Molecular composition and properties of impact propylene copolymers

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Abstract. Impact polypropylene copolymers (IPCs) are important commercial materials, but their morphology and molecular architecture are not yet fully understood. In this study the focus was on selectively removing specific fractions from the original IPC, recombining the remaining fractions, and studying the properties and morphology of these recombined polymers. It was found that some properties of the samples changed remarkably, depending on the fraction of material that was removed before recombination. In a similar fashion, morphological changes could be observed. For example, the degree of phase separation and the crystalline morphology of the recombined materials varied noticeably. It was further established that specific copolymer fractions present in the original polymer affect not only the morphology of the final polymer, but also the hardness and impact resistance.

Keywords: mechanical properties, impact propylene copolymers, temperature rising elution fractionation, molecular composition, morphology

1. Introduction

The complex nature of impact propylene copolymers (IPCs) is well documented. Due to the complex nature of the polymer, it is not that easy to understand the relationship between the molecular structure and the physical (macroscopic) properties of the polymers in question.

Numerous groups have studied the polymerization kinetics and morphological development of polypropylene (PP) with solid catalysts. This relates to the final product obtained during the preparation of IPCs, as the first phase comprises the preparation of an isotactic polypropylene (iPP) matrix. The iPP particles comprise agglomerated granules that are, in turn, made up of microparticles that are bound together [1–11]. Between the microparticles there are sub-micron sized pores, while micron-sized pores are present between the granules. By contrast, only a handful of papers on the morphology or kinetics of IPCs have appeared in the open literature. Examples are those of Kakugo et al. [12], and Simonazzi et al. [13]. An excellent, independent study was conducted at the University of Wisconsin-Madison, and reported by Debling and Ray [14]. Additional papers that deal with the morphology of the IPCs are those by McKenna and coworkers [15, 16] and Urdamilleta et al. [16]. From the available literature it is quite clear that the morphology of the ‘as-polymerized’ reactor powders is quite different from the morphology that is obtained after the first processing step [17]. This is an aspect of the morphological and chemical composition development that still needs more investigation, but one that is not dealt with in this paper. It can, in general, be concluded that the preparation of an IPC comprises, after the preparation of the iPP phase as
microparticles, the formation of a ‘copolymer phase’, which comprises rubbery as well as crystalline materials. This copolymer phase is not trapped inside the microparticles, but flows into the sub-micron pores and into the larger pores between the granules. The extent of this migration depends on both the nature of the copolymer phase (molecular weight and molecular weight distribution) and the chemical composition distribution of the copolymer phase. The chemical composition aspect is one which will, inter alia, determine whether or not there is some ‘compatibilization’ between the iPP matrix and the rubbery phase at work [18, 19]. There have been a number of papers on morphology of physical blends of iPP with other polymers [20–25], as well as the macroscopic relationship between structure and property of the IPCs, and it is clear that the impact properties of these polymers are influenced by the size and distribution of the rubber particles in the polymer after processing [26–34]. The final morphology of the polymer can also be influenced by processing parameters [35–38].

In our view, there is still a lack of fundamental understanding of how the molecular composition of the polymer influences the macroscopic properties of the IPCs. In this paper we report the results of a study where we selectively removed fractions of a commercial IPC and studied the effect thereof on the morphology and selected properties of the IPCs. We did not investigate the relationship between the morphology of the reactor powders and the final morphology of the processed polymer; that is in fact part of an on-going investigation. We have in the past successfully fractionated commercial polyolefins by preparative temperature rising elution fractionation (prep-TREF) [39, 40]. We therefore applied prep-TREF to a commercial IPC and selectively removed fractions of the polymer before recombining the rest of the material for analysis and testing.

