DEVELOPMENTS IN POLYPROPYLENE FOR ROTOMOLDING

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Abstract

The position of polypropylene (PP) as a material for rotational molding is reviewed and a general specification is proposed for a suitable rotomolding grade. Attempts to achieve an improvement in the impact strength of PP, by formulation with impact modifiers, are described and the effects on other physical properties of such modifications are highlighted. A novel approach to improving the impact strength of PP is introduced, which utilizes a two-layer technique. Initial results from testing two-layer structures look promising.

Introduction

The history of rotomolding over the last three decades has been characterized by strong growth, fuelled by the inherent design flexibility of the method, innovative process developments and a steady supply of new applications. Rapid growth is continuing in new markets such as Eastern Europe, Latin America and the Far East. However, on-going growth in mature markets, like Europe and North America, will depend on new applications for the process continuing to be established.

Another characteristic of rotomolding is the limited range of polymer types that can be used to produce a successful part. During the process, virtually no shear is imposed on the polymer melt and relatively few polymers have suitable rheological characteristics to enable them to sinter and flow successfully under zero shear conditions. An additional factor is the harsh environment that the polymer must withstand during the process, with relatively long cycle times compared to, say, injection molding or blow molding.

Polyethylene (PE) has long been the predominant polymer used in rotomolding, due to its ease of processing and its optimum balance between stiffness and toughness. The various forms of polyethylene account for over 95% of the materials used in rotomolding. Other polymers in current use include polyvinyl chloride, polycarbonate, polyamide (often known as “nylon”), polyoxymethylene (often known as “acetal”) and polypropylene.

This paper describes a long-term development project, conducted at Matrix Polymers, to evaluate possible options for the use of polypropylene in rotomolding.

The Need for Rotomoldable Polypropylene

Linear medium density polyethylene (LMDPE) is an excellent rotomolding material and deserves its pre-eminent place in the selection of materials for the process. However, LMDPE has its limits and product designers and end-users often call for rotomouldable materials that have properties that are different to PE.

Recently a market research exercise[1] was conducted across a wide spread of European rotational molders using conjoint or “trade-off” analysis[2]. This survey indicated significant demand for a material with the following general characteristics:

Table I: Product Requirements	
Stiffness and hardness	Significantly greater than LMDPE
Impact strength	At least 30% of LMDPE at room temperature
Operating temperature	90 – 110 °C (continuous)
Acceptable processing characteristics	Moderately difficult compared to LMDPE
Maximum price	£5 / kg (US$4 / lb)

The last requirement, which is commercial and not technical, tends to be the most restrictive parameter to finding suitable candidate materials. For example, a rotomolding grade of the material polyamide 12 is available that surpasses all of the technical criteria given above. However, this material has a very high unit price and its applications are confined to specific market niches. There is no doubt that, for widespread adoption, a polymer is required that meets the technical requirements specified above but can be purchased at a more moderate unit price, albeit significantly higher than PE.

Of all the polymer types currently available, polypropylene (PP) appears to have the most promise to provide the vehicle for significant expansion of the roto market. A few grades are available commercially, but as yet no supplier has offered the industry anything with sufficiently good technical properties to make a significant breakthrough.

Issues with Polypropylene

Grades of PP currently offered to the rotomolding industry, on both sides of the Atlantic, all share the same significant defect - they are extremely brittle. This is the case even at room temperature conditions and, as a result, impact strength is very poor. Typically a 3mm thick sample plaque will have no measurable impact strength when subject to the standard industry impact test, the ARM Drop Dart Test[3]. To pass the impact strength criterion showed in Table 1, a candidate material would need an impact strength of at least 30J.

One practical problem is that the standard ARM Drop Test, even at its lowest height setting, delivers an impact energy significantly in excess of what currently available polypropylene grades can provide. Therefore this test cannot be used as a research tool to differentiate between candidate materials. In response to this difficulty, a Low Energy Drop Dart test was developed; this has been reported elsewhere[4].

The key reason for the brittleness of PP is related to its glass transition temperature, T_g. This property represents the temperature at which the molecules in the amorphous

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[1] Matrix Polymers, Internal document, 2004.

[2] Crawford,M. & Di Benedetto, A., New Products Management, Ch. 7, 135 – 152, McGraw Hill Irwin, (2003).

[3] Association of Rotational Molders International, Low Temperature Impact Test Method.

[4] Henwood, N.G., Proc., ARM 28th Spring Meeting, (2005).

phase have very low mobility. At temperatures near T_g the material assumes a glass-like state and is unable to undergo plastic deformation. In these circumstances it will be brittle.

Homopolymer PP has a T_g at around minus 5 ºC, so at room temperature the material is near to its T_g and has a tendency to be brittle. In comparison, the T_g of PE is around minus 85 ºC, which is far below normal service conditions. This is the reason for the observed ductility of PE materials[5].

Impact modified grades of PP (see next section) have values of T_g that are lower than standard homopolymer PP, down to minus 20 ºC.

