Study and Control of the Distribution of Elastomer in High Impact Polypropylene

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Summary: In an initial step, different techniques were used to investigate the distribution and properties of the rubbery domains inside individual high impact polypropylene particles. Both Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were used to visualise the local of rubber nodules as a function of the quantity of ethylene propylene rubber (EPR) in the final product. It was demonstrated that the EPR forms first as nodules near the centre of the homopolymer particles, and then accumulates as the rubber quantity increases.

Keywords: elastomer; high-impact; poly(propylene); rubber

Introduction

Semi-crystalline isotactic polypropylene (PP) can be toughened by dispersing rubbery domains in the homopolymer matrix. In commercial processes this is usually done in at least two different reactor steps as suggested in the schema below. PP homopolymer is made in the first step (usually, but not always) in a slurry of liquid monomer. The resultant particles are flash dried and sent to a gas phase reactor in a second step. Here, a mixture of ethylene and propylene is fed to the reactor, leading to the formation of ethylene propylene rubber (EPR) nodules dispersed in the PP matrix at low to moderate rubber concentrations (it is possible that there is a sort of phase inversion that occurs at high rubber contents,[1] but that point is beyond the scope of the current work). Since EPR is highly soluble in most hydrocarbons, this second step is always done in the gas phase. Since the polymerisation step is highly exothermic, problems of agglomeration, fouling and eventually melt-down can be common in the gas phase polymerisation step – especially at high rubber contents, or under other conditions where EPR can be found on the surface of the particles. It is therefore extremely important to understand where the rubber phase is produced, how its distribution evolves during the reaction, and whether or we can control the arrival of rubber on the particle surface. Considerable knowledge of the morphological development of heterophasic copolymer such as impact grade polypropylene has most likely been gathered at the industrial level; however there are relatively few studies of hiPP morphology in the academic literature. Catalyst, product and process confidentiality are likely (some of the) reasons. We therefore decided to use different types of microscopy to investigate the evolution of the distribution of EPR inside the growing particles.

Experimental

The polymerisation procedure is the same as that described by Kittilsen and McKenna.[2] Briefly, the continuous two reactor process is replaced by a series of two semi-batch reactions in a spherical stainless steel reactor at 8 bars of monomer. In the first reaction, propylene monomer is polymerised in heptane slurry at 80° for different lengths of time (to obtain different

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PP particle sizes). The mixture is then degassed thoroughly, followed by a second gas phase polymerisation step. With the commercial Ziegler-Natta catalyst used here it is sufficient to fill the reactor with 8 bars of a monomer mixture containing 37 mol% ethylene, and then feed the reactor with a 50:50 molar mixture of ethylene and propylene in order to obtain an elastomeric copolymer with an equimolar composition.[3]

AFM analysis of the individual high impact polypropylene particles was performed as discussed by Bouzid et al.[4] The principle behind this nanomechanical analysis is to measure the snap-on and snap-off force (attractive and adhesive forces) between the AFM probe head and the surface of the polymer, as well as the spring constant (resistance to deformation) of the material as the probe head is pushed into the surface. This type of analysis allows us to easily differentiate zones covered by EPR from those where there is just PP. In addition, it is possible to use snap-on and snap-off forces to evaluate the mechanical properties of the EPR phase. Force measurements were obtained at room temperature, using a commercial atomic force microscopy (Thermomicroscope Explorer ECUPlus, Veeco Instrument S.A.S). The silicon nitride microlever from TM Microscopes (Veeco, Ref MLCT-EXMT-BF) had a spring constant of $0.5 \pm 10\%$ N/m according to the measurement on a cantilever of known force constant (Veeco, Ref CLFC-NOBO). Deflection-Piezo displacement curves were recorded in contact mode at the rate of $0.1\ \mu m \cdot s^{-1}$ on the micrometric region identified on an optical digital camera. Raw curves acquired by AFM consisted of voltage measured on the photodiode as a function of the piezo displacement.