2. Experimental section
The equipment used for the preparative TREF experiments was designed and built in-house [36]. The polymer (3 g of propylene impact copolymer CMR 648, Sasol Polymers, Secunda, South Africa, ethylene content 14.87%) was dissolved in 300 mL xylene (Technical grade, KIMIX Chemicals, Epping, South Africa) at 135°C. Stabilizer (2% w/w mixture of Irganox1010 and Irgafos168, supplied by Sasol Polymers, Modderfontein, South Africa) added to limit degradation. After complete dissolution the polymer solution was added to pre-heated sand (~50±70 mesh grade of Silica Sand, Sigma Aldrich, Munich, Germany) in a 1L reactor. The sand/polymer solution mixture was then cooled at 1°C/hour from 130 to 25°C. The sand was separated from the solvent, and the polymer remaining in solution isolated by removing the solvent under reduced pressure. This was denoted the 25°C fraction. Further fractions were collected in the second step at given temperature intervals (40, 60, 80, 90, 100, 110, 120, 130 and 140°C) by eluting the polymer from the sand with xylene at the required temperature. Polymer fractions were isolated by precipitation with acetone and drying under reduced pressure.

A reference material was prepared (E-REF) by recombining all the fractions from a prep-TREF experiment. In a series of other experiments, one fraction was removed from the material isolated from the prep-TREF experiment and the rest of the fractions recombined. The notations for all the materials prepared in this fashion are presented in Table 1. For further analyses, samples were prepared by injection moulding disks (Haake Minijet II, Thermo Scientific, USA). These disks were used for hardness measurements, DMA analyses, DSC analyses and 13C NMR spectroscopy in selected cases. Sections of the disks were used for SEM analyses (surface analyses only) and small sections were used to anneal samples in the DSC prior to microtoming, staining and TEM analyses. It needs to be pointed out that roughly 3–4 g was used in each TREF experiment, so the amount of material that could be obtained after fraction removal and recombination was very limited. This obviously also limits the amount of physical testing that was possible, and as such tensile tests, impact toughness etc could not be conducted.

The bulk and the recombined materials, as well as the fractions obtained from TREF experiments were fully characterized by 13C NMR, DSC, high-temperature SEC.

High temperature 13C NMR analyses were done on a Varian Unity Inova, 600 MHz NMR spectrometer, with 1,1,2,2-tetrachloroethane d2, (Sigma Aldrich, Munich, Germany) as solvent.
Molecular weight determinations were done with a PL-GPC 220 high-temperature chromatograph (Varian Polymer Laboratories, USA), measurements were performed at 160°C (1, 2, 4 trichlorobenzene stabilized with 0.0125% 2, 6-di-tert-butyl-4-methylphenol (BHT)) at a flow rate of 1 mL/min⁻¹. Columns were packed with a polystyrene/divinylbenzene copolymer (PL gel MIXED-B [9003-53-6]) from Varian Polymer Laboratories.

Morphology was studied by both transmission electron microscopy (TEM) and scanning electron microscopy (SEM). A Reichert Ultracut S microtome were used to prepare samples (previously annealed in the DSC) for TEM (Leo® 912 TEM). Ruthenium (III) chloride hydrate powder (Merck Chemicals, Darmstadt, Germany), were used to prepare a ruthenium oxide vapour to stain the samples prior to the TEM analyses. A Leo® 1430VP Scanning Electron Microscope was used to do the SEM analysis on the samples, with sample disks being prepared by injection moulding (Haake Minijet II, Thermo Scientific, USA). Thermal analyses were conducted using a Q100 DSC, (TA Instruments, New Castle, USA). The DSC was also used to perform isothermal heat treatment for selected samples before TEM analyses.

DMA analyses were conducted using a Perkin Elmer 7e DMA (Perkin Elmer, Waltham, USA). Samples were cooled to –80°C and then heated to 140°C. The heating rate was 5°C/min and a nitrogen purge gas with a flow rate of 28.0 mL/min was used. The static force used was 110 mN, with a static force tension of 120%. The dynamic force was 100 mN, the amplitude 10.0 µm, and the frequency 1.00 Hz.

Hardness values were determined using a UHL type VMH-002 microhardness tester (AMS Laboratory Technologies, Cape Town, South Africa), using an indentation load of 10 gf (0.01 N), an indentation speed of 25 um/s and a dwell time of 15 seconds for each sample. An average of 10 measurements was used.