It should be noted that, in addition to poor impact strength, currently available grades of PP have some other disadvantages when compared to PE. Firstly, PP is more sensitive to heat degradation than PE; therefore PP grades need more powerful (ie more expensive) stabilization packages to make them suitable for rotomolding. Secondly, PP is more difficult to pulverize into a fine powder than PE; ambient grinding can be too slow to be economical and cryogenic grinding is usually required. Finally, rotomolders who use currently available grades of PP generally report a range of molding difficulties and higher scrap rates than when using PE.

Despite all of the above difficulties, PP has been used successfully to supply some niche roto applications. The barrier to wider application usually comes back to its brittleness and poor impact strength.

Impact Modification of Polypropylene

Large amounts of PP are used in processes such as injection molding for the production of durable, impact resistant products. The grades of PP used in these applications are invariably versions of standard PP that have been *impact modified* by the addition of more flexible minority component. If this is effective for injection molding, then clearly there must be a case for trying the same technique for rotomolding.

The additional component can be introduced directly into the polymer chain during the polymerization process (ie within the reactor). Alternatively, it can be introduced post-reactor by compounding a flexible minority component into the surrounding PP.

A major program of research and product development is underway at Matrix Polymers to assess whether it is possible to produce an impact modified grade of PP that can be satisfactorily rotomoulded.

It was decided that testing a large number of candidate reactor grades and extruder blends by rotomolding would be too time consuming and that progress would be unacceptably slow. Therefore a test protocol was developed to screen candidates for physical properties and for processability using small scale evaluation techniques based around solid state and melt phase rheometry. In this way a large number of possible reactor grades and compound blends could be evaluated and only promising performers would be progressed to testing by rotomolding. Most of the results of this work are proprietary and the program is, of necessity, long term. However, we have been able to draw several general conclusions so far:

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[5] Cowie, J.M.G., *Polymers: Chemistry & Physics of Modern Materials*, 262, Stanley Thomas (Publishers) Ltd., (1991).

- The majority of reactor impact modified PP grades we have tested have proved to have unsuitable rheological characteristics and could not be rotomolded.
- Impact modification via extruder blending can raise the impact strength substantially, whilst retaining moldability. So far, we have managed to increase the impact strength to approx 10J, from a figure for standard grades that is essentially zero. For some applications, this can make the product sufficiently viable to be used, although clearly it is still well below the general level specified by market research (ie 30J).
- Successful impact modification will lower T_g but this will cause a corresponding reduction in the other desirable properties of the PP.

The final point is especially significant, since it represents a likely overall restriction on the options that can be formulated. In effect, there seems to be a direct trade-off between improving impact properties and simultaneously retaining other desirable properties, such as tensile strength, stiffness and temperature resistance. This is illustrated in Figure 1, which compares the impact strength at room temperature and tensile strength at yield for four different PP formulations. The trend is clearly observed that, as improved impact strength is achieved, tensile strength decreases.

Our program is ongoing and we do believe that it will be possible to produce PP grades with tailored combinations of properties for specific rotomolding applications. However, the “holy grail” of an impact-modified grade with universal applicability to rotomolding still seems a rather remote possibility. In particular, an impact strength of 30J at Room Temperature remains a very challenging goal.

