

A BETTER MOUSETRAP? A NEW LOOK AT SOME OLD ISSUES

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ABOUT THE AUTHOR

Albert van Reenen was born in Stellenbosch in 1957. He obtained both his MSc (1985) and PhD (1988) in polymer science at Stellenbosch University under the supervision of Prof Ron Sanderson. He joined Stellenbosch University as a researcher at the Institute for Polymer Science in 1989 and was subsequently appointed as senior lecturer in the Department of Chemistry. From his early research, which focused on polymeric membranes for waste water treatment, an interest in understanding the fundamental relationship between polymer microstructure and macroscopic material properties developed.

Coupled with a long-standing collaboration with local industry, Prof van Reenen's research has been primarily focused on the structure-property relationship in commercially important thermoplastics, in particular the polyolefins. Related to this are research projects that encompass wood-polymer composites, polyolefin nanocomposites, and the study of solution crystallisation of polymers. A new focus area that is being developed at present is the use of bioactive polymers or polymer systems in packaging applications. Over the past 10 years, these activities have resulted in 19 MSc and 17 PhD students completing their research under Prof van Reenen's supervision. The collaboration with industry has also allowed him to leverage substantial funds for the purchase of analytical equipment that is essential for successful research. He regularly publishes in peer-reviewed journals and has been actively involved in the organisation, in South Africa, of an annual international conference on macromolecules and materials. He has a keen interest in furthering polymer science education in Southern Africa and through a collaborative effort with colleagues regularly presents short courses and workshops in both academia and for local industry.

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Dedicated to my wife Carol

INTRODUCTION

It has been stated that we live in a material age¹. With material science, the understanding of the structure-property relationships is at the centre of the discipline. It is important to be able to correlate the macroscopic properties of the material in question with the molecular architecture present.

This is a simple question but one that is at the same time extremely complex and difficult to fully understand: When we discuss the molecular structure of a material, at what level do we need to evaluate the structure? We also need to bear in mind that in many cases the analytical techniques that we use give us information that is very easy to misinterpret (or maybe it is sometimes just convenient to do so!).

There is a common adage that states, “If it ain’t broke, don’t fix it.” From a material science perspective, we have to add the proviso, “If it does break, you need to know why it broke and how to fix it.” It is true that people tend to worry only about the properties of a material once it fails to function as expected. In the case of polymer science, as in many other branches of science, technological advances are often driven by need and fundamental understanding is often neglected as rapid product development dominates. One classical example of this is the development of polythene (polyethylene) during the 1930s and 1940s². The first eight grams (thought to be the first significant amount) of ‘polythene’ were made in December 1935. The development of the polymer as industrial material was slow, and initially this material was identified as a possible insulation material for submarine cables. The advent of the Second World War and the need for an insulating material for flexible high-frequency cables for ground and airborne radar equipment really led to the hastened industrialisation of this polymer. It was only some years later that the true complexity of the seemingly simple polymer, derived

from ethylene gas, was elucidated. In fact, the highly branched nature of this polymer (now known as low-density polyethylene) is still one of the challenges faced in the quest to fully analyse the molecular structure of commercial thermoplastic polymers.

In this paper, I will highlight how the development of analytical techniques can impact our understanding of the behaviour of seemingly commonplace materials and how the available techniques can enhance our understanding of systems that may be of prime importance in the quest for a greener, sustainable future.

PROPYLENE HOMO- AND COPOLYMERS

Propylene is a simple prochiral 3-carbon monomer that we can polymerise to produce polypropylene. The spatial arrangement of the methyl group in the polymer backbone can be random (atactic polypropylene) or ordered (isotactic polypropylene [iPP] or syndiotactic polypropylene). The atactic form of the polymer has little or no commercial value. The advent of transition metal catalysed polymerisation of propylene led to the development and industrialisation of isotactic polypropylene in the 1950s³. This discovery led to the Nobel Prize in Chemistry being awarded to Karl Ziegler and Giulio Natta in 1960⁴. Developments in homogeneous transition metal catalysts by Ewen in the 1980s led to the commercialisation of syndiotactic polypropylene⁵. The type of tacticity (isotactic or syndiotactic) and the extent of the tacticity (usually expressed as a percentage) are factors that influence the properties of the polypropylene. Even a seemingly simple polymer such as this can be quite complex, and very similar materials can be substantially different on a molecular level. This can be seen if we fractionate similar materials⁶.

