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Creating New Recycling Options for Post-Consumer Bottle Grade HDPE

Final Report

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Kevin Thomson, Almar Postma and Ruxandra Rosu*



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ABSTRACT

Reactive extrusion has been used to convert post-consumer recycled HDPE from milk bottles, into a grade which can be injection moulded into large products such as crates and mobile garbage bins. The modified materials have been successfully injection moulded at a level of 100% modified recycled HDPE, without blending with other materials, using conventional equipment and tooling. Physical properties approach that of virgin materials but still require further improvement to meet all performance criteria.

EXECUTIVE SUMMARY

Approximately one third of the HDPE used in Australia to make blow moulded bottles (eg 15,793 tonnes from the 49,000 tonnes used in 1997) is recycled. It is estimated that the market for post-consumer recycled HDPE milk and other bottles could be expanded by 10,000 tonnes if there was an economic process for converting the low melt flow index (MFI) bottle grade HDPE to a range of higher MFI injection moulding grades. Such a process would allow the greater use of recycled HDPE in the production of large injection moulded items such as bins and crates using conventional injection moulding equipment and tooling. Currently, the low MFI of milk bottle grade HDPE allows it to be used at a maximum level of only about 30% by blending with higher flow HDPE. Alternatively, it can be blended with other materials but this introduces higher costs and the possibility of lower physical/mechanical properties due to incompatibilities. Other processes, such as injection/compression can use higher levels of recycle but require significant investment in specialised processing equipment and tooling.

Through an initiative of the CRC for Polymers, with contributions from CSIRO Molecular Science, Nylex, Monash University Materials Engineering and EcoRecycle Victoria, a research project was undertaken to develop and commercialise technology for economically increasing the melt flow rate of recycled HDPE. The specific aim was to utilise reactive extrusion to establish an economical process for producing recycled HDPE with a high melt flow rate and good physical/mechanical properties suitable for large injection moulded products at a level of 100% modified recycled HDPE.

Utilising several reactive extrusion conditions, extrusion blow moulding HDPE was converted into grades with suitable MFI for injection moulding, and these were used to manufacture kerbside recycle collection crates. The physical/mechanical properties of the crates were evaluated, yielding promising results. An improved grade, also produced by reactive extrusion, was chosen for injection moulding large mobile garbage bins. This full-scale trial was successful, showing no problems with injection into the mould under standard conditions; however, the mechanical properties of the modified HDPE need improvement.

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1. INTRODUCTION

In 1997, approximately 49,000 tonnes of high density polyethylene (HDPE) was used annually in Australia to make blow moulded bottles, but only approximately one third of this (15,793 tonnes) was recycled. The market for post-consumer recycled HDPE milk and other bottles could be expanded by 10,000 tonnes per annum if there was an economically viable process for converting the low melt flow index (MFI) bottle grade HDPE to a range of higher MFI grades suitable for use in injection moulding. The economic incentive is particularly important in applications using large amounts of polymer such as the production of injection moulded mobile garbage bins (MGBs) and kerbside recycle collection crates.

Current approaches to the use of recycled HDPE are:

- Blending with standard higher flow HDPE. This is only practical at a maximum level of about 30%. It requires higher processing pressures which increase wear on the injection moulding equipment and tooling.
- Blending with other polymers. Blending with other materials can produce mouldable materials with up to about 70% recycled HDPE. However, this does introduce concerns regarding mechanical properties due to possible incompatibility.
- Alternative processes. Various injection/compression processes can work with low MFI materials. Current practice indicates that the achievable recycle content is well below 100%. A large investment in specialized equipment and tooling is also required.

An alternative approach investigated in this study is to effect the conversion of low MFI HDPE to higher MFI grades by chemically reducing the molecular weight of the high molecular weight blow moulding grade. The commercial recycling of bottle grade HDPE already involves an extrusion step which is used to remove some contaminants while converting the material into a pelletized form. A reactive extrusion process, achieved either by addition of a small dose of additives, particular process conditions, or a combination of both, could be included as part of the current recycling extrusion step, using extrusion equipment currently available and installed at Visy Plastics or other HDPE recyclers. It is anticipated that such new technology could be employed without major capital acquisition or plant modification.

While technology exists for chemically increasing the MFI of polypropylene, there is no similar process for HDPE. Under normal processing conditions, the MFI of HDPE tends to decrease due to chain branching. However, a background literature study conducted by the CRC for Polymers and Nylex led to the conclusion that development of the required process may be technically feasible.

