Solvent recycling of polypropylene : 1. Properties of the recycled polymer

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Stabilized isotatic polypropylene film was recycled using a solvent technique, i.e. by its dissolution in tetrachloroethylene with subsequent solvent removal. By this method the film was reduced to a powder which could be extruded to reform the film. Degradation after multiple recycles using this technique was minimal and was not manifest in the physical properties of the film.

INTRODUCTION

A considerable amount of work has been carried out on the dissolution of polymers in organic solvents. In their extensive work Ueberreiter and Asmussen[1–9] used polystyrene and poly(methyl methacrylate) as examples of amorphous polymers. Low crystalline materials such as poly(ethylene succinate) have recently received attention[10]. The work of Blackadder and Le Poidevin has amplified and extended the theoretical details of the dissolution of polypropylene in a wide spectra of organic solvents[11–14]; this work has opened up the possibility of technical utilization of polymer dissolution.

The use of solvents as a method of reclaiming and recycling polymers offers many advantages over traditional reclamation methods. Firstly, the dissolution of a plastic in a suitable solvent will cause a massive decrease in the bulk volume of the plastic. Secondly, the precipitated polymer is in a more acceptable form for re-use, e.g. a powder or granule instead of film, sheet or specific articles. Thirdly, any insoluble contaminants can be removed by filtration leaving the polymer clean for further reprocessing. Finally, solvent processes can be used to separate mixtures of plastic materials[15]. With the exception of this latter use little or no use has been made industrially of solvent reclamation processes.

To this end a study has been made to determine the effects of solvent recycling on the mechanical and molecular properties of polypropylene as well as any changes in additives which might be present in the polymer. Further work is also underway to study suitable processes such as filtration systems to accommodate hot viscous polymer slurries as well as cost effective methods of solvent removal and recovery.

EXPERIMENTAL

Materials

Stabilized polypropylene granules (Shell KY61) were used throughout. Unstabilized polypropylene powder of the same molecular weight distribution as KY61 was obtained as a gift from Shell Chemicals (U.K.) Ltd.

Tetrachloroethylene was purchased from Hopkin and Williams Ltd. All other chemicals were general reagent grade chemicals.

Preparation of virgin film

In this work isotactic polypropylene in the form of oriented film was used as the virgin starting material. This was fabricated from a batch of polypropylene granules using a small film extruder (Plasticisers – Mk 1). The extrusion conditions were chosen to simulate a large commercial extruder.

Barrel Zone Temperature	200°C, 210°C
Die Head Temperature	220°C
Screw Speed	20 r.p.m.
Chill Roll Temperature	Dew point
First Godet, Haul-off Roll Speed	5 ft/min
Second Godet, Drawing Roll Speed	25 ft/min
Drawing Roll Temperature	132.5°C

The extruder barrel was flushed with fresh polymer granules prior to use and no film was collected until it was seen to be free of contamination. The extruder rolls were cleaned with white spirit to accomodate the production of a smooth film and to prevent film breakage.

Polypropylene recovery by the solvent process

300 g of polypropylene film were dissolved in 3 l of tetrachloroethylene. This was achieved by heating at boiling point (121°C) under reflux in a 5 l polymer reaction vessel, fitted with a stirrer. The vessel was heated in an oil bath controlled at 130°C. After approximately 15 minutes a clear solution of relatively low viscosity was obtained. The low viscosity allowed good agitation thus giving a homogeneous solution, as well as preventing froth formation.

The hot solution was poured into a beaker containing 2 l of acetone. The result of this quenching operation was a precipitate of a white flaky, open-textured gel. The gel was mechanically squeezed and broken into lumps and dried at a low temperature (60°–70°C) in a vented hot air oven. Finally the dried lumps of polymer were reduced in size to

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a fine powder in an Apex type 314 Hammer Mill. This powder was then extruded to form a film under the same conditions as for virgin film.

Tensile strength and elongation at the break

These tests were performed on an Instron Universal Model 1102 Tensile Testing Instrument.

Viscosity measurements

Viscosity-average molecular weights for the samples were calculated using the Mark–Houwink correlation using intrinsic viscosity data. Decalin at 135°C was used as the solvent for the polypropylene. The viscometer used was an ASTM No. 1, Ubbelohde type.

Molecular weight distribution

The molecular weight distribution of the virgin and recycled polymer film was determined by gel permeation chromatography. This work was carried out by RAPRA using a Waters 200 GPC with a differential refractometer as the detector.

The resulting chromatograms were analysed by a computer technique and the results obtained enabled plots of molecular weight distribution to be made and values assigned for $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_v$ and $\bar{M}_z$ for each sample.

Infra-red spectra

Infra-red spectra of polypropylene films were recorded by use of a double beam, Perkin Elmer 337 grating spectrophotometer. Scanning took place over wavelengths 400–600 cm^{-1}.

Hydroxyl and hydroperoxide group formation gave a broad shoulder centred at 3400 cm^{-1}; carbonyl formation peaked at 1730 cm^{-1}.

