Materials engineer Dr Davide De Focatiis discusses the finer points of polymers, and gives a structural overview of his work towards optimising their properties for a wide variety of applications.

When did you become interested in processed polymers?

During my PhD, I worked on the mechanics of a needleless powder injection device that made use of the rapid deformation of a small injection-moulded dome-shaped polymer component to accelerate drug powder. In this process, I began to collaborate with Professor Emeritus Paul Buckley of the University of Oxford, UK, in developing biaxially stretched versions of these domes that were substantially stronger than the injection-moulded originals. I found it fascinating that by tailoring the process to orient the molecules in this component, it was possible to obtain a substantial improvement in performance, although this concept is used readily in many everyday oriented polymer products like packaging films and polyethylene terephthalate (PET) bottles.

Have these interests developed over time?

After my PhD, I continued my polymer research together with Professor Buckley. Much of my work has focused on understanding and developing tools to predict orientation and its effect on the properties of polymers. It is undoubtedly the case that exploiting polymer orientation can lead to significant improvements in the applications of polymers in a very wide array of industry sectors.

How do you use small-angle neutron scattering (SANS) in your research?

We use SANS as a molecular probe that tells us about the dimensions of polymer molecules, which is a measure of how stretched they have become following a process. Collaborating with experienced synthetic chemists, it is possible to obtain polymers whose hydrogen atoms have been replaced with deuterium. This makes them less visible to neutrons, and allows us to selectively look at different molecules within a specimen.

We developed a new technique that allowed us to probe the dimensions of long and short molecules simultaneously within the same blend. Studying these dimensions after polymer specimens have been subjected to different processes helps us develop models of the mechanisms by which the molecules within these blends orient with flow, and how they interact with each other.

You have created a toolbox to predict birefringence and craze initiation stress in monodisperse polymers. Have your predictions been close to experimentally measured quantities?

Our predictions of birefringence in monodisperse oriented polymers turned out to be very precise, and gave us great confidence that the methodology behind the model was correct. Predicting craze formation is somewhat more challenging, partly because of the many factors that influence it. But we were nonetheless able to obtain good correlations between craze formation and parameters output from the model in monodisperse polymers. The challenge is to extend these models to allow the same quality of predictions in more complex polymer systems.

In 2009, you were awarded the Dutch Polymer Institute award for excellent research, and you were recently invited to deliver a keynote lecture at the 26th Annual Meeting of the Polymer Processing Society. What do you consider your greatest achievement to date?

Both the award and the keynote lecture were concerned with the computational model I developed in collaboration with Professor Buckley and as part of the Microscale Polymer Processing consortium, an interdisciplinary collaboration between several UK universities and industry partners. This was the first time that a model had been proposed combining solid-state deformation and rheology with molecular awareness; the parameters of the model consisted of information about the length of the polymer molecules, which directly influenced the process and product performance.

Demonstrating that this was possible, and validating it with experiments on model polymers, has been a substantial undertaking and is definitely the highlight of my career to date. This achievement has been the foundation of several other projects attempting to widen the applicability of this model to more complex polymer systems, and more recently to apply this understanding to nanocomposites and degradable medical polymers.

Terminology

- Craze initiation stress – crazing is a phenomenon that takes place in glassy polymers where small crack-like objects appear over time when the polymer is subjected to a stress. They are precursors to true cracks, and also detract from the appearance of transparent polymers by making the part appear milky in colour. But they are also important elements of energy dissipation, such as in high-impact polystyrene, from which many children's toys are made.

- Birefringence – the difference in the refractive index in perpendicular directions. Birefringence is important in optical applications of polymers, such as lenses.
OF ALL THE materials created by man, plastic must be among the most infamous. Irrevocably associated with environmental concerns based on its inability to decompose, and often used in substandard products due to its low cost, for many, plastic has become a symbol of the worst aspects of manufacturing. Although this view is based on valid concerns, it may not be entirely fair; plastic bags, for example, may be the scourge of wildlife when improperly disposed, but they weigh about 5 g and can carry as much as 2,000 times their own weight. This is not a function that can easily be achieved using other materials, even half a century after the first plastic carrier bag was patented. Plastic is a triumph of engineering, regardless of its misuse by the population at large.

Plastics have negative associations because of their ubiquity, but they are ubiquitous because they are cheaper, more versatile and more facile than almost any other group of materials; that, after all, is why we called them plastics. What is more, despite their bad public image, plastics continue to be integral to modern manufacturing and living – and this is reflected in their production. In the UK, the polymer industry employs almost 200,000 people across 7,400 companies and, far from shrinking, it is actually growing at a rate of approximately 2.5 per cent every year. This large industry is responsible for processing 4.8 million tonnes of plastics annually, and in 2010 it contributed 2.1 per cent of UK GDP.

IMPROVING ON SUCCESS

The success of this national industry is primarily based on the versatility for which plastics are named; as well as being conducive to moulding, the polymers that make up plastic can be manipulated in various ways to produce different material properties. In plastics composed of molecules of uniform length, known as monodisperse polymers, it is possible to predict the solid-state properties of the finished material based on its rheological (flow) properties when melted. However, commercial plastics are polydisperse, and consequently their properties are much more difficult to predict. In order to effectively model polydisperse polymers, and save this important industry from costly trial and error, significant advances are needed to ascertain how polymer molecules of different lengths interact to produce material properties.