3. Results
A typical prep-TREF profile is presented in Figure 1.

It is clear that about 25% of the material remains soluble at room temperature (25°C fraction). About half the polymer sample elutes at 110 and 120°C. The soluble part of the polymer is normally assumed to be rubbery and non-crystalline in nature, while the fractions eluting at the higher temperatures are more highly crystalline. The fractions of the material that elute in the range 40 to 80°C are less crystalline than those that elute at higher temperatures, and are regarded as being propylene/ethylene copolymers of limited crystallinity.

The overall contribution of these so-called copolymer fractions to the total weight of the polymer is between 15 and 20%, 50–60% by weight is crystalline iPP and 25% is soluble, rubbery material, possibly non-crystallisable PP-PE copolymers, or low molecular weight isotactic PP and EPR rubber. For the purpose of this study, we decided to take each the fractions of each TREF run, remove a specific fraction and then to recombine the rest of the material. The fractions that were to be removed were the 25°C fraction, the copolymer fractions at which elute at 60, 80 and 90°C, and the 100, 110 and 120°C fractions, which comprise mostly the iPP matrix of the impact copolymer. Of real interest to us was the effect that removing the copolymer fractions would have on the properties of the resultant recombined materials. For practical purposes the polypropylene matrix (crystalline fractions) and the rubbery material need to be present, as these fractions give the material its main properties.

The overview of the properties of some of the fractions (as an example of a typical TREF run) are shown in Table 1. Due to limited amounts of material, full characterization by 13C NMR was not possible for all the fractions.

As was expected, most of the ethylene is present in the soluble (25°C) and the copolymer fractions (60 and 80°C). Also of interest here is the wide molecu-
lar weight distribution in the copolymer fractions (4.3–10). It must be noted that the ethylene content is given as a concentration, and that one needs to take into account the size of the fractions that were analyzed in order to get a complete picture of the distribution of ethylene in the copolymer, and whilst the 40°C fraction is not considered here, the distribution of the ethylene that we did analyze is also shown in Table 2, where it is displayed as a percentage of the whole. From this it is quite clear that almost all the ethylene is in the soluble (25°C) fraction. It must also be noted that the ethylene content quoted is determined by 13C NMR, and does not distinguish between the molecular species where the ethylene is found. There are distinct differences between the spectra of the 25 and the 60°C fractions, for example (Figures 2a and b). See for example here the area indicated by the rectangle on the spectra. The peaks in this area relate mostly to different configurations of ethylene and propylene units occurring in copolymers of the two monomers.

The peak assignments for the 13C NMR spectra are given in Table 3. These assignments were made according to literature [41–45]. Assignments for the methylene carbons in Table 3 are identified by the letter S and a pair of Greek letters that indicate its distance in both directions from the nearest tertiary carbons. A methyl carbon is identified by the letter M and a tertiary carbon is labelled by the letter T.

### Table 1. Characterization data for selected fractions obtained by prep-TREF

<table>
<thead>
<tr>
<th>TREF fraction</th>
<th>M_w</th>
<th>PD</th>
<th>Ethylene content</th>
<th>Fraction weight</th>
<th>Ethylene in fraction</th>
<th>T_m [°C]</th>
<th>X_c [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>123 902</td>
<td>1.85</td>
<td>38.9</td>
<td>0.8268</td>
<td>82.00</td>
<td>116.26</td>
<td>49.89</td>
</tr>
<tr>
<td>60°C</td>
<td>73 914</td>
<td>1.70</td>
<td>34.1</td>
<td>0.1175</td>
<td>10.30</td>
<td>105.46</td>
<td>35.7</td>
</tr>
<tr>
<td>80°C</td>
<td>112 201</td>
<td>4.33</td>
<td>20.3</td>
<td>0.1375</td>
<td>6.67</td>
<td>104.56</td>
<td>12.1</td>
</tr>
<tr>
<td>90°C</td>
<td>211 376</td>
<td>10.0</td>
<td>4.49</td>
<td>0.1083</td>
<td>1.03</td>
<td>94.66</td>
<td>35.7</td>
</tr>
<tr>
<td>100°C</td>
<td>168 959</td>
<td>7.15</td>
<td>n/d</td>
<td>0.1384</td>
<td>n/d</td>
<td>154.00</td>
<td>49.8</td>
</tr>
<tr>
<td>110°C</td>
<td>93 841</td>
<td>2.13</td>
<td>n/d</td>
<td>0.4521</td>
<td>n/d</td>
<td>154.2</td>
<td>59.2</td>
</tr>
<tr>
<td>120°C</td>
<td>426 752</td>
<td>2.81</td>
<td>n/d</td>
<td>1.3309</td>
<td>n/d</td>
<td>161.4</td>
<td>66.9</td>
</tr>
</tbody>
</table>