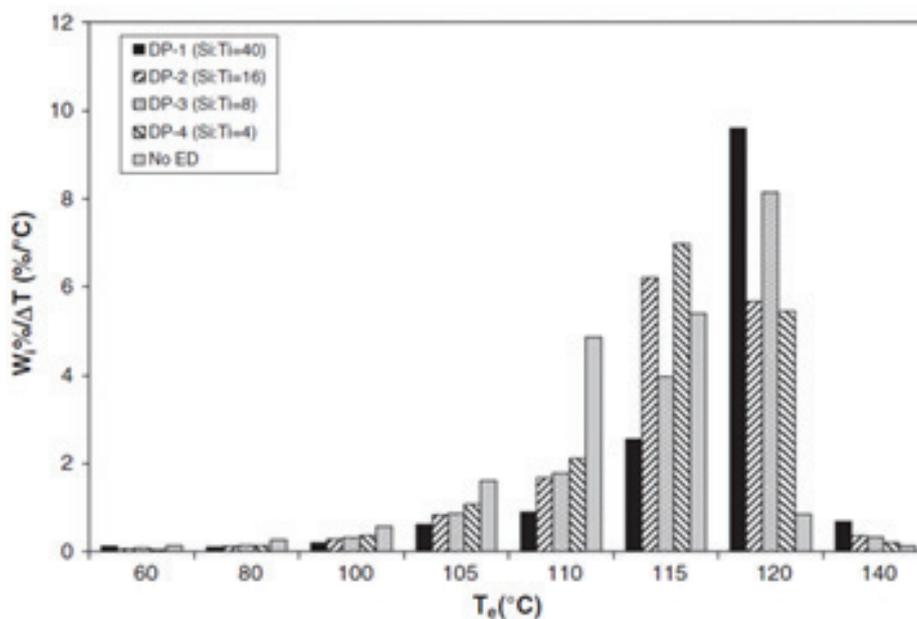


Figure 1: Temperature rising elution fractionation for five isotactic polypropylene samples. Samples DP1 – 4 have similar melting points and crystallinity⁶

Here we can see (Figure 1) that materials that have apparently similar properties do in fact have a different molecular makeup, as evidenced by the comparison of the temperature rising elution fractionation (TREF) profiles.

Polypropylene is a useful thermoplastic but suffers from the drawback of being quite brittle. As a result, the so-called impact copolymers (or heterophasic ethylene-propylene copolymers [HEPCs]) were developed. These are complex materials, effectively an in-reactor blend of isotactic polypropylene (made in a first-stage gas-phase transition metal catalysed polymerisation) and a mixture

of rubber and semicrystalline polymers (synthesised inside the iPP particles from the first reactor, in a second [cascade] gas-phase reactor). During this second stage, some ethylene gas is introduced with propylene, this being designed to form a rubber (ethylene-propylene rubber [EPR]) within and around the primary particles. After the polymer has been melted, the rubber and the iPP phase separate, with the resultant material existing as an iPP matrix with finely dispersed rubber particles. This is shown in Figure 2, together with a schematic depiction of what is shown in the electron micrograph. The ethylene-propylene copolymer acts as an interphase between the EPR and the iPP.

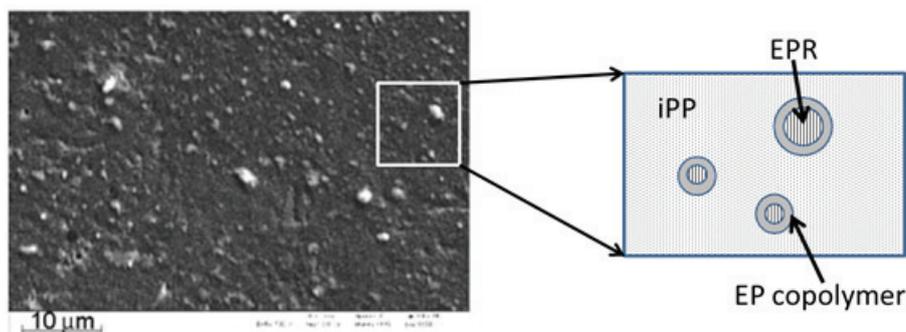


Figure 2: Scanning electron micrograph of the surface of a propylene impact copolymer, with a schematic representation of the visible features

Take, for example, a case where an impact copolymer (HEPC) is made by two different technologies to yield apparently similar materials, yet the properties differ. The example shown in Figure 3 is of two polymers with different impact properties⁷.