The research described in this report was conducted as a collaborative project within the CRC for Polymers. It involved contributions from researchers at CSIRO Molecular Science (development of laboratory scale reactive extrusion technology), the Materials Engineering Department of Monash University (rheological and mechanical properties), and Nylex (product trials and product evaluation).

EcoRecycle Victoria financial support allowed the employment of an additional researcher (AP) for the project.

2. TECHNICAL BACKGROUND

HDPE is the product of ethylene polymerisation resulting in polymers with densities from 0.940 to 0.958 g/cm³. HDPE is usually a copolymer of alpha olefins, with ethylene predominating, but can also be a homopolymer. The alpha olefins are typically 1-butene or 1-hexene. They are deliberately introduced to give a small number of short chain branches, reducing crystallinity which in turn increases impact strength and reduces stiffness.

Two main catalysts are used in the production of HDPE: those based on chromium oxide (Phillips catalysts) and those based on Ziegler-Natta systems. Other known catalysts are based on a wide range of transition metals and metal complexes. These catalysts are then employed in three processes available for HDPE manufacture: solution, suspension and gas-phase polymerisation. Solution polymerisation is employed primarily for producing HDPE in the low molecular weight range, suspension polymerisation (the oldest and most widely used) produces the full range of molecular weight grades, and gas-phase polymerisation (the newest) provides the most cost effective method for producing HDPE.

The low melting point and the chemical inertness of HDPE lends itself to conventional processing techniques like extrusion, injection moulding and blow moulding. Blow moulding and injection moulding in packaging applications are by far the largest uses of HDPE resins, with blow moulding using about half as much as injection moulding. Due to its inertness and absence of toxicity, HDPE is used mostly for food and drug packaging purposes, with food containers, milk bottles, housewares and toys the main end products. It is also used to make crates, pails, pipes, and films.¹

In the blow moulding process a low MFI, high average molecular weight, high melt strength grade (and thus high viscosity) HDPE is required to form a parison as part of the moulding process. In injection moulding, a higher MFI grade HDPE is required to aid the polymer movement through narrow channels in the moulds. Recycled blow moulding grade HDPE has an MFI of around 0.8 which needs to be increased to around 3.5 for its satisfactory use in injection moulding. This change in MFI allows injection pressures, clamp forces and temperatures to be kept to a practical level for conventional injection moulding and tooling.

HDPE has a predominantly saturated linear hydrocarbon structure which generally exhibits high chemical stability and is also relatively stable to heat. At processing temperatures of 290-300°C, in vacuum or an inert medium, HDPE will start to break and cross-link its polymer chains, in a similar manner to thermocracking of hydrocarbons. In the presence of oxygen, thermo-oxidation occurs with oxygen attacking the polymer backbone, leading to complex events like chain scission, cross-linking and molecular enlargement which can either improve physical/mechanical properties or lead to degradation.²⁻⁷ Under most conditions chain branching and cross-linking predominates with HDPE (unlike PP), leading to an increase in molecular weight in a polymer (a decrease in MFI), but under certain extreme conditions chain scission is more likely to occur.

Johnston and Morrison⁴ used batch mixing, temperature and time dependent changes in vinyl and vinylidene concentrations, relative oxidation rates and possible vinylene

concentration to develop a kinetic model that allows estimation of dominance of cross-linking relative to thermal scission.

Using a single screw extruder, Hirata *et al.*⁸ observed cross-linking to dominate over scissioning in early stages of mixing, but with further mixing the situation changed to favour branching.

Sakai² found chain scissioning occurring with processing temperatures above 280°C on a high-speed twin screw continuous intensive mixer, also noticing an increase in MFI and a narrowing of the molecular weight distribution. Sakai² also describes the effect of the polymer's initial MFI and the effect of shear induced scission with different screw configurations. Rideal and Padgett⁹ also noted that melt temperatures over 290°C caused a decrease in melt viscosity and narrowing of polydispersity index, with an increase in long chain branching and molecular enlargement (occurring below 290°C) causing an increase in melt viscosity. Dontula *et al.*¹⁰, using a co-rotating intermeshing twin screw extruder and processing temperatures above 300°C, also observed chain scission to occur. Dontula *et al.*¹⁰ also looked at the effects of barrel temperature profile, screw speed, percentage feed rate and residence times. Chain scissioning was found to increase with an increase in screw speed and feed rate, as long as the increase in these parameters offsets a decrease in residence time.