Selective poisoning was performed in two ways: (1) an intermediate, slurry phase poisoning where the degassing stage between the two steps is interrupted half way through, and a poison is briefly mixed with the concentrated slurry (approximately 10 minutes at 1 bar absolute propylene). The mixture is then thoroughly degassed and the gas phase reaction begun; (2) a gas phase poisoning step where the reaction procedures as normal, expect that the poison is injected into the reactor at the beginning of the gas phase reaction.

Results and Discussion

Morphology and Rubber Distribution

Particles were first obtained by polymerising at 8 bars propylene and 80 °C in a heptane slurry, then at 8 bars total monomer at 70 °C for different times to add controlled amounts of EPR copolymer. Individual particles were randomly selected, embedded in resin then microtomed at low temperatures when examined with scanning electron microscopy (SEM), or simply cut with a scapel in liquid nitrogen for examination with atomic force microscopy (AFM – without embedding in resin). The evolution of the morphology of hiPP particles is shown as a function of the rubber content Figure 1. These (representative) images reveal at least two interesting points (N.B for the polymerisation conditions given above, and for the particular ZN catalyst system used in this work): (i) the rubber phase seems to form initially in the centre of the particles; (ii) it begins to form as identifiable, individual islets, or nodules that grow to form semi-continuous networks of rubber as the quantity of EPR increases. This first result, while unexpected, was confirmed by Bouzid et al.[4] in their study on the use of AFM to characterise the distribution of EPR in the PP particles.

Mechanical properties obtained with AFM measurements provide a real observation of polymer blends, and allow direct quantification of phase volume fractions and computation of domain interface of various morphologies. It is necessary to note that the compositional representation of the rubber will be made in a continuous mode. Note also that in the case where the surface under examination is not well defined enough to allow for the reconstruction of visual images (e.g. when poorly microtomed), force curve features can still be used to differentiate between EPR and

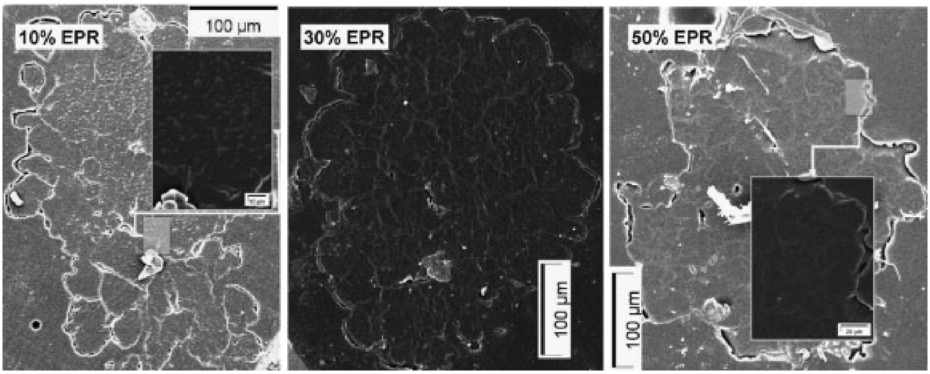

Figure 1.
SEM images of three individual hiPP particles with varying rubber contents (10, 30, 50% w/w total particle mass). EPR phase polymerised at 70 °C, 8bar total monomer. At 10% EPR, the rubber is present in nodules. These grow to touch each other and form a semi-continuous network by 30%. By 50% we can still distinguish the EPR network, but the rubber seems to cover most of the interface.

PP zones, and to know if the mechanical nature of the copolymer (e.g. higher/lower average molecular weight) is the same everywhere inside the particle. Another point of interest that can be estimated is the thickness of the layer of copolymer which covers the PP fragments.