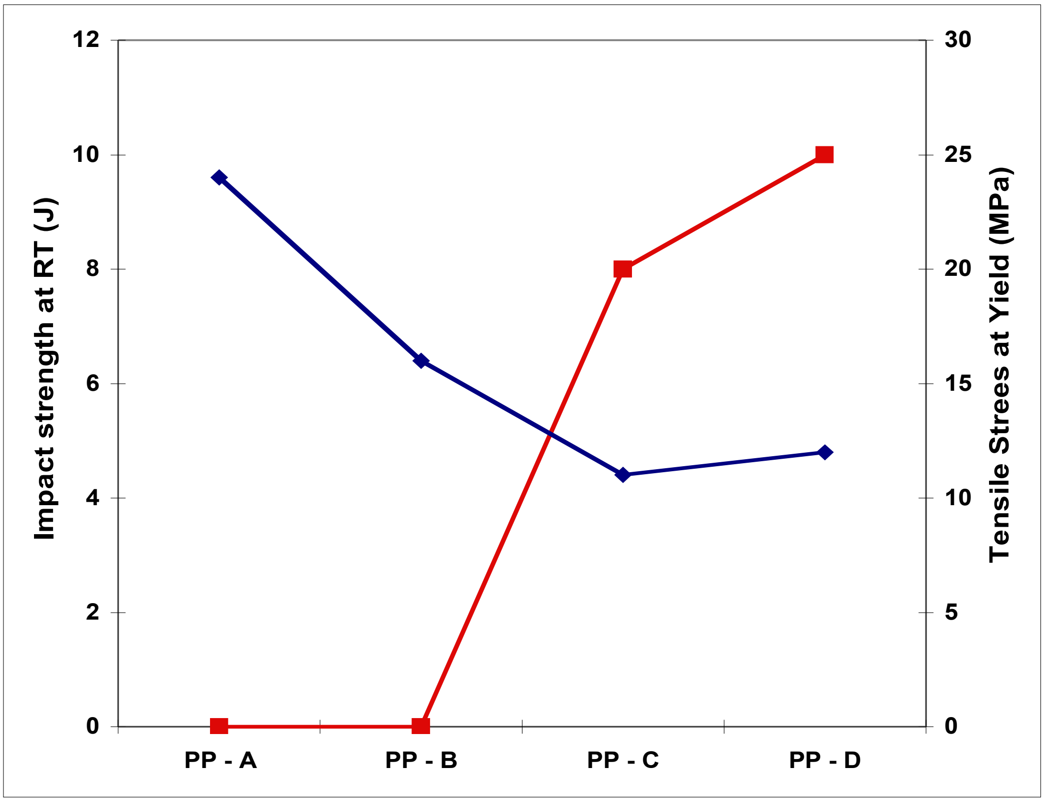

Figure 1: Effects of Impact Modification on Tensile Properties of PP

The EXPLORE® CT Concept

We have acknowledged significant difficulty in finding an optimum balance of performance and processability in an impact modified grade of PP and, whilst we are still positive about improvements in the long term, the rotomolding industry is interested in solutions today. We need an alternative strategic approach to the problem.

One possible strategy is to use PP, to deliver the required properties of stiffness, hardness and heat resistance, in conjunction with a *second* layer of material that will provide an impact strength that is generally acceptable.

The use of two-layer technology in rotomolding is well established for producing articles with an outer skin of standard PE and an inner layer of foamable PE. More recently, applications have been reported[6] (for motorcycle fuel tanks) that incorporate a polyamide 12 outer skin with a layer of modified polyolefin material (MPO) to provide impact resistance at low temperatures.

Matrix Polymers offer such two-layer structures as the *EXPLORE® CT* product family. The principle by which these systems operate is quite simple (see Figure 2). When a molded part sustains a heavy impact, the energy of impact travels through the wall thickness and the rear face of the part is caused to fail by stretching and the initiation of micro-cracks. These micro-cracks propagate backwards into the thickness of the material and, if the impact is of sufficiently high energy, the part fails. Therefore it would seem logical that, by backing a fragile material with a much tougher material, the impact energy will be absorbed by the rear layer and micro-cracks will not form and will not propagate. This principle has been demonstrated to be extremely effective if a correctly designed two-layer structure is used.

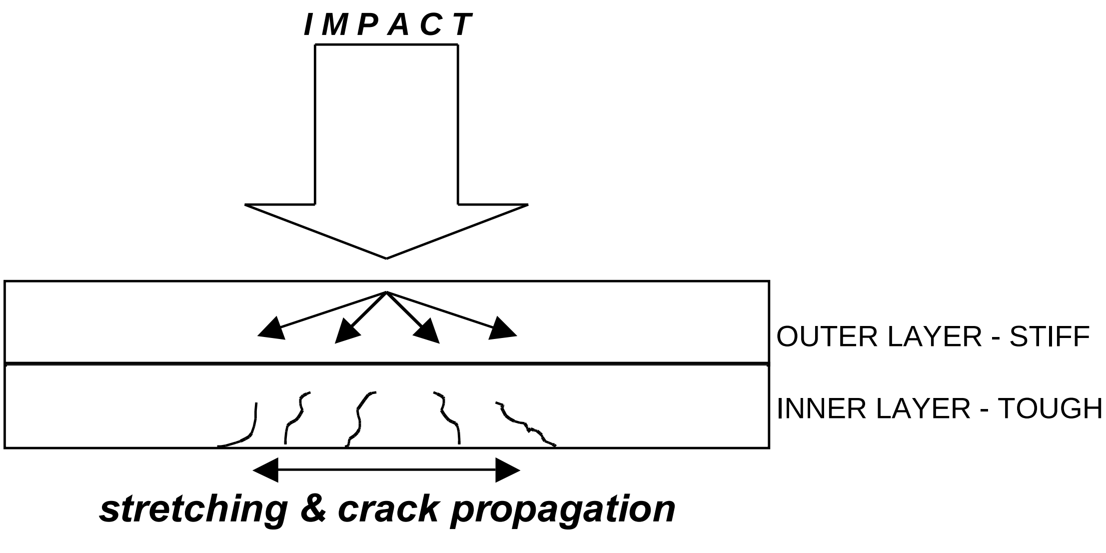

Figure 2: How EXPLORE® CT Works

[6] Henwood N.G., Rotation, Jan - Feb, 32 - 33, (2003).

Therefore the EXPLORE® CT principle has the potential to incorporate relatively fragile materials into structures that provide acceptable overall impact strength. However, the success of such a structure depends critically on two additional elements.

The bond between the two layers must be extremely efficient; otherwise the structure will not behave as one entity. De-lamination of the layers will occur on impact and the more fragile material will be unprotected by its backing layer, resulting in failure. Bonding polyolefins to each other, or to other substrates, is inherently difficult and requires some very precise chemical and physical formulation.

A similar type of behaviour has been observed if the outer layer is so brittle that it cannot transmit the energy of impact to the backing layer without failure. In this case, the outer layer will crack on its own, even though the backing material retains its integrity.

Both of the