Several papers^{5,6,9} have noted the effect of air (oxygen) causing scissioning, and thus molecular weight reduction, but also branching, chain extension and crosslinking. The presence of small amounts of dissolved O₂, always present in polyethylene exposed to air, was shown by Hinsken *et al.*⁵ to cause scissioning under severe conditions. Holmström and Sörvik¹¹ noted thermo-oxidative degradation of HDPE films under nitrogen atmospheres with low oxygen content, with temperatures between 284°C and 355°C giving both molecular enlargement and scissioning.

Moss and Zweifel¹² have shown that catalyst type used in production of HDPE has an influence on the reactive processing behavior of HDPE. Ziegler-Natta HDPE (Ti catalysed) favoured chain scissioning while Phillips HDPE (Cr catalysed) showed a tendency towards cross-linking, which was more evident with multiple extrusions. Harlin and Vainio¹³ observed molecular enlargement with Phillips HDPE, mainly caused by the high residual vinyl content of this type of PE. Moss *et al.*¹² and Drake *et al.*¹⁴ also showed that molecular weight increase can be prevented with the addition of antioxidant, phosphite and hindered phenol stabilisers. The dependency of the type of HDPE (catalyst, additives) on the amount of MFI change was also observed by Sakai².

The melt processing of HDPE with peroxides can have the effect of chain scissioning, chain branching, chain extension or cross-linking through the formation of polymeric radicals and the resulting competitive reactions^{5,12,14}.

Methods Examined for Reducing the Molecular Weight of HDPE

It was decided to conduct a systematic study of all the possible approaches, suggested by the literature review, for reducing the molecular weight of recycled HDPE. In addition, some novel approaches were also evaluated.

3. EXPERIMENTAL

Polymers Used

The recycled blow moulding grade HDPE, H1 (Visy Plastics, MFI=0.7), is the material to be converted through reactive extrusion to an injection mouldable grade and was one of the polymers used in the study. Most of the initial reactive extrusion experiments were performed on HD 5148 (Qenos, MFI=0.8) blow moulding grade HDPE which is used to make blow moulded bottles. This was used in the comprehensive study, comparing a wide range of conditions, in preference to H1, since it is a purer material. It is without the variable level of contaminants that may be present in recycled HDPE, and which could interfere when experimentally assessing the effects of the differing processing conditions. After the best processing conditions were identified, they were applied to H1 to prepare materials for the production trials. The virgin injection moulding grade HDPE currently used to make mobile garbage bins is LBH 1103 (Qenos, MFI=3.5). The reactive extrusion conditions were varied in attempts to produce modified HDPEs with properties the same as this commercially available polymer.

Twin Screw Extruder

Experiments were conducted using a Japan Steel Works 30 mm diameter twin screw extruder (JSW TEX 30) of L/D ratio 42 operating in the co-rotating mode (see Fig. 1). The HDPE resin was added at controlled rates between 5 and 20 kg/h to the feed throat of the extruder via a gravimetric feeder.

The twin screw extruder barrel was maintained at a variety of temperature profiles around the range 200°C to 300°C. Screw speeds were varied from 100 - 400 rpm with the motor current ranging from 12 - 34 amps. A vacuum port at the end of the barrel was generally operated to vent volatiles.

Under all run conditions the hopper(s) and feed throat are kept under a positive pressure of gas (usually nitrogen).

