DEVELOPMENT OF HIGH QUALITY RECYCLED POLYETHYLENE RESINS FOR THE REPLACEMENT OF VIRGIN RESINS

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Abstract

Dairy and fruit juice bottles are a major source of post consumer recycled high density polyethylene (PCR HDPE). The recycled HDPE has limited post-consumer applications due to its poor stress crack resistance (SCR). This paper presents a review of a test method for SCR and some preliminary results of the development of recycled HDPE blends with improved SCR. The improvement has been achieved with the addition of a modifier, and results indicate that there is a potential to incorporate the use of recycled HDPE in non-pressure pipe applications. These customised blends have been tested for SCR according to the Notched Constant Ligament Stress (NCLS) test. The NCLS test is a new test method (ASTM F17.40) which is currently under development. The NCLS test will be used to determine the susceptibility of HDPE resins to slow crack growth (SCG) under a constant ligament stress in an accelerated environment. The results from the test will subsequently be correlated with field performance results.

Introduction

One of the major problems facing the plastics industry in Australia and around the world is the large variety of plastics and plastic products available. At present, the plastics recycling industry in Australia is primarily concerned with the recycling of rigid plastics; milk bottles and detergent bottles, which are commonly available and easy to recognise. The recycled plastics can be used in the manufacture of a limited range of products because of the reduced quality and limited properties of such plastics. One of the limiting properties of recycled dairy bottle resin is poor stress crack resistance (SCR), as it is a highly crystalline homopolymer, thus making it more susceptible to environmental stress cracking.

With a market share of 20% of the total plastic consumption and with a relatively low added value, pipes are a natural product for the economic re-integration of plastics into the materials stream [1]. HDPE has been used in pipe applications for more than 40 years. Over this time, HDPE has proven itself to be lightweight, chemical, corrosion and abrasion resistant. Furthermore, HDPE is easy to manufacture and install and subsequently bears low maintenance cost.

HDPE intended for pipe applications must provide superior resistance to failure that typically occurs by a slow crack growth mechanism, which can significantly affect long-term strength. Brittle-type slow crack growth is the paramount mode of field failure for polyethylene piping systems. The development of brittle failure starts with crack initiation, which is followed by a slow crack growth period. The initiation period constitutes a vital part of the total time of failure. The lifetime of these HDPE pipes is therefore controlled by material, environmental and loading factors. Hydrostatic pressure testing is the method specified for determining the lifetime of a plastic pipe. However, pressure testing is expensive and time consuming. Therefore it is necessary to establish an alternative, less time-consuming test method.

Currently, the material specification for testing stress crack resistance (SCR) of HDPE resins is the ESCR test, ASTM D1693. In 1997, ASTM D3350, the standard for Polyethylene Plastic Pipe and Fittings Materials, adopted a new test, ASTM F1473 (PENT test) to evaluate the SCR of polyethylene gas pipes [2]. As a result, there are two methods included in the ASTM D 3350 standard, irrespective of their SCR property.

In addition to these two test methods, a supplementary test method has been established to evaluate the SCR specifically for HDPE pipe resins. Based on ASTM D5391 (standard test method for Evaluation of Stress Crack Resistance of Polyolefin Geomembranes Using Notched Constant Tensile Load), ASTM F17.40 has emerged as the new standard for the Notched-Constant Ligament Stress (NCLS) test. The NCLS test is used to determine the susceptibility of HDPE resins or corrugated pipe to slow crack growth under a constant ligament stress in an accelerated environment. The test method measures the failure time associated with a given test specimen at a constant, specified, ligament stress level. This paper will focus on the importance of the NCLS test in evaluating SCR of recycled HDPE, for implementation into non-pressure pipe applications.
**Slow Crack Growth**

Medium and high density polyethylenes used in the manufacture of pipes and pipe components, experience premature failure in field conditions. Environmental stress cracking (ESCR) can be defined as premature initiation of cracking due to simultaneous action of stress, particularly a biaxial stress situation and contact of specific liquids [3]. ESCR of polyethylene has been a failure phenomenon of notable importance since it was first observed in the early 1950’s [3].

The NCLS test is a measure of brittle failure in HDPE. Brittle type slow crack behaviour occurs over prolonged periods of time at lower stress levels, as opposed to ductile deformation. Comprehensive studies have shown that the slow crack growth (SCG) process includes the formation of craze-like damage at the notch tip, fibril growth, crack initiation and crack growth. HDPE is a semicrystalline polymer in which the lamella crystals are bounded by the tie molecules and entanglements. The tie molecules and entanglements are responsible for passing the stress into the crystals. At low stress levels, the tie molecules relax, disentangling themselves from the crystals, resulting in the failure of the fibrils. Thus, the disentangling rate depends on the strength of the crystals. This behaviour is accelerated with the addition of a lubricant, like Igepal.