Crystallinity and melting ranges

(a) A Perkin Elmer DSC 1B Differential Scanning Calorimeter was used to determine the melting points and heats of fusion of the samples. The latter results enabled the percentage crystallinity of the samples to be calculated.

(b) The method of Natta *et al.*[16] was used to determine the percentage crystallinity from data obtained from wide-angle X-ray diffraction patterns. The equipment used was a Philips wide-angle X-ray Diffractometer, Model P.W. 1050 with a Rigaku–Denki 2c X-ray tube.

RESULTS AND DISCUSSION

Recovery of polypropylene by the solvent method

It was found that the dissolution of 10% w/v isotactic polypropylene film in boiling tetrachloroethylene was time dependent. Work on the dissolution process showed that small amounts of the thin film began to soften and swell in the solvent at 70°C and became totally dissolved at 90°C. Film which was introduced at 90°C or above was dissolved immediately. Polymer samples of a more compact nature e.g. thick films, chips or granules did not dissolve quickly at 90°C but underwent initial softening followed by swelling at the surfaces which gradually progressed inwards until complete dissolution was achieved. These observations suggested that the rate of dissolution was controlled by the ability of the solvent to penetrate the polymer matrix and that the greater the surface to volume ratio of the solid the faster was the dissolution.

The extensive work of Blackadder and Le Poidevin on the mechanism of dissolution of polypropylene in organic solvents shows this to be the case. Dissolution was shown to occur according to a two part rate curve. There was first an induction period during which the rate of dissolution gradually increased; there then followed a period in which the rate was essentially constant. The rate determining stage for steady dissolution was either the rate at which polymer molecules escaped from the solvent–swollen surface layer or the rate at which solvent penetrated and destroyed the crystallites in the solid polymer. The induction period increased and the rate of the constant dissolution process decreased with increased polymer density (or crystallinity) and decreasing temperature.

These theories underline the observations of a time period required to dissolve a batch of thin film in the recycling process. The thin film did not dissolve immediately since the first stage of the dissolution involved softening and 'curling-up' into lumps. These lumps were dispersed into solution at a finite rate as the solvent penetrated inwards. In theory agitation of the lumps should have helped their dissolution, however, in practice this was not the case. The gelatinous lumps clung to the solid surfaces of the reactor and the impeller; thus agitation at this stage slowed down the rate of dissolution. However, when dispersion of the lumps was attained agitation was begun which effectively completed the total dissolution of the lumps throughout the solvent.

The hot solution of polymer was then quenched with acetone. The ability of the acetone quenching process to yield a flaky brittle product was attributed to three factors. (a) Acetone is a non-solvent for polypropylene and causes its precipitation from solution. (b) Acetone and tetrachloroethylene are miscible and hence the acetone may remove some solvent from the polymer. (c) Acetone is a highly volatile liquid and absorbs its heat of evaporation from the solution resulting in rapid and subsequent crystallizing out of the polymer.

Properties of the recycled polymer

The dried powder was re-extruded and the resulting films from the first and subsequent recycles are from now on termed Film 1, Film 2 . . . etc. An extensive study of the properties of these films was undertaken to determine how much, if any, degradation had occurred during the recycling process. The mechanical and physical properties of the films are shown in *Table 1.* From these results it can be seen that recycled films have comparable strength and physical properties with the starting material. The elongation-at-break of recycled material, however, is lower than that of virgin material. Values of tenacity (or strength) are calculated per unit film denier and, therefore, these results account for variations in film thickness and width. Elongation-at-break values are quoted directly as measured and no account is taken of variations in film thickness or width. If corrections are made for these parameters by calculating values of elongation-at-break per denier it then appears that elongation-at-break remains virtually unaffected by recycling. The crystallinity and melting ranges of the recycled films show no appreciable deviation even after four recycles. Thus, from these investigations there appears to be no large scale degradation occurring as a result of the dissolution and re-extrusion of the films.

Degradation occurring in polymers would be revealed in measurements of molecular weights. To this end differential

Table 1 Mechanical and physical properties of virgin and recycled films

Film	Tenacity g/denier	Elongation-at-break %	Elongation-at-break/denier	Melting range °C	Crystallinity % D.s.c.	Crystallinity % X-ray
Virgin	3.07	34	0.03	139–167	26	44
1	2.73	26	0.03	141–166	23	45
2	2.92	29	0.04	141–168	24	40
3	3.18	23	0.03	141–166	25	44
4	3.25	25	0.04	140–167	27	42

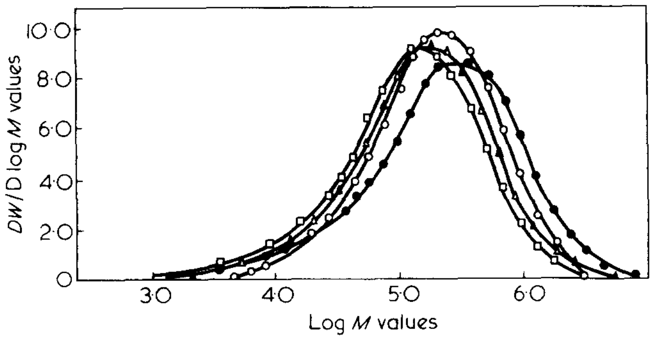

Figure 1 Differential molecular weight distributions of virgin and recycled polypropylene films: ○, virgin film; ●, film 1; △, film 2 and 3; □, film 4