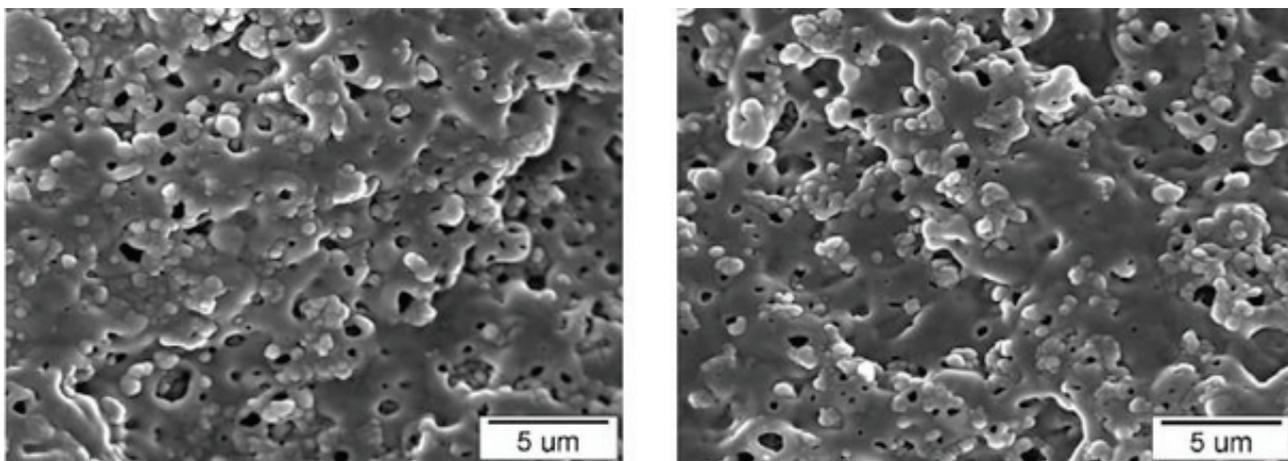


Figure 3: Scanning electron microscope (SEM) image of two HEPCs with the left showing a good dispersion of rubber particles and the right a poorer dispersion of rubber particles (represented by the holes where the particles were extracted)

If the macroscopic parameters (molecular weight, dispersity and ethylene content) are similar, why do the properties and morphology differ?

It is commonly known that the dispersion of the EPR (reflected by rubber particle sizes and interparticle distances) can be translated into the physical performance, specifically the impact toughness, of the polymer⁸. Vital to being able to control rubber particle size and distribution is an understanding of how the rubber phase develops relative to the existing homopolymer matrix and how the semi-crystalline copolymers facilitate compatibility between the clearly incompatible homopolymer and rubber. These are, again, related to the chemical composition distribution of the species present in the commercial HEPC materials. We can, if need be, easily determine the composition distribution

by fractionation (by TREF, for example) of the products made by different technologies.

The fact that we can observe these differences in the final product (see Figure 3) must be related to the differences in macroscopic properties, but this is in itself of little comfort to the manufacturer of the polymer in question. The real question is, Why does this happen? How can the problem be solved?

In recent studies, we were in the fortunate position to be able to study the morphological development of HEPC particles inside an industrial reactor and to observe the change in chemical composition distribution (CCD) as a function of the reaction conversion. The nascent iPP particles as they emerge from the first reactor (for two different technologies) are shown as SEM images in Figure 4. The difference in apparent porosity is immediately obvious.

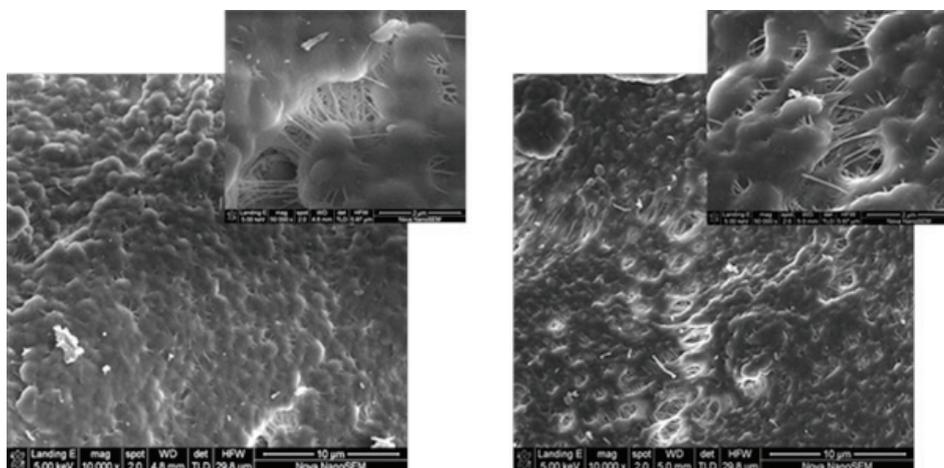


Figure 4: SEM images for the surface of nascent iPP particles produced by two different technologies⁹

We could monitor the development of the rubbery morphology as a function of the ethylene content (see Figure 5, Set 1 shown), and we could similarly gain a very good indication of where the ethylene that was incorporated would in fact find itself (Figure 6, both sets). In addition to that, we could by carefully fractioning each sample drawn from the reactor gain insight into the development of the chemical composition distribution

of the complex polymer during the actual conversion process. We can see that in the case of Set 1, the development of long ethylene sequences is delayed to the latter part of the reaction while it happens much more rapidly in the Set 2 samples. It is also clear that for Set 1, the average particle diameter increases and the interparticle distance decreases as the ethylene content increases. This is not the case for the other sample (not shown here).

