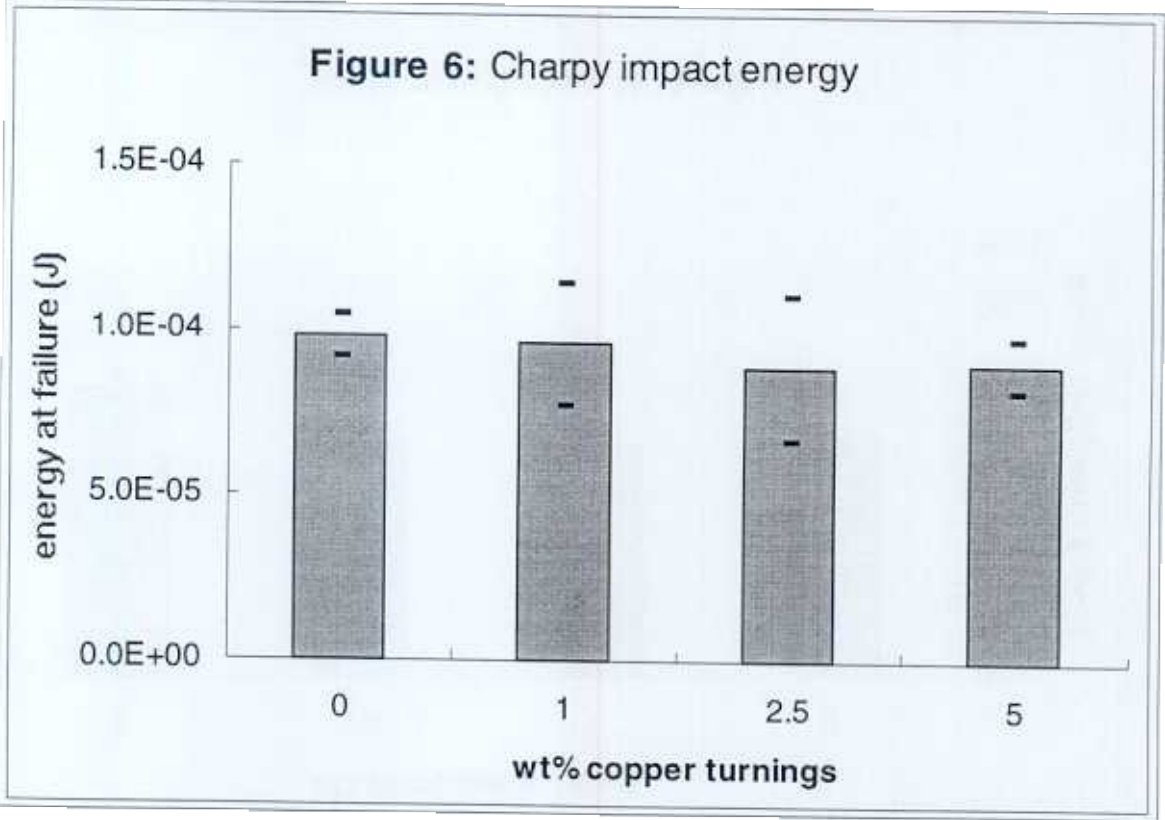


Figure 8: Falling weight impact energies (0°C)

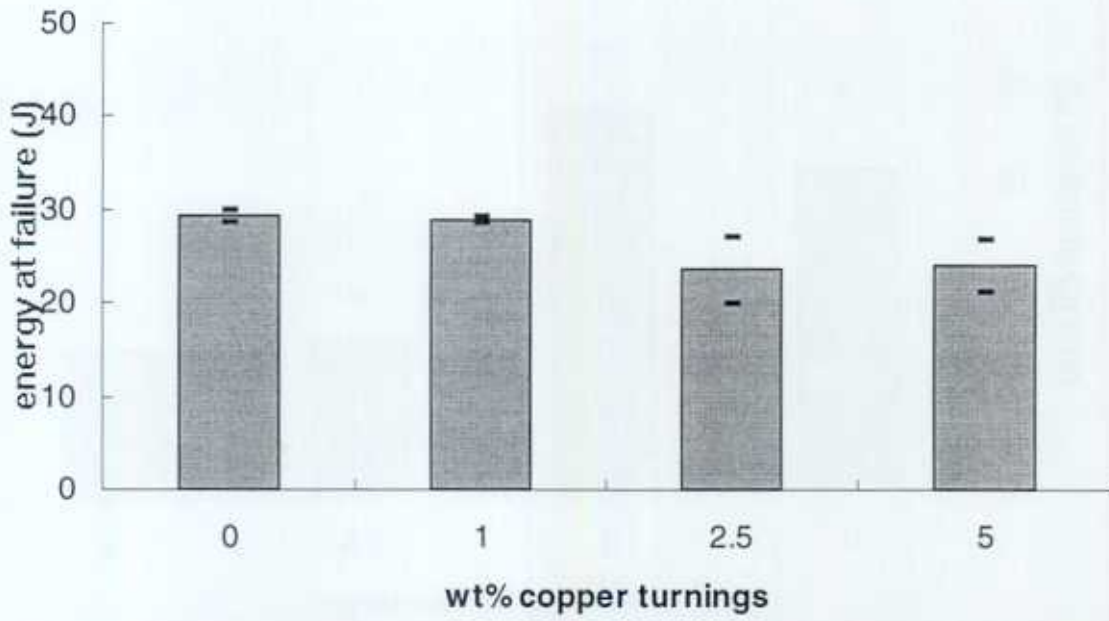


Figure 9: Falling weight impact energy (-70°C)