Topographic AFM images of hiPP particles containing 10% rubber and 50% rubber are shown in Figure 2 (these images are taken from spots near the centre of cross sectional microtomed particles). The bright spots in the topographic images shown here represent the rubber phase and the darker areas the PP homopolymer. The graphs shown in this figure represent force-displacement curves for the AFM measurements (for more information on the meaning of these curves see Bouzid et al.[4]) Briefly, the microscope probe head is placed above the surface of the polymer and slowly lowered (this is the zone between 200 nm and close to zero). Here, no external force is exerted on the probe head and the slope of this force distance curve is of course zero. As the probe head gets close to the surface, it is attracted (more or less strongly) to the polymer. To simplify, it can be said that the probe head is pulled down to the surface. This is the snap-on force (indicated on the graphs for 50% rubber). The magnitude of the snap-on force is a function of the physical nature of the surface. It is close to zero for the semi-crystalline PP homopolymer, and quite measurable for the amorphous EPR as can be seen from this figure. The slope of the subsequent section (solid line) is the intrusion section – it represents the material resistance of the polymer surface to the probe head being pushed into it. The higher the slope of this force-displacement curve, the more resistant (less elastic) the surface is. PP will have a sharper slope than EPR – in fact the slope of this curve for PP homopolymer is very close to the spring constant of the probe given by the manufacturer of the AFM.[4] For the sake of clarity we have only included the intrusion curves on the graphs. There are analogous retraction curves and snap-off, or adhesive forces that have also been measured (cf. Figure 3).

It can be seen from the top section of Figure 2 that, for low EPR contents of 10% or less, the rubber domains are well defined, and interspersed in a continuous PP matrix just as was shown in the SEM images in Figure 1.

If we consider the upper of the 2 graphs for the 10% Rubber particle (the graph corresponding to the measurement made in the rubber nodule), we can see three