1 Determined by 13C NMR; 2 Determined as weight% of the total amount of ethylene present in the 25, 60, 80 and 90°C fractions; 3 Calculated from DSC compared to perfectly crystalline PP. n/d Not detected

### Table 2. Selected data for the materials prepared by fraction removal and recombination

<table>
<thead>
<tr>
<th>Polymer</th>
<th>TREF fraction removed</th>
<th>Material removed [%]</th>
<th>M_w</th>
<th>PD</th>
<th>T_c [°C]</th>
<th>T_m [°C]</th>
<th>X_c [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-REF</td>
<td>None</td>
<td></td>
<td>252 971</td>
<td>4.06</td>
<td>116.26</td>
<td>160.54</td>
<td>49.89</td>
</tr>
<tr>
<td>Less 25C</td>
<td>25°C</td>
<td>27.50</td>
<td>140 850</td>
<td>2.45</td>
<td>114.92</td>
<td>159.33</td>
<td>54.85</td>
</tr>
<tr>
<td></td>
<td>40°C</td>
<td></td>
<td>-</td>
<td>-</td>
<td>114.92</td>
<td>159.33</td>
<td>54.85</td>
</tr>
<tr>
<td>Less 60C</td>
<td>60°C</td>
<td>3.33</td>
<td>173 536</td>
<td>2.63</td>
<td>116.16</td>
<td>155.20</td>
<td>54.79</td>
</tr>
<tr>
<td>Less 80C</td>
<td>80°C</td>
<td>3.90</td>
<td>157 116</td>
<td>2.49</td>
<td>113.36</td>
<td>159.79</td>
<td>43.28</td>
</tr>
<tr>
<td>Less 90C</td>
<td>90°C</td>
<td>3.07</td>
<td>165 685</td>
<td>2.33</td>
<td>106.5/109.8</td>
<td>148.70</td>
<td>35.20</td>
</tr>
<tr>
<td>Less 100C</td>
<td>100°C</td>
<td>3.93</td>
<td>163 587</td>
<td>2.53</td>
<td>107.1/111.6</td>
<td>149.30</td>
<td>23.10</td>
</tr>
<tr>
<td>Less 110C</td>
<td>110°C</td>
<td>12.83</td>
<td>117 200</td>
<td>2.31</td>
<td>105.6/110.1</td>
<td>149.30</td>
<td>37.40</td>
</tr>
<tr>
<td>Less 120C</td>
<td>120°C</td>
<td>37.77</td>
<td>202 950</td>
<td>2.98</td>
<td>107.1/111.6</td>
<td>149.30</td>
<td>23.10</td>
</tr>
<tr>
<td></td>
<td>130°C</td>
<td>5.76</td>
<td>-</td>
<td>-</td>
<td>107.1/111.6</td>
<td>149.30</td>
<td>23.10</td>
</tr>
<tr>
<td></td>
<td>140°C</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
<td>107.1/111.6</td>
<td>149.30</td>
<td>23.10</td>
</tr>
</tbody>
</table>

1 These fractions were not removed to create recombined materials. 2 Determined by DSC, relative to 100% crystalline PP. 3 One crystallization peak observed.
the more crystalline fractions constitute the bulk of the material, and as such cannot be removed without altering the nature of the material significantly. Using the values presented in Table 3 and the spectra presented in Figure 2, we can see that, for example the 60°C prep-TREF fraction shows that the ratio of the EEP:PEP peaks at around 37–38 ppm is different to that of the 25°C fraction, Similarly the presence of the peaks associated with PP homopolymer (20.5–21., 27.5–28.7 and 45–46 ppm is much more evident in the 60°C fraction. This illustrates the difference in chemical composition distribution of a partially crystalline fraction and the soluble fraction.