This is the central focus of a team of polymer engineers based at the University of Nottingham (UoN), UK, and led by Dr Davide De Focatiis. It was De Focatiis who, together with Professor Emeritus Paul Buckley as part of the Microscale Polymer Processing consortium (μPP), was first able to formulate a coupling between molecular rheological constitutive equations and solid-state constitutive models in monodisperse polymers, allowing scientists to predict their solid-state properties. Now working alongside UoN mathematics lecturer Dr Richard Graham and polymer chemist Dr Lian Hutchings of the University of Durham, UK, De Focatiis is engaged in a new project to create a functional model for predicting the properties of polydisperse polymers, including bimodal blends.

APPROACHES TO ORIENTATION

When a polymer part is being produced, it is common practice to process it in the melt. Virtually all polymer materials encountered in everyday life have undergone this process, which involves pushing the melt through narrow channels so that it shears and stretches, giving
Optical polarised transmission micrograph of an oriented polymer specimen illustrating fringes produced by a compensator used to measure optical retardation, and hence birefringence.

In order to be as economic as possible, the melt is then quickly cooled, locking in the orientation of the individual molecules. The problem with this process is that oriented polymers are anisotropic; like a piece of wood which splits more readily along the grain than against it, individual polymers have different properties in different orientations. Therefore, predicting how a processed polymer will behave is very difficult and hugely dependent on molecular orientation—and when the polymers involved are polydisperse, it becomes even harder.

De Focatiis’s current project focuses on bimodal blends—polymer mixes that contain molecules of two different lengths, representing the simplest form of polydisperse polymers. In order to investigate the relationship between flow and solid states in these blends, the researchers process samples of various blends and analyse the orientation of their polymers in the solid state using small-angle neutron scattering (SANS). This method allows them to examine the effect of processing on polymer orientation, and the impact that different lengths of polymer have on each other as part of this process. The team has also been responsible for developing new and more comprehensive methods for analysing the finished plastics.

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**AN INSIGHT INTO INDUSTRY**

A large part of the UoN group’s approach is their close collaboration with industry. Lucite International and Styrolution, two industry leaders in the polymer sector, are assisting with this particular project. As De Focatiis explains: “Virtually all of the polymer research we undertake involves some aspect of collaboration with industry, and there is always mutual benefit in this.” In fact, the programme of research is designed specifically with industry in mind.

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Improved modelling systems, which the researchers ultimately hope to make compatible with existing software used by manufacturers, will have a huge impact on the manufacturing process, saving time and money for large and small businesses alike. Equally, without models to fall back on, the industry has a huge body of experience gained from trial and error, and this has resulted in the development of ‘rules of thumb’, some of which are invaluable to the researchers. For example, in industry it has been known for some time that the mechanical properties of some polymer parts can be enhanced by adding small quantities of higher molecular weight polymers, but it has been difficult to predict how much is required, or what effect this will have both on the process and final product. These rules of thumb are not always well-connected to their scientific bases, but they can provide De Focatiis and his collaborators with time-saving clues as to what to look for, thus helping them to further their research and the efficiency of the industry in the process.

**Technical toolbox**

Before being appointed Lecturer in Polymer Engineering at UoN in early 2009, Dr Davide De Focatiis was a postdoctoral researcher at the University of Oxford in the research group of Professor Emeritus Paul Buckley. It was in this position that he conducted his research into the link between rheological and solid-state characteristics in monodisperse polymers. Since leaving Oxford, he has continued to work with Buckley in a long-term collaboration that has remained fruitful.

In 2011, this joint effort culminated in the development of numerical models for the prediction of birefringence and craze initiation stress in oriented monodisperse linear amorphous polymers. These models built upon the output of the constitutive model they proposed in 2010, consisting of a combination of rheology and solid-state polymer theory. With the help of polymer chemist Dr Lian Hutchings, they were able to compare their predictions to experimental data on model polymers, and found excellent agreement between simulations and experiments.

Numerical models of this kind are aimed at predicting solid-state properties of processed polymer parts, such as extrusions and injection mouldings. Since the models are partly based on molecular rheology, they are inherently molecularly aware and can accurately predict the effect of a given choice of polymer grade on a finished article. Although properties can only be predicted accurately for monodisperse polymer systems at present, the success to date is an encouraging step towards achieving a predictive toolbox for more general polymer systems.

**INTRODUCTION**

Solid-state property predictions for oriented bimodal and polydisperse glassy polymers.

**OBJECTIVES**

To develop the tools necessary to assemble and validate a constitutive model enabling solid-state property predictions for oriented bimodal and polydisperse glassy polymers.

**KEY COLLABORATORS**

Emeritus Professor C Paul Buckley, Department of Engineering Science, University of Oxford, UK • Dr Urs Gasser, Laboratory for Neutron Scattering, Paul Scherrer Institute, Switzerland • Dr Richard Graham, School of Mathematics, University of Nottingham, UK • Dr Lian Hutchings, Department of Chemistry, Durham University, UK • Dr Olga Smerdova, Department of Engineering, University of Cambridge, UK

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**DR DAVIDE S A DE FOCATIIS** graduated in Engineering from the University of Cambridge, UK, in 1999, and obtained his doctorate in Engineering Science at the University of Oxford, UK, in 2003. Between 2004 and 2008, De Focatiis conducted postdoctoral research as part of the Microscale Polymer Processing consortium in the Solid Mechanics and Materials Engineering group in the Department of Engineering Science at the University of Oxford. In 2009, he was appointed Lecturer in Polymer Engineering in the Faculty of Engineering at the University of Nottingham. Within the division of Materials, Mechanics and Structures and as part of the Polymer Composites research group, he leads a team of researchers focused on numerical and experimental aspects of the solid-state properties of polymeric, composite and nanocomposite materials.