**Comparison of SCR Tests**

According to ASTM D3350 specification, ASTM D1693 Condition B should be used to evaluate SCR of Polyethylene pipes. The test is performed using ten notched specimens, which are bent and submerged in 10% Igepal at 50°C. Test specimens are taken from moulded plaques. The test allows for a maximum of 50% failures after a 24-hour test period. However, there are disadvantages of this test, some of which include:

1. The failure time of an individual test specimen can not be recorded.
2. Lab to Lab reproducibility value of 193% [2].
3. Stress condition is unknown throughout the test.

Likewise, ASTM F 1473 (PENN test) is practiced to evaluate SCR of HDPE resins used in pressure pipes for quality control. In order to obtain short failure times, the compression-moulded plaques are subjected to slow cooling rates to accentuate crystallinity and the test is performed at 80°C. This is the maximum allowable test temperature limit for SCR tests without varying the property of the material [2]. However, the PENN test is believed to be extreme for use on corrugated pipes.

Our investigations have shown that some of the advantages of the NCLS test procedure are:

1. The test is applicable to both HDPE resins and corrugated pipes.
2. Determines slow crack growth under a constant ligament stress in an accelerated environment.
3. Measures the failure time associated with a given test specimen at a constant, specified, ligament-stress level.
4. Reproducibility rates are greater (at 135%), when compared to the ESCR test, ASTM D1693 (193%) [2].

**Experimental**

**NCLS System Features**

System features of the NCLS are illustrated in Figure 1. Features include a stainless steel temperature controlled bath (a) and frame which supports twenty arm levers in total. The aluminium arm levers with a ratio of 3:1, include adjustable loading containers are connected to the levers. Each station has a self-powered, restable digital timer (c) per lever, which is halted upon sample failure.

**Material Properties and Blends**

Two classes of recycled HDPE; Dairy bottles which included Polypropylene (PP) caps in the recycling process (H1) and recycled dairy bottles without PP caps (H2) were tested, in addition to two commercial resins; virgin HDPE and Medium Density Polyethylene (MDPE). Some of their characteristics are presented in Table 1. Compositions of the tested blends are shown in Table 2.

**Sample Preparation**

Five dumbbell shaped test specimens at 1.65mm ±0.05mm thick were tested from each of the six formulations. The test specimens were cut from compression moulded plaques with a die cutter. The plaques were compression moulded in accordance with ASTM D 1928 – Procedure C, and can be moulded in either pellet form or from pipe sections. Holes of 6.5mm diameter are then drilled at both ends of the dumbbell (as shown in Figure 1). However, it is important to note that the test specimen geometry specified in ASTM F17.40 was found to be inconsistent with our calculations. Our calculations show that the overall length of the test specimen is in fact 70mm, not the 60mm specified in the standard. The revised specimen geometry, which our test specimens were modelled by, is shown in Figure 2.
Notch depth typical of our test specimens was 0.33mm ± 0.1. The notch depth of the test specimens is calculated as 20% of the nominal thickness of the specimen. A fresh razor blade was inserted every twenty test specimens.

Annealing of the samples was carried out at 80°C for a period of three hours once the samples had been fully prepared. Annealing was introduced as part of the testing process as it increases the crystal strength and lifetime [4]. At a temperature of 80°C most thick crystals will not melt, and any stress induced through notching will be relieved.

Test Conditions
Tests were conducted under an applied stress of 15% of the yield stress of the material. The applied stress was calculated based on the remaining ligament cross-sectional area [2]. An applied stress of 4.05MPa was then used to calculate the load to be placed on each lever:

\[
\text{Load (g)} = \frac{S \times (T-a) \times W}{(MA) \times (9.81)} \times 1000 - CF \times \frac{MA}{MA}
\]  

(1)

Where:
- \(a\) = Notch Depth (mm)
- \(S\) = Constant Ligament Stress (MPa)
- \(T\) = Specimen Thickness (mm)
- \(W\) = Specimen Width (mm)
- \(MA\) = Mechanical Advantage of the apparatus
- \(CF\) = Correction Factor of the arm weight

The equation given in ASTM F17.40 was not applicable in our test method. The following equation was therefore derived to determine an appropriate correction factor for the equipment [5].

\[
CF = \frac{W_B(MA-1)}{2}
\]  

(2)

Where:
- \(W_B\) = Weight of the Aluminium Arm

The calculation of the correction factor is a crucial step in the experimental process. Inaccurate calculations will ultimately lead to incorrect failure times. However, further calculations and observations proved that additional frictional forces acting between the arm and the bearings needed to be considered along with the weight of the arm and sample assembly. As a result the following equation was derived and used as part of our load calculations:

\[
CF = \frac{\text{Load Balanced on the Arm}}{MA}
\]  

(3)

Test Specimens were immersed in a test solution of 10% Igepal CO-630 and 90% de-ionised water, at a test temperature 50°C ± 1°C. After an equilibration period, the test was started, where the test runs for duration of 24 hours. Failure times are recorded individually to 0.1 of the hour.