The mechanical properties of the materials are presented in Figures 3 and 4. Figure 3 gives the hardness values for the materials. The hardness of the reference material is given in the bar on the left. The values are given as relative hardness values (HV) and are derived by the instrument.

It is quite obvious that removing the rubbery, soluble material completely leads to a large increase in hardness (Less 25C sample), but this is expected and has little practical significance, as the rubbery material is an essential part of the material. The

Table 3. 13C NMR assignments for propylene and ethylene sequences in IPCs

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Chemical shifts [ppm]</th>
<th>Sequence type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{uu}$</td>
<td>45.14–46.32</td>
<td>PPP</td>
</tr>
<tr>
<td>$S_{uy}$</td>
<td>37.70–37.90</td>
<td>PEP</td>
</tr>
<tr>
<td>$S_{uy}$</td>
<td>37.08–37.70</td>
<td>EEP</td>
</tr>
<tr>
<td>$T_{56}$</td>
<td>33.03–33.20</td>
<td>EPE</td>
</tr>
<tr>
<td>$T_{05}$</td>
<td>30.40–30.78</td>
<td>PPE</td>
</tr>
<tr>
<td>$T_{so}$</td>
<td>30.00–30.31</td>
<td>PEP</td>
</tr>
<tr>
<td>$S_{66}$</td>
<td>28.61–29.79</td>
<td>EEE</td>
</tr>
<tr>
<td>$T_{p}$</td>
<td>27.49–28.66</td>
<td>PPP</td>
</tr>
<tr>
<td>$S_{p}$</td>
<td>27.20–27.40</td>
<td>PEP</td>
</tr>
<tr>
<td>$M_{pp}$</td>
<td>20.45–21.58</td>
<td>PPP</td>
</tr>
<tr>
<td>$M_{pp}$</td>
<td>20.60–20.98</td>
<td>PPE</td>
</tr>
<tr>
<td>$M_{pp}$</td>
<td>19.90–20.70</td>
<td>PEP</td>
</tr>
</tbody>
</table>
same is true for removing the 60°C fraction, as this is essentially also rubbery material, but with some crystalline material present. Of real interest is that we can remove the 80 and 90°C fractions and still maintain hardness values that are similar to that of the reference material. This is particularly interesting if we take into consideration the DMA results. The DMA results are presented in Figure 4. In order to relate these results to the impact resistance of the polymers we used the size (area under the curve) and peak position of the tanδ peaks for the reference material and the recombined polymers to give a 3D plot (Figure 4a) as well as a 2D projection of the 3D plot of the same data (Figure 4b).

Figures 4a and 4b shows how the T_g (tanδ) transition regions shift from the one sample to the next, and also clearly maps the broadness and separation of the samples. From the top down of the map in Figure 4b we can see that removing the crystalline materials leads to an increase in the intensity of the tanδ transition, without significantly altering the position of the transition. This is to be expected, as removing the crystalline material should have that effect. Removing most of the polymer is, however, of little practical significance, and in this regard we find the effect of removing the 60 to 90°C fractions (sample ID 3-6) significant. We can see real changes in the position and number of tanδ peaks, which indicates that these fractions play a significant role in the final morphology of the polymer in question. It appears as if the removal of the copolymer fractions influences the degree of phase separation between the more rubbery material and the crystalline iPP matrix. In the case where the 60°C prep-TREF fraction is removed, the tanδ peak moves to a significantly lower value, and the entire transition becomes much broader. The tanδ peak value moves closer to the expected T_g value for EPR rubber, which would be in the region of –30 to –40°C. This indicates that there is now a significant phase separation between the iPP matrix and the rubbery EPR phase. The broadness of the transition (–30 to 8°C) also suggests that the DMA shows that this peak is due to both the EPR phase as well as the iPP phase. If the 80°C prep-TREF fraction is removed the tanδ peak moves back to around the same value of the reference material. This indicates that this molecular fraction does not influence the phase behaviour of the EPR fraction to the same extent as the 60°C fraction. When both the 60 and 80°C are removed (sample ID 5) there is significant phase separation, with a well-developed tanδ peak at around –30°C. Whilst these changes do necessarily represent measurable changes in physical properties, they do represent changes in morphology, which could conceivably be related to changes in impact behaviour of the polymer in question. If this is taken in conjunction with the hardness values, we can see that we can affect the hardness properties without adversely affecting the (as evidenced by the DMA data) impact properties of the polymer, particularly in the case of removing the 60 and 80°C fractions individually or together (sample ID 5). These two fractions represent about 7% of the total of the polymer.