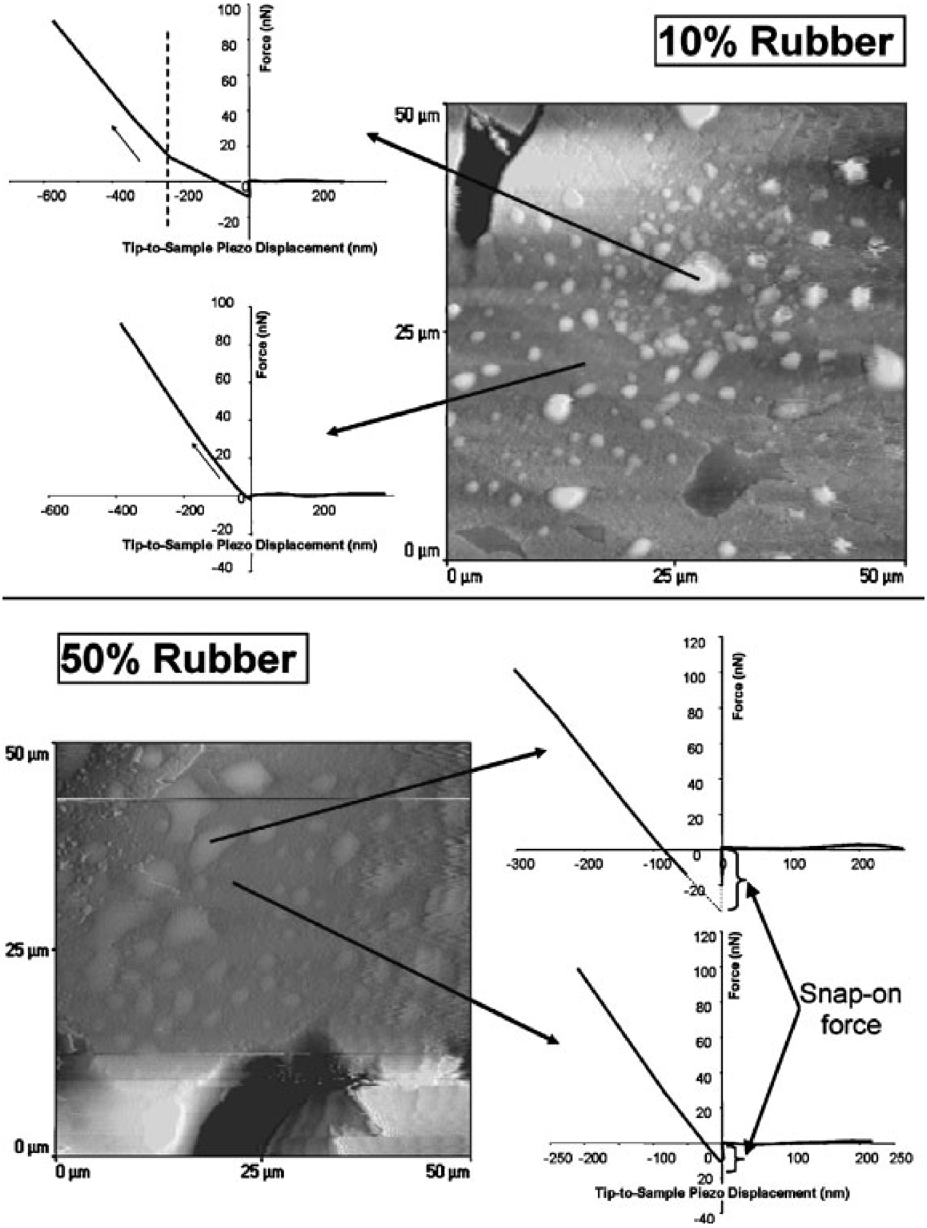

Figure 2.
AFM images of the cross section of an hiPP particle containing 10% EPR (top) and 50% EPR (bottom) by total weight. The white spots correspond to EPR phase, and the darker areas to PP homopolymer. The direction of the arrows on the top figure represent the direction of the displacement of the microscope probe with respect to the surface being examined. Solid curves are intrusion measurements and dotted lines are retraction measurements.

well-defined zones. At the particle surface, there is a clearly measurable snap-on force, showing that we are probing an EPR domain. Subsequently the intrusion curve shows two straight sections with different slopes; the first section having a much lower slope than the second. This indicates that the rubber nodule at the point of measure-