Table 2 Molecular properties of virgin and recycled films

Film	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_v$
Virgin	0.92×10^5	3.32×10^5	7.97×10^5	2.89×10^5
1	0.58×10^5	5.08×10^5	16.61×10^5	4.20×10^5
2	0.45×10^5	2.92×10^5	9.21×10^5	2.45×10^5
3	0.32×10^5	2.85×10^5	8.61×10^5	2.42×10^5
4	0.21×10^5	2.32×10^5	6.74×10^5	1.96×10^5

Table 3 Amount of hydroxyl and carbonyl functional groups in virgin and recycled films

Film	Hydroxyl absorbance at 3400/cm	Carbonyl absorbance at 1730 cm^{-1}	Hydroxyl absorbance per unit film thickness	Carbonyl absorbance per unit film thickness
Virgin	0.010	0.010	0.101	0.101
1	0.013	0.012	0.130	0.125
2	0.009	0.008	0.128	0.126
3	0.010	0.012	0.130	0.152
4	0.005	0.011	0.066	0.162

molecular weight distribution curves of virgin and recycled films were constructed, these are shown in *Figure 1*. Value for $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_v$ and $\bar{M}_z$ average molecular weight values were calculated from these curves. The results are shown in *Table 2*. From these results it can be seen that there is an increase in molecular weight for Film 1 and thereafter a progressive decrease.

The tendency of molecular weight distribution to move towards higher molecular weight values after one recycle is probably due to the formation of crosslinks at the high processing temperatures. The initial increase is then offset by the effects of thermal degradation in later recycles and the molecular weight values begin to fall progressively. This effect has also been noted recently in other polyolefins[17]. Furthermore, since the measurements of molecular weight involves the dissolution of the polymer in solvents at high temperature, films containing reduced amounts of stabilizer may be further degraded. It seems probable that the stabilizer content is reduced by the multi-recycling procedures and therefore the reduction of molecular weight for recycled film may be partly due to the degradative effects brought about during its determination.

The infra-red spectrum of virgin film contains small peaks at wavelengths of 3400 cm^{-1} and 1730 cm^{-1} indicating the presence of small amounts of oxidative degradation products. These products are probably produced during polymerization and thermal processing operations. The spectra of the recycled polymer films reveal similar patterns and the quantities of these products are recorded in absorbance units in *Table 3*. On comparing results for virgin and recycled films the quantity of degradation product per unit film thickness increases with each recycle. It has been argued by Carlsson and Wiles[18] that degradation of polypropylene films takes place mainly at the surface and therefore the term 'quantity of degradation products, per unit film thickness' may be considered misleading. However, the recycling system mixes the polypropylene at each stage and even if degradation products were produced only at the film surfaces during extrusion they will eventually become dispersed into the bulk of the recycled films.

The recycling process can be divided essentially into three separate operations, *viz* dissolution, drying and extrusion. It is of some importance to identify which of these operations contributed most to the slight degradative effects noticed in the preceding analyses. In order to investigate and locate where degradation was occurring, samples of stabilized and unstabilized films were dissolved in tetrachloroethylene and refluxed (120°C) for periods up to 48 h. In the case of the stabilized film samples, the initial clear solution changed through a yellow colour after one day and eventually became a deep red. The presence of this colour was probably due to the conversion of the stabilizer, a substituted phenol, to phenoxy-radicals[19]. Samples taken from both solutions after various times were dried and examined by infra-red spectroscopy and viscometry. The results obtained, *Table 4*, show that little or no degradation has occurred with either film even after two days of refluxing. Considering that unstablized film degrades extensively in air at 120°C in 2–3 hours, it is reasonable to assume that the solvent vapour acts as an inert environment to prevent degradation in the recycling operation. Hence, as the drying operation is carried out at relatively low temperatures (60°–70°C) most of the degradation occurring during the recycling procedure must be effected during the extrusion operation.

Table 4 Properties of stabilized and unstablized polypropylene films under reflux

	Stabilized polypropylene		Destabilized polypropylene	
Reflux time (days)	$\bar{M}_v$	Carbonyl group absorbance per unit film thickness	$\bar{M}_v$	Carbonyl group absorbance per unit film thickness
0	2.43×10^5	0.101	2.18×10^5	0.165
1	2.40×10^5	0.112	2.07×10^5	0.182
2	2.30×10^5	0.172	2.05×10^5	0.202

CONCLUSIONS

(1) Polypropylene film has been recycled by dissolution of the polymer in tetrachloroethylene. The polymer was precipitated out of solution and subsequently re-extruded.
(2) The quality of the recycled film as compared to virgin film does show some evidence of degradation having taken place. However, the extent of the degradation is slight and is not manifest in the overall properties of the film.

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