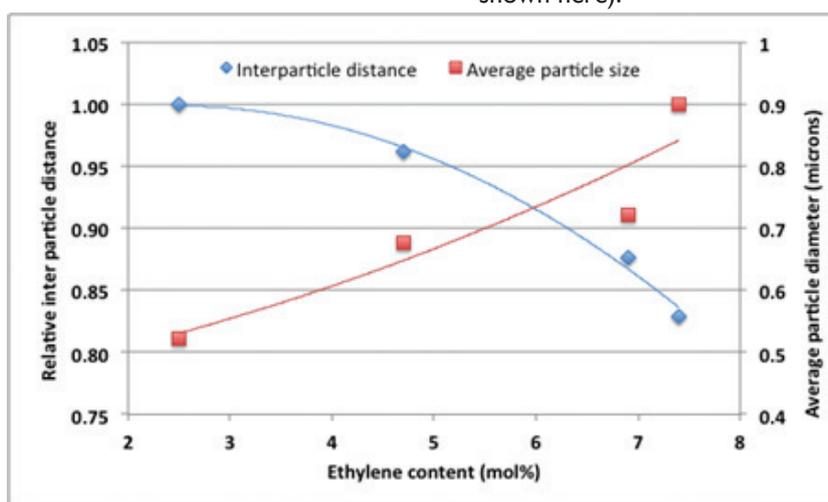


Figure 5: Rubber particle size and interparticle distance as a function of ethylene incorporation for HEPC⁹

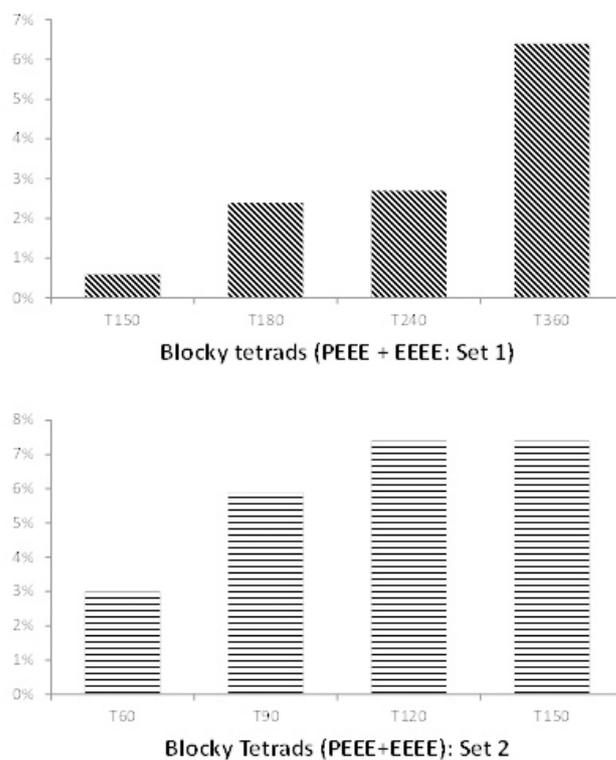


Figure 6: The distribution of ethylene in the HEPC copolymer as a function of total ethylene content. Blocky tetrads were determined by ¹³C NMR

If we take the morphology (rubber particle size and distribution) and the average chemical composition development during polymerisation into consideration and we couple these with the development of the physical properties of the material (Figure 7), a picture starts to emerge. It appears that in the case of the one technology, the impact properties develop far more rapidly than in the case of the other.

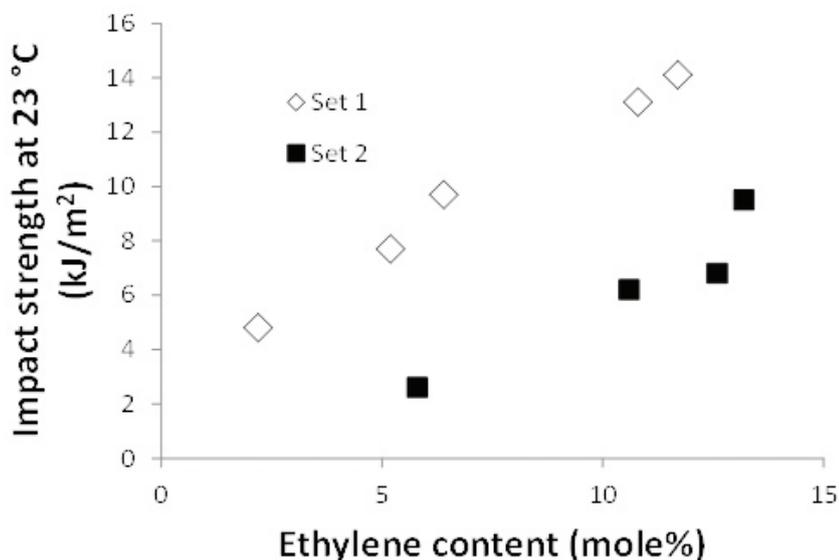


Figure 7: The development of impact properties as a function of ethylene content (HEPCs made by different technologies)

One of the challenges that we face when analysing any polymer is that we either tend to make use of solution-based techniques to attain some average composition information (for example solution ^{13}C NMR spectroscopy) or we fractionate from solution in order to obtain samples that we may analyse in a number of different ways. On bulk samples we may obtain macroscopic mechanical property data (such as tensile or impact properties) or we may visualise the morphology, for example by microscopy or SEM. It may even be possible to form some idea of the chemical composition distribution of a specific material by FTIR microscopy. It is, however, very difficult to gather information on chemical composition and morphology in a solid, unaltered sample and to be able to link this to changes in morphology brought on by changes in temperature. To link this to the present topic, if we have reactor particles, can we see and link the morphology and chemical composition of that artefact (without dissolution or fractionation)?