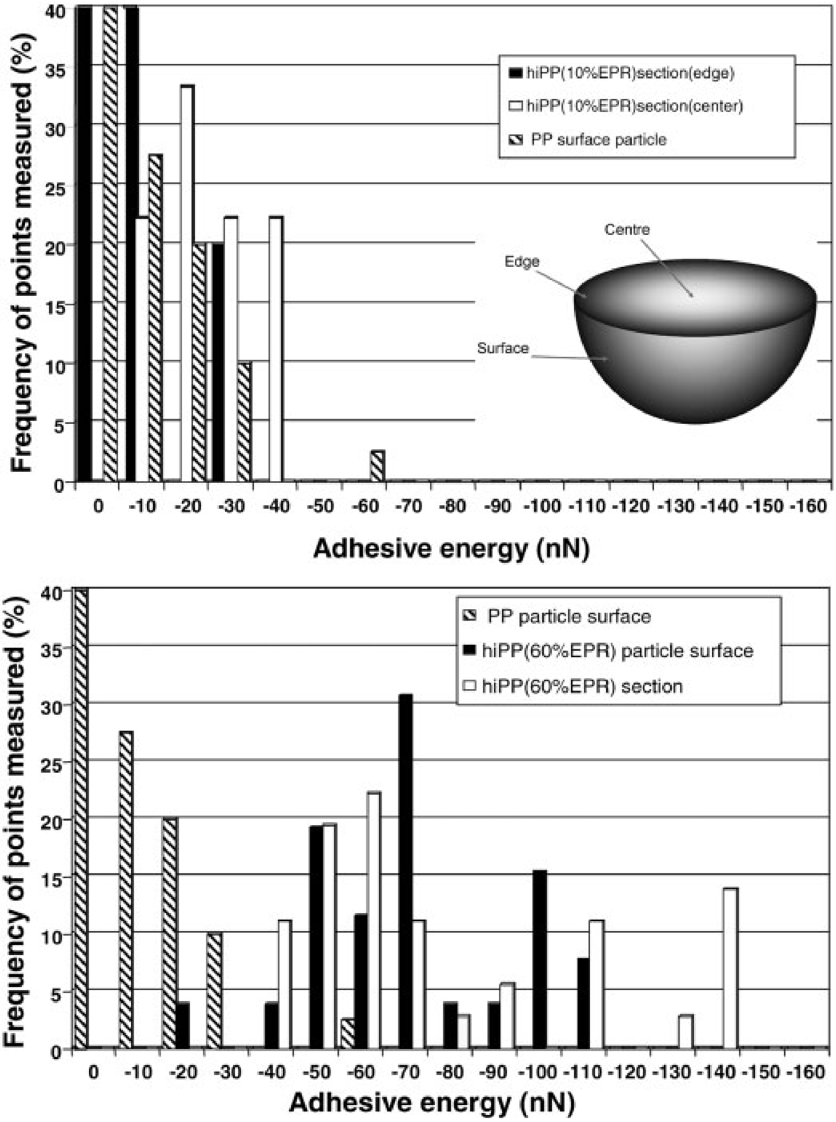

Figure 3.

Distribution of adhesive energy for a series of measurements in tapping mode on PP homopolymer particles and at different points near the surface and the centre of a cross sectional cut of hiPP particles with 10% EPR and 60% EPR (top and bottom respectively).

ment is around 250 nm thick. The lower slope of the first section between 0–250 nm shows that we are indeed ‘‘pushing’’ into a rubber domain. However beyond this limit, the probe head encounters a much stiffer material – most likely PP homopolymer. Indeed, if we compare the slope of this third section with that of the intrusion curve of the material between the nodules, it can be seen that the two are identical in terms of their mechanical resistance. Finally, in the second graph of the 10% rubber image, we can also see that there is essentially no interaction between the probe head and the surface in terms of a snap-on force. As was indicated in early work, this is entirely indicative of polypropylene homopolymer.[4]

If we consider the bottom half of Figure 2, it can be seen that rubber nodules and the interstices between the clearly defined nodules both exhibit the same mechanical resistance (slope of the intrusion curve) and both show a measurable snap-on force. The slopes of the intrusion curves are the same as those of the well-defined rubber nodule at 10%. These observations also strongly support the interpretation of the SEM images offered above: that the EPR begins to form a semi-continuous network at high rubber contents.

As shown in Figure 3, the distribution of the histograms of adhesive (snap-off) force measured at different spots (on the surface, near the edge and in the centre of cross sectional slices) in individual particles depends greatly on where the measurements were made and on the quantity of rubber in the particles. Note that to gather this data a significant number of different measurements were made in each zone. If we compare the adhesive forces at the surface of an hiPP particle with 10% rubber to those of a PP homopolymer, the difference is minimal – in other words if the snap-off forces are similar that means that the physical nature of the surfaces are similar. It can be seen from the top part of this figure that the centre of the particles with 10% rubber is slightly stickier in spots, but in others it is identical to the PP homopolymer. This confirms that the rubber nodules are well isolated as ‘‘islets’’ in a PP ‘‘sea’’. If we compare the adhesive forces of a particle containing 60% EPR to those of a homopolymer, it can be seen that there is a big difference (as one would expect). However, it is interesting to note that no isolated domains of PP were found anywhere on the surface or on the cross-section. In other words, the rubber seems to have spread pretty much everywhere within the particle (although it does appear to be more concentrated in some spots than others). These observations once again reinforce the interpretation of the SEM images in Figure 1.

Furthermore, the bottom graph in Figure 3 suggests that the distribution of adhesive forces is different in the centre of the particle, and at the edge. This supposition is confirmed by the results shown in Figure 4. The two force displacement curves shown in this picture were measured on separate rubber nodules in a cross