Results and Discussion

Table 3. shows the results obtained from the test performed on the six blends. Samples that have exceeded a 24-hour testing period are classified as successful for use in corrugated pipe applications. 24 hours is the recommended testing period by both ASTM F17.40 and the National Highway Cooperative Research Program (NHCRP).

NCLS test results are displayed in Table 3. The test demonstrates as expected, long failure times for samples tested from 100% virgin material (Blends 1 and 2). All five test specimens from Blends 1 and 2 had not failed at 350 and 200 hours respectively. Conversely, samples made from 100% recycled material (Blends 3 and 4) both failed before the specified 24 hour period. This can be attributed to the fact that the recycled material is a milk bottle blow moulding homopolymer grade and therefore, has a deficient SCR. Moreover, the average failure time was somewhat lower for Blend 3, in comparison to Blend 4. The explanation for this is that the recycled material that was used for Blend 3 is primarily milk bottle resin with PP cap contamination. Whereas, the composition of Blend 4 is essentially milk bottles, thus this recyclate stream is characterised as having a homogeneous melt flow.

Further examination of the results in Table 3. reveal the SCR of the recycled HDPE can be improved with the addition of a modifier. When compositions of 75% Recycled HDPE and 25% virgin HDPE or MDPE were blended and tested, the NCLS test data displays a significant improvement in the SCR of the recycled material. In which case, adding polyethylene grades that are known to have a particularly good stress crack resistance, can increase the SCR of recycled HDPE resin.

The test results show the NCLS is capable of determining and differentiating between HDPE materials of different SCR. The most important fact being that the NCLS test failure time can be directly related to the SCR performance of the blends.
Conclusion

The determination of failure times in the Notched Constant Ligament Stress test using an accelerated environment was found to be a qualified experimental method to characterise environmental stress cracking of HDPE pipes and resins. Given that a suitable criterion for good acceptable field performance for non-pressure pipes is stated as 24 hours, then this test method is suitable for the rapid lab assessment of polymer blends for pipe applications.

Results from the NCLS test confirmed that the incorporation of a modifier to recycled HDPE increases the stress crack resistance of recycled HDPE. This improvement in stress crack resistance of recycled HDPE blends has lead to the production of high quality products from regenerated plastics, for example; non-pressure pipes.

Moreover, the large difference in failure times demonstrates the effectiveness of the NCLS test in identifying SCR of different pipe materials, and different materials intended for pipe manufacture.

Acknowledgments

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References

5. Private communication with Edward Kosior.

Key Word Index

Slow Crack Growth, Environmental Stress Crack Resistance, Notched Crack Ligament Stress, Polymer Recycling

<table>
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<th>Property</th>
<th>HDPE</th>
<th>MDPE</th>
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<th>H2</th>
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<td>MFI (g/10min)</td>
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**Table 1. Material Characteristics**

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<thead>
<tr>
<th>Blend No.</th>
<th>Composition</th>
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<tr>
<td>1</td>
<td>100% MDPE</td>
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<tr>
<td>2</td>
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<tr>
<td>3</td>
<td>100% H1</td>
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<td>100% H2</td>
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<td>5</td>
<td>75% H1 + 25% MDPE</td>
</tr>
<tr>
<td>6</td>
<td>75% H2 + 25% HDPE</td>
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**Table 2. Composition of Blends**

**Figure 1. NCLS System Features**

Note. Illustration is Courtesy of BT Technology Inc.

**Figure 2. Specimen Geometry**

Note – Dimensions are in millimetres to accuracy of 0.02mm.
<table>
<thead>
<tr>
<th>Blend</th>
<th>Load (g)</th>
<th>Applied Stress (MPa)</th>
<th>Avg Failure Time (hrs:min)</th>
<th>Std. Dev</th>
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<td>6.96</td>
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* Denotes test was stopped at this time. All five test specimens had not failed when the test was stopped.

**Table 3. NCLS Test Results**

Table 3. NCLS Test Results
* Denotes test was stopped at this time. All five test specimens had not failed when the test was stopped.