Based on the ethylene-dependent changes observed for the HEPCs as well as some semi-crystalline TREF fractions (see Figure 8), further variable-temperature solid-state ^{13}C NMR experiments were done to observe temperature-dependent shifts in localised mobility within the bulk samples during a heating/melting profile. From

these experiments, the development of amorphous polypropylene signals was observed with increasing temperature, which could indirectly be related to the introduction of ethylene defects. It was also observed that polypropylene components with high rigidity remained at high temperatures for the HEPCs but not for the homopolymer. $T_{1\rho}$ experiments were used to differentiate between changes in crystalline and non-crystalline phases based on ethylene incorporation as well as during melting. An interesting observation from this study was that the polypropylene homopolymer could experience increasing segmental mobility around defects as the temperature was increased. This can significantly alter its interactions with other more mobile copolymer segments during melting, influencing phase separation and the distribution of the rubbery copolymer, which ultimately influences the polymer's mechanical behaviour¹¹.

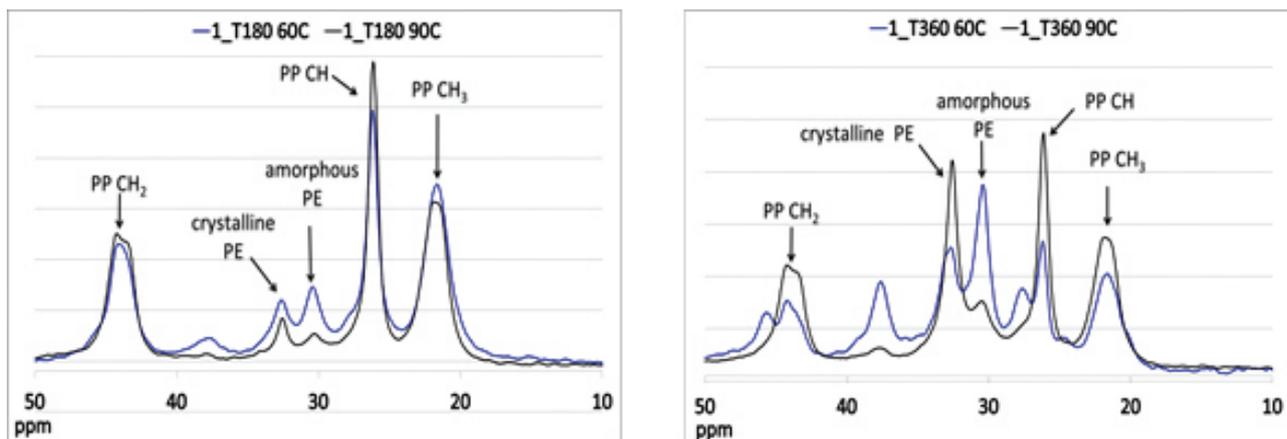


Figure 8: Solid-state spectra indicating conformational development within the 60 °C (blue) and 90 °C (black) TREF fractions for two samples with different ethylene content¹⁰

LASER LIGHT SCATTERING: CONVENIENT, QUICK AND INEXPENSIVE

As was pointed out in the initial section of this paper, being active in the field of polyolefin analyses means relying quite heavily on fractionation techniques, whether analytical (such as crystallisation analysis fractionation [Crystaf]) or preparative (such as preparative temperature rising elution fractionation [prep-TREF]). Both Crystaf and prep-TREF are available to in-house, and both techniques work according to the principle that crystalline polymers can be dissolved at elevated temperatures and then fractionated by crystallisation by means of controlled cooling. Depending on the type of

polymer analysed, the data obtained in this way can be related in some way to the CCD of the material. These methods are all subject to one constraint: they are time consuming.

Following a paper by Shan et al¹² (and preceded by some discussion on this topic between Erich Rohwer and myself), we decided to construct an instrument that is able to follow the crystallisation from solution upon cooling and the dissolution (or solution melting) upon heating of suitable semi-crystalline thermoplastics. We decided that every technique should have a suitable acronym, so we came up with 'solution crystallisation analysis by laser light scattering' or Scalls¹³. A basic schematic of this instrumentation is shown in Figure 9.