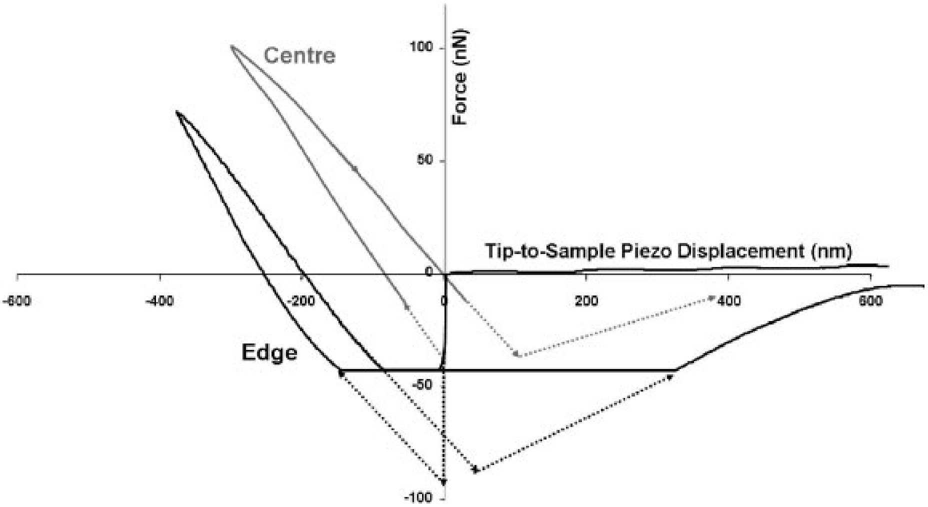

Figure 4.
Force-displacement curves two rubber nodules in an hiPP particle containing 50% rubber by total mass. The nodules were located in a cross-sectional cut of the particle, one near the centre, and one closer to the edge.

sectional cut of a particle containing 50% rubber by total mass. One nodule was located near the edge of the particle, the other nearer the centre.

Since there is no observable change in slope of the intrusion curves, and since the slope has roughly the same value as that measured for the EPR regions in Figure 2, we can be fairly certain that we are measuring the physical properties of EPR rich zones (N.B. it is not unusual to see hysteresis between the intrusion and retraction curves, most likely due to the adhesion of the tip to the material). However, the snap-on and snap-off forces of the two sets of measurements are quite different. This, along with the data shown in Figure 3 suggest that as the rubber accumulates in the particles one can find rubber domains with different properties at different spots inside the particles. This last point needs to be explored in more detail, but might be attributable to:

- Change (drift) in the reactivity ratios of the active sites as a function of time.
- A spatial distribution of types of active sites.
- Concentration gradients in the particle that provoke a composition distribution in the rubbery phase.

While it is not entirely surprising that the rubber formed near the centre and at the surface might have different mechanical properties for the reasons cited above, it remains somewhat counter intuitive that rubber nodules would accumulate first in the centre, then at the edges of the particles. A partial explanation for this fact might also be attributable to a spatial distribution of active sites. Let us consider a polymer particle produced with a spherical supported catalyst particle having a perfectly uniform distribution of active sites per unit volume. If the outer portions of this particle fragment first and grow faster during the initial homopolymerisation step, then it is entirely possible that the number of sites per unit volume of particle would be higher near the centre than the exterior when the particle is injected into the copolymerisation phase of the process. In this event, even if all of the sites polymerised at the same rate, there would be a higher concentration of rubber molecules nearer the centre. If these molecules are produced relatively close to each other then surface tension would incite them to form a separate phase (i.e. nodules) at the centre before this happened at the edge of the particles.

Of course, this explanation remains purely conjectural for the moment as more work is needed in terms of looking at the influence of the PSD, reaction and fragmentation conditions (in addition to perhaps refining the analysis of mechanical properties with the AFM probe).