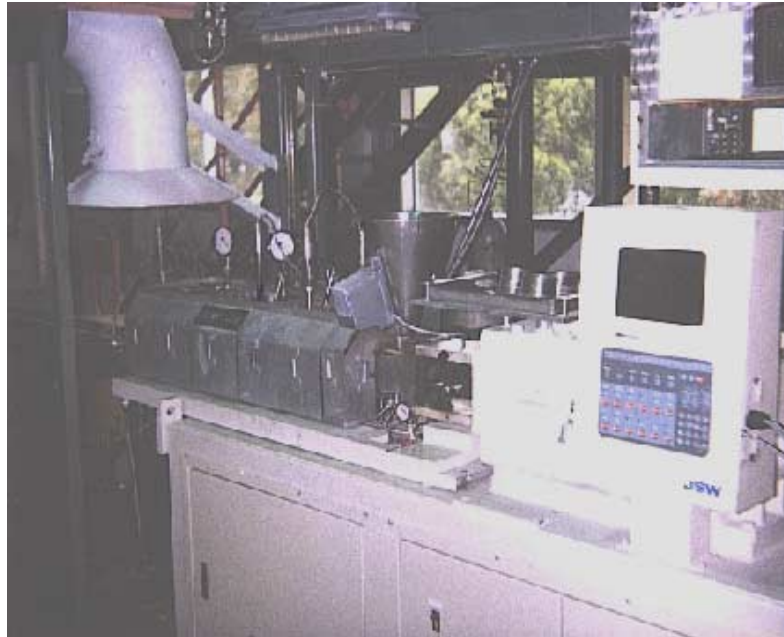


Figure 1: The reactive extruder at CSIRO Molecular Science, Clayton

Melt Flow Index (MFI)

Standard MFI measurements were carried out to routinely examine the rheology of the modified HDPEs.

The calculation of MFI is a variation of the capillary viscometer experiment with a standard diameter (2.095mm) and length (8.00mm) of a capillary die. The amount of polymer forced through the die (measured in grams) in 10 minutes is the MFI, and a high MFI means a low viscosity.

Mechanical Testing

The modified HDPEs were pelletised and subsequently injection moulded into specimens suitable for performing tensile testing, Izod impact and falling dart impact testing. The mechanical properties of the modified resin were measured and compared to those of the polymer typically used to injection mould mobile garbage bins (LBH 1103).

Sample Characterisation

The modified HDPEs were characterised using a variety of techniques, including:
High Temperature Gel Permeation Chromatography (H.T.GPC)
Fourier Transform Infrared spectroscopy (FTIR)
Nuclear Magnetic Resonance spectroscopy (NMR)
X-ray Photoelectron Spectroscopy (XPS/ESC)
Elemental analysis
Steady state shear rheology
Capillary and dynamic rheology measurements
Modulated Differential Scanning Calorimeter (MDSC)
Environmental stress cracking.

The overall aim of these characterisation tests was to determine the molecular weight of the modified material, to detect any degradation products or impurities, to determine properties relevant to future processing, and to assist in determining if the properties of a final product were likely to be satisfactory.

4 RESULTS AND DISCUSSION

The initial stage of the study involved carrying out a systematic examination of the effect of the various reactive processing conditions, identified by the literature survey, on the melt rheology and mechanical properties of the modified HDPEs prepared from the extrusion blow moulding grade of HDPE sold by Qenos for producing milk bottles (HB 5148). Then combinations of conditions and some new approaches to achieving chain scission were investigated.

The mechanical properties of some of these modified HDPEs produced under a wide range of processing conditions are shown in Figure 2, and are compared with HB 5148, H1, LBH 1103 and a PP composition used to make recycle crates. The results show that reactive extrusion can increase the MFI of HB 5148 from 0.8 to values in the range of injection moulding HDPE (3-4) and to even higher values (>6). Data for the modified HDPEs has been depicted in four groups based on the MFI of the modified HDPEs: <3, 3-4, 4-6 and >6. The results show that increasing the MFI of blow moulding grade HDPE (HB 5148) by reactive extrusion reduces its impact strength but generally increases its tensile modulus. They also show that it is possible to produce grades with MFIs (3-4) similar to LBH 1103 (the virgin HDPE currently used to make mobile garbage bins) that also have comparable tensile modulus and impact strength. Some of these modified HDPEs have mechanical properties that are similar to those of the polypropylene currently used to make kerbside recycle collection crates.