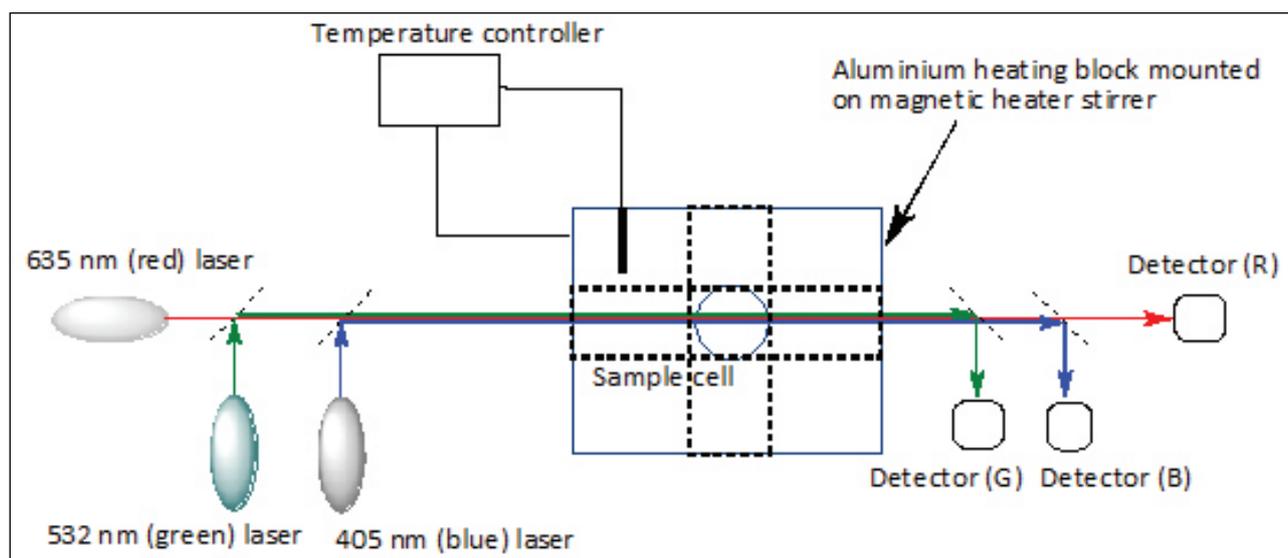


Figure 9: Schematic representation of the Scalls instrumentation

The major advantage that this instrumentation has is that of utilising lasers of different wavelengths simultaneously. As the ability to scatter light is dependent not only on the size of the scattering particle but also on the wavelength of the light, using lasers of 405, 532 and 635 nm simultaneously allows for the tracking of crystal growth in solution, which in turn relates to the kinetics of crystallisation. Similarly, the rate of dissolution upon heating can be tracked. The first derivative of the raw voltage data is normalised and plotted. Figure 10 below depicts one of the iPP samples discussed in Figure 1¹³.

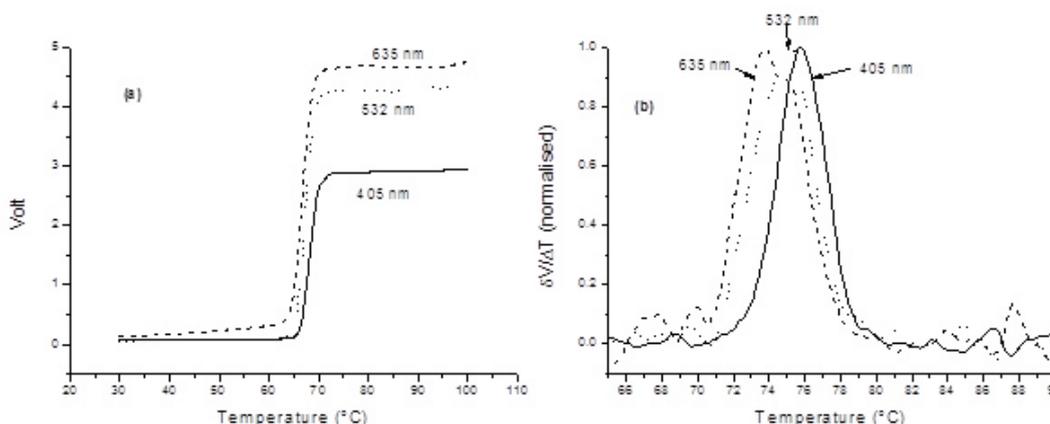


Figure 10: The raw voltage data (a) and normalised first derivative data (b) for the crystallisation from solution of an iPP sample as determined by Scalls

We have shown that the Scalls technique can, quickly and accurately, provide as much information about the crystallisation of polyolefins as the conventionally accepted technique, but more recently we have shown that we can also use this technique to probe the crystallisation behaviour of one of the more commercially important biopolymers, poly(lactic acid). This biodegradable material is a candidate for replacing fossil fuel-based materials in everyday use, yet there are some practical drawbacks that hamper the commercialisation of this polymer. The most important of these is the extremely low rates of crystallisation of the polymer.

Poly(lactic acid) can be found in three forms: Polymerisation of the enantiomeric L- or D- forms of the monomer results in poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA). Both these forms can crystallise. Polymerising a racemic mixture of the two enantiomers results in an amorphous form of the polymers. We used Scalls to study the solution crystallisation/recrystallisation of the enantiomeric forms individually as well as selected blends of PLLA and PDLA. Here we were able to show that blending the materials resulted in the formation of a high-melting stereocomplex crystalline structure, which could be used to increase the rate of crystallisation and the extent of crystallinity of the PLLA (see Figure 11).