Surface Modification: Selective Poisoning

As mentioned earlier, one of the major difficulties encountered when making hiPP is the stickiness of the powder, which increases as the rubber content of the final particles increases. The reason for this is the accumulation of the rubber on the surface of the particles, most likely through a dual mechanism of production of rubber by active sites near the surface, followed by an eventual diffusion of rubber from the inner confines of the particles, through the pores to the surface. Nevertheless, at low to moderate rubber contents of (10–35% w/w), the active sites near the particle surface are certainly the principal causes of the presence of the EPR layer covering hiPP particles. As we saw above, rubber begins to accumulate more and more at the surface as the EPR phase continues. The question remains is there is some sort of migration of rubber from the centre to the surface, or is the rubber found at the surface only produced there. In order to study this, we developed a procedure to kill the existing catalytic sites on the particles surfaces.[5,6] To perform selective poisoning of the catalytic sites on the surface without adversely influencing the overall kinetics pushes us to look for a large molecule. Ethylene glycol dimethyl ether (Glym) was found to possess the properties susceptible to allow us to achieve this goal, yet to attain

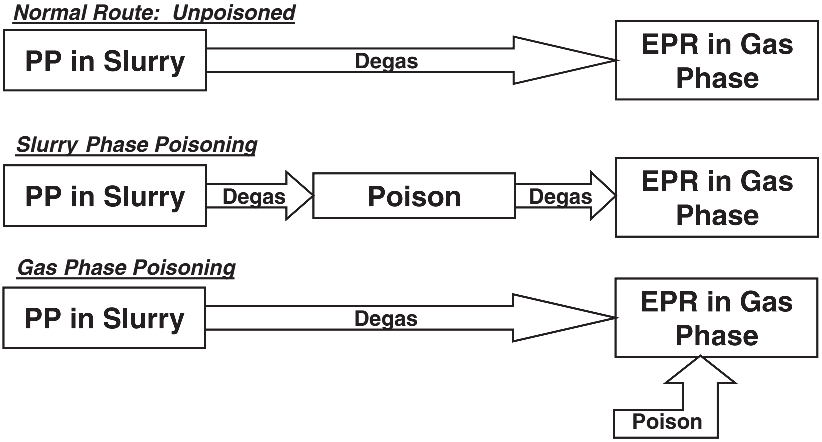

Figure 5.
Different routes used to selectively poison particles during hiPP production.

a final polymerisation where the overall kinetics remains relatively unchanged (with respect to unpoisoned systems). A second, proprietary antistatic agent (CASA for Commercial AntiStatic Agent) was also found to work well. Since the results of the selective poisoning study have been published elsewhere,[4] we will only briefly review the concepts involved and cite an example of how the poisoning study elucidates aspects related to particle morphology. The different routes used to selectively poison the surface of the active PP polymer/catalyst complexes are illustrated in Figure 5. Both Glym and CASA were used in identical fashions, and injected under the conditions described in the experimental section above.

It can be seen from Figure 6 that the different routes used to selectively poison

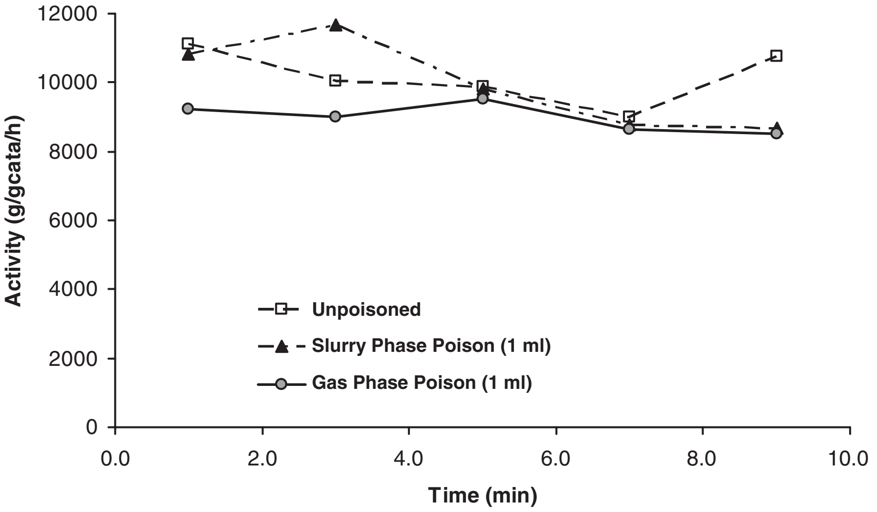

Figure 6.
Polymerisation rates of an ethylene-propylene copolymerisation step at 3 bars ethylene, 5 bars propylene, 70 °C with different poisoining routes: none, slurry and gas phase. EPR content 50% with respect to total mass at 9 minutes.