Mechanical properties summary
REX modified HB 5148

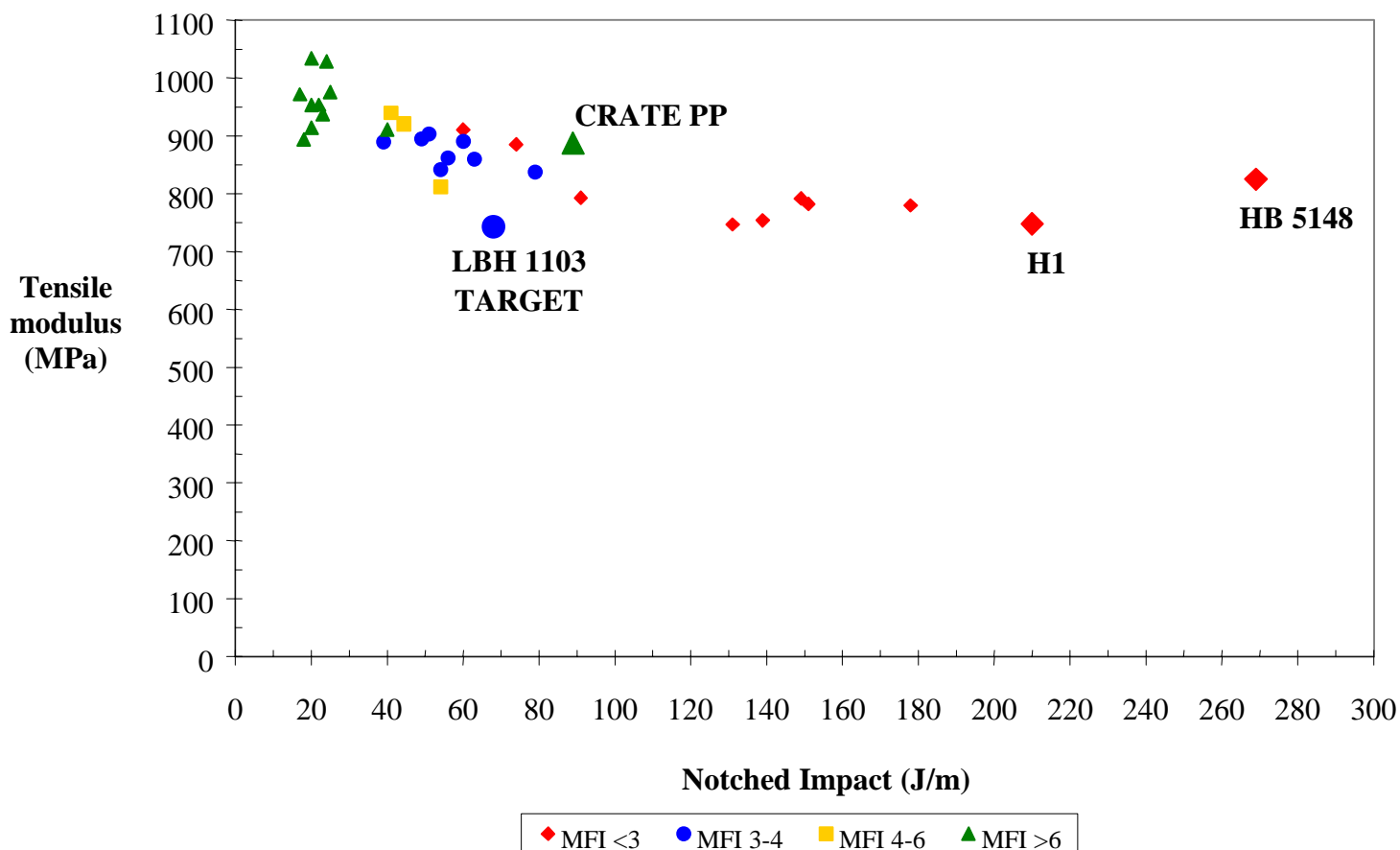


Figure 2: A plot of the tensile modulus versus notched impact results for modified HDPEs with a range of MFIs (as indicated by the legend).

The extensive study of the effect of a range of reactive extrusion conditions on melt flow index, melt rheology and mechanical properties of the modified HDPEs led to the selection of two modified HDPEs for production trials to assess their suitability for use in the production of mid-sized moulded products. The conditions used to produce both materials were practical for larger scale production, with acceptable throughput rates and operating temperatures. However, the MFI was targeted at 3.5 whereas the polypropylene compound currently used in the production of the selected mid-sized moulded product has a significantly higher MFI. Fifty kilogram quantities of each composition were prepared from recycled HDPE (H1) for evaluation in a production trial to assess the processability of these compositions in injection moulding of large items. It was decided to firstly evaluate these materials in the production of recycle crates before attempting a production trial to produce the larger mobile garbage bins.