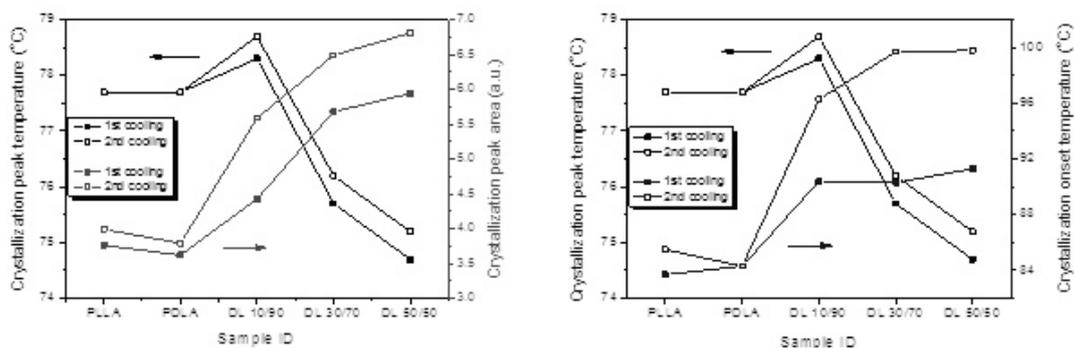


Figure 11: Scalls data for first and second cooling of homopolymers and blends (left), crystallisation peak temperature and crystallisation area (right), crystallisation peak temperature and crystallisation onset temperature¹⁴

In addition, it could be demonstrated that using blending of another biopolymer, poly(butylene succinate) (PBS), with PLLA could alter the rate and extent of the crystallisation of the PLLA. Crystallisation of the PLLA could be increased significantly (blending low levels of PBS) or suppressed completely (higher levels of PBS).

WOOD-POLYMER COMPOSITES

The use of waste materials to produce useful products is always an attractive prospect. In this respect, wood-polymer composites have received a great deal of attention and in particular the use of polyolefins in this application. Little is known about the interaction of the hydrophobic polymers with the essentially hydrophilic wood surface, which is usually facilitated by the use of compatibilising polymers. While we could show the effect of the wood composition and the compatibiliser for a simple polymer such as linear low-density polyethylene^{15,16}, the advent and growth of fluorescence microscopy (and spectroscopy) allowed for the visualisation (for the first time) of the interface of the wood fibres, the compatibiliser and the polymer itself¹⁷. This is shown in Figure 12.

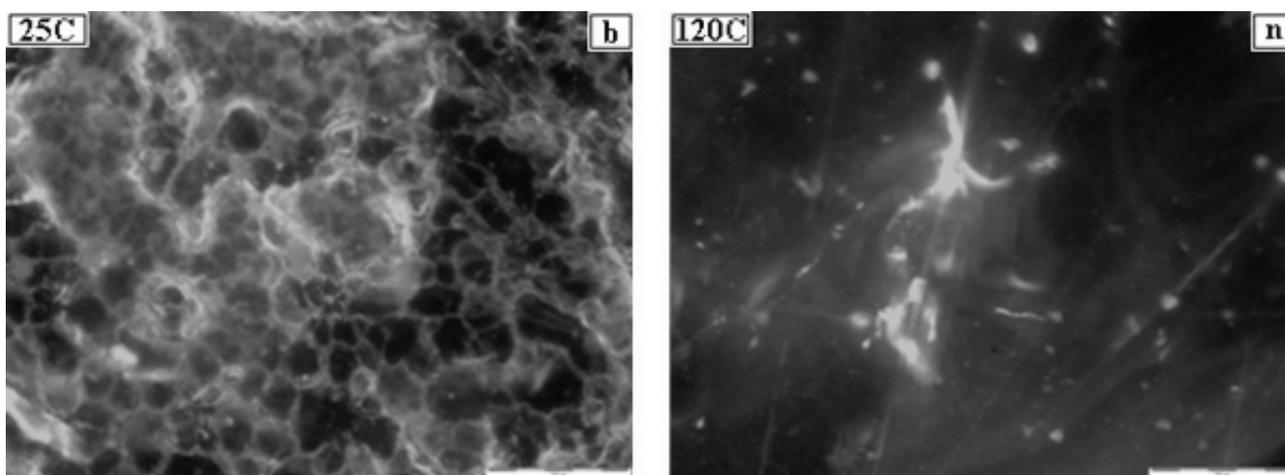


Figure 12: The interaction of a fluorescein isocyanate (FITC)-labelled ethylene-vinyl alcohol copolymer compatibiliser (light areas) with (b) the EPR and (n) the iPP fractions of an HEPC polymer. Fractions were obtained by TREF.

CELLULOSE AND NANOCRYSTALS

Moving from composites to nanocomposites is a logical step, and with the ability to produce nano-sized fillers such as carbon nanotubes, the field of polymer nanocomposites became the place to be (remember the famous saying, “There is plenty of room at the bottom”). One of the developments in this area was the use of cellulose nanocrystals. These are isolated from microcrystalline cellulose via acid hydrolysis and extraction of the non-crystalline materials, leaving the required nanocrystals behind:

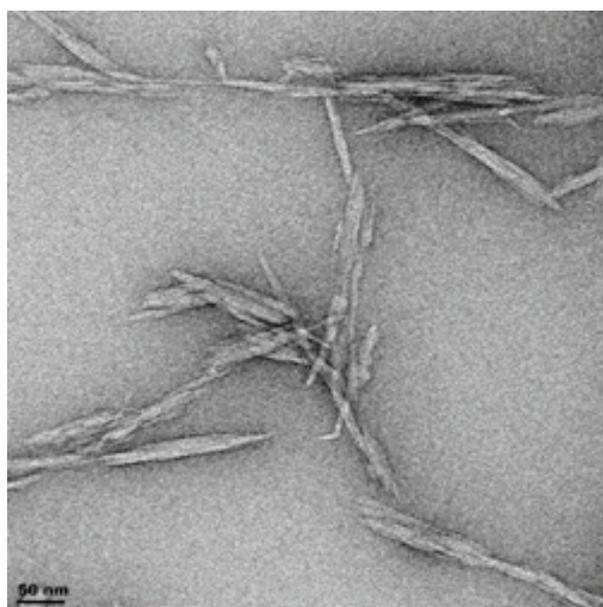


Figure 13: Transmission electron microscopy image of cellulose nanowhiskers (CNW). The scale bar is 50 nm.

The problem with utilising these nanocrystals in composite materials is the distribution of the nanofibres in a polymeric matrix. This is especially true if the polymer and the fibres are incompatible. Incompatibility aside, the very size of the nanocrystals and the viscosity of a molten polymer make it extremely difficult to disperse these reinforcing fillers into a polymer. In addition, the small sizes make evaluation of the dispersion of a filler in a composite difficult without resorting to transmission electron microscopy (in which sample preparation is tedious and analyses could be selective and non-representative). The ability to attach a fluorophore to the nanocrystals makes it possible to visualise the distribution of the nanofiller via fluorescence spectroscopy (Figure 14). More importantly, however, the lack of dispersability of the nanofillers opens up the possibility to use these materials as nanosized probes to help visualise the morphology of complex polymers such as the HEPCs.

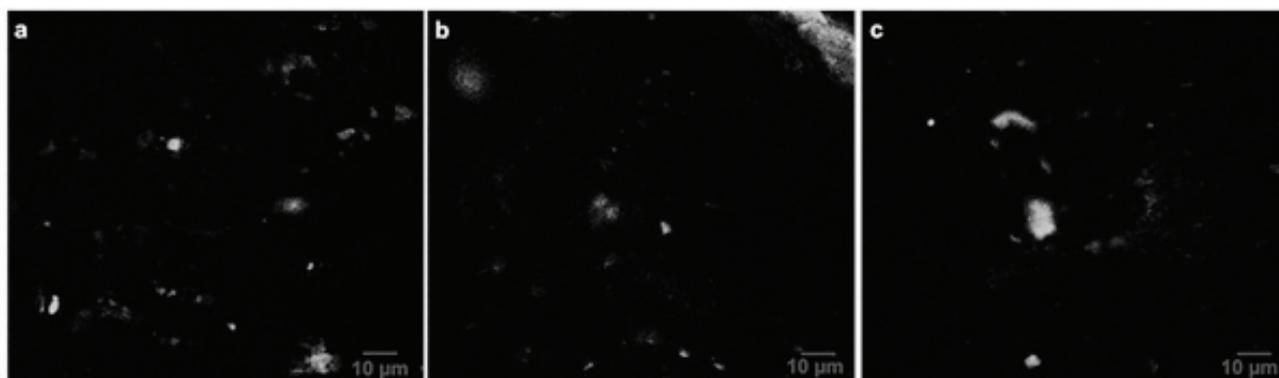


Figure 14: Confocal fluorescence microscopy images of FITC-labelled CNW dispersed in the EPR (rubbery) particles of an HEPC. The light areas depict the distribution of the rubber particles

WHERE TO NEXT?

Some long-standing problems still exist. One of the most used and abused commercial thermoplastics is PVC. There are inherent molecular defects present in this polymer that are responsible for the inordinate amounts of additives that we need to add to the material in order to make it useful. Yet we still do not understand exactly why these defects develop during industrial production. Advances in spectroscopic techniques as in the case of solid-state NMR should allow us to unravel some of the puzzles presented by this fascinating polymer.

Apart from the old, there is also the new. Research in polymer science is undergoing a significant expansion with the growth in bioactive polymers and polymer systems. Advances in analytical techniques are allowing us to design and understand complex macromolecular architectures. There are significant challenges and opportunities that could be embraced. Functionalised polymers and complexes of polymers have the potential to be used as sensors. There is scope for the application of this technology in sustainable food production, for example in postharvest technology to monitor ripening of fruits and as early detectors of food spoilage.

A WORD OF THANKS

At this stage, all of what has been done has been made possible by a very special group of people. The results that are so casually reported have been made possible by the hard work of many postgraduate students. For those who have come and gone, thank you. For those who are here now, thank you for electing to become part of our research family. There are exciting times ahead.

I must also give thanks to all those people whom I have been able to collaborate with over the years; thank you for being willing to share your knowledge and insights. A special word of thanks to my erstwhile supervisor and mentor, Prof Ron Sanderson, for introducing me to the wonderful world of macromolecules and to my friend and colleague in the United States of America, Lon Mathias, for showing me what it means to be an academic.

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