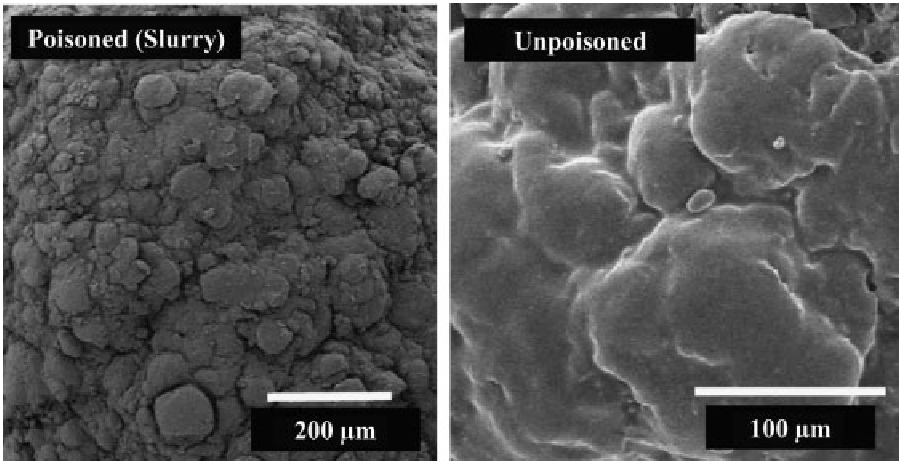

Figure 7.
Close-up SEM images of the surface of a slurry-poisoned hiPP particle (left) and an unpoisoned particle (right). Both particles were polymerized under identical conditions and contain 50% EPR by total particle weight.

the active catalysts did not influence the copolymerisation kinetics in any noticeable manner, however the close-up SEM images shown in Figure 7 show very clearly that the selective poisoning step stops the formation (and accumulation) of rubber on the surface of the particles for EPR contents as high as 50%. In other words, it should be clear from these images that the rubber that is found on the surface of the particles is polymerised there, and that it does not flow from the inside to the outside of the PP matrix while it is being produced - at least in the specific cases studied here.

Conclusions

The study presented in the current paper builds on previously published results to show how the EPR phase of a high impact polypropylene ‘‘block copolymer’’ evolves as a function of time. Counter intuitively, the rubber seems to form first in the centre of the particles in the form of well-defined nodules, and then to spread outward to the surface of the particles as the EPR content increases. As the amount of rubber in the particle increases, the EPR spreads out until it is found to have penetrated the entire PP homopolymer matrix issued from the first step of the reaction. These conclusions are strongly supported by both SEM and AFM investigations. Furthermore, selective poisoning studies (intended to improve the flowability of the product) reveal that no noticeable amounts of rubber are found on the surface of poisoned particles (regardless of how the poisoning step takes place). This indicates that for rubber contents of up to 50%, no bulk movement of the EPR phase takes place inside the particle. Any rubber found at a given spot is therefore likely to have been produced there.

While these results are quite interesting, it is clear that more work needs to be done. First of all, one needs to be aware of the fact that the conclusions drawn here obviously depend to a large extent on the morphology of the initial PP product (which in turn is a complex issue), and therefore on the catalyst and polymerisation process used here. It is entirely possible that altering the catalyst, and therefore PP morphology will cause different behaviour in other systems. For example, the PP produced on the ZN catalyst used here was relatively porous (bulk densities of around 0.4 g/cm^3). If the PP matrix were significantly less porous, it is possible that the hydraulic forces generated inside the particle would cause the rubber to flow out. Additionally, we have also shown in a companion paperm[3] that hydrogen provokes more ‘‘pooling’’ of

EPR on the particle surface, likely due to the much lower molecular weights. It would therefore be of use to continue with studies such as the one presented here, and include the viscosity of the rubber phase as a controlled variable.

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