Nylox Seaford Injection Moulding Trial: Recycle Crate

A production trial to produce recycle crates was conducted at Nylox, Seaford plant (10.08.00). The overall results obtained using the two reactive modified HDPEs were comparable with the results obtained for a polypropylene composition routinely used to mould these items. Good mouldings were obtained with the modified HDPEs (Figure 3), indicating that the compositions should have the correct melt rheology for producing large mouldings. The crates prepared from the modified HDPEs showed

good mechanical properties and passed the drop test used at the plant to evaluate the mechanical properties of the final product. A correlation between empirical tests and industrial tests was identified. The crates moulded from reactively modified HDPE showed isotropic impact strengths whereas the crates made using the PP showed much higher impact strengths 90° to the flow (perpendicular), indicating some difference in the materials. Nevertheless, the trial showed that it may be feasible to develop a higher flow recycle material which could be suitable for crates.



Figure 3: A crate moulded entirely from reactively modified recycled milk bottle HDPE

Trials at Huntingdale, Nylex: Moulding of Mobile Garbage Bins

A large-scale trial (100 kg) was conducted at Huntingdale, Nylex (19/12/00) for the production of mobile garbage bins, using modified recycled milk bottle HDPE resin. Complete mobile garbage bins were moulded successfully (see Figure 4 and 5), using the same moulding parameters as used by Huntingdale for routine production. However, these bins failed the drop test used by Nylex to assess impact strength, and the results are currently being analysed. This trial has shown that it is possible to use reactive extrusion to produce modified HDPEs that can be used to mould mobile garbage bins. The remaining development challenge, which will be addressed in ongoing research, is fine-tuning the reaction conditions to produce a polymer with adequate mechanical properties and aging properties.



Figure 4: A mobile garbage bin in the injection moulding machine prior to removal, made entirely from reactively modified recycled milk bottle HDPE



Figure 5: A collection of garbage bins made from modified milk bottle HDPE

5. CONCLUSIONS

This research has shown that it is possible to convert blow moulding bottle grade HDPE, recovered from the waste stream, into grades suitable for injection moulding large items (kerbside recycle collection crates, mobile garbage bins) at a level of 100% recycled HDPE using standard injection moulding equipment and tooling. The reactive extrusion conditions selected are considered to be practical and suitable for economic use in existing extruders that are routinely used in HDPE recycling plants as part of the current recycling process. The materials evaluated in trials had adequate properties for use in recycle crates, but would need a higher MFI. The processing conditions need to be further refined to produce modified HDPE grades with adequate impact strength for use in the production of mobile garbage bins. Further research to improve the mechanical properties is required and is being undertaken. The cost effectiveness of the reactive extrusion process also needs to be established when conditions have been optimised.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

1. Kroschwitz, J. I. *Concise Encyclopedia of Polymer Science and Engineering*; John Wiley & Sons, A Wiley-Interscience Publication: Brisbane.
2. Sakai, T. *Japan Steel Works Tech. News* **1975**, *11*, 7-13.
3. Casale, A.; Porter, R. S. *Polym. Eng. Sci.* **1985**, *25*(3), 129-143.
4. Johnston, R. T.; Morrison, E. J. *Polymer Durability: Degradation, Stabilization and Lifetime Prediction* **1996**, *249*, 651-682.
5. Hinsken, H.; Moss, S.; Pauquet, J.-R.; Zweifel, H. *Polym. Deg. Stab.* **1991**, *34*, 279-293.
6. Spinks, G. M.; Ayrton, S. *Mater. Forum* **1992**, *16*, 137-140.
7. Bernardo, C. A.; Cunha, A. M.; Oliveira, M. J. *Polym. Eng. Sci.* **1996**, *36*(4), 511-519.
8. Hirata, S.; Hasegawa, H.; Kishimoto, A. *J. Appl. Polym. Sci.* **1970**, *14*, 2025.
9. Rideal, G. R.; Padget, J. C. *J. Polym. Sci.: Symp.* **1976**, *57*, 1-15.
10. Dontula, N.; Campbell, G. A.; Connelly, R. *Polym. Eng. Sci.* **1993**, *33*(5), 271-278.
11. Holmström, A.; Sörvik, E. M. *J. Polym. Sci.: Symp.* **1976**, *57*, 33-53.
12. Moss, S.; Zweifel, H. *Polym. Deg. Stab.* **1989**, *25*, 217-245.
13. Harlin, A.; Vainio, T. *Polym. Deg. Stab.* **1993**, *39*, 29-34.
14. Drake, W. O.; Pauquet J. R.; Todesco, R. V.; Zweifel, H. *Angew. Makromol. Chem.* **1990**, *176/177*, 215.