In order to correlate the mechanical and chemical analyses of the materials with the morphology, we conducted SEM and TEM analyses. Some selected results are presented in Figures 5a–c and 6a–c. The SEM micrographs show the rubbery particles present as small white bumps in the reference material (Figure 5a). For the Less 60C and Less 80C samples we see crevices in the surface of the material (Figures 5b and 5c. The crevices appear larger for the sample where the 60°C prep-TREF fraction
was removed. This indicates phase separation on the molecular scale. The TEM micrographs of samples that were isothermally crystallized indicted phase separation on a completely different scale to the SEM images. Here the rubbery particles are about 20–30 nm in diameter, which indicates the way that phase separation occurs also at a much smaller scale than can be seen in the SEM micrographs. What interested us here was the apparent phase separation amongst crystalline regions in the copolymer.

In Figure 6a the reference material quite clearly shows small amorphous, rubbery inclusions spread through the more crystalline matrix. Where copolymer fractions have been removed, the isothermally crystallized fractions clearly show a distinct phase

Figure 6. TEM micrographs of (a) E-REF, (b) Less 60C and (c) Less 80C. Polymers were isothermally crystallized and stained. Darker areas indicate more amorphous materials. Dark arrows indicate crystalline structures while the light arrows indicate rubbery particles.

Figure 7. TEM micrograph of the Less 110C material (a) scale bar = 100 nm, (b) scale bar = 50 nm
separation between different crystalline phases (dark arrows in Figures 6b and c), as well as distinctly separate rubbery segments (Figure 6c), indicated by the light arrows. In Figure 6c, in particular, we see a complete segregation of the rubber particles and two distinct crystalline phases. These TEM micrographs clearly show that the copolymer fractions play a role not only as compatibilizers between the more rubbery and the more crystalline areas in the impact copolymer, but also between materials of differing crystallizability. For interest’s sake, we also include a TEM micrograph of the Less110C material, where a significant amount of the crystalline material was removed before recombination (Figure 7).

In Figure 7 we can see that we now have structures that almost resemble ‘core-shell’ particles, where there appears to be crystalline material encapsulated in a rubber matrix.

4. Conclusions

Overall, it was found that removing fractions and recombining material led to significant changes in morphology (as observed by SEM and TEM), as well as mechanical properties. The IPC materials are designed to be impact resistant materials that retain their temperature resistance and strength properties of the parent iPP, so removal of the EPR phase and the highly crystalline phase of the polymer are academically interesting, but of little practical significance. It is therefore the effect of the removal of the copolymer fractions (constitutes 20–25% of the overall polymer material) that is of the most interest from a practical standpoint. It is quite clear that the effect of removing those fractions that were isolated by TREF at 60, 80 and 90 °C could have practical implications. These copolymer fractions clearly influence the phase-separation behaviour of the material significantly. It therefore appears that we could alter the hardness/impact balance of this particular copolymer by subtle alterations to those molecular species present in the copolymer that elute in the 60 to 80 °C range during TREF separation.

Results of TEM studies on the isothermally crystallized samples were quite revealing. A staining regimen was developed that allowed us to see distinct phase differences on the samples analyzed. Removal of the copolymer fractions could be seen to have significant effects on the morphology of the samples, and clear phase boundaries could be seen in the absence of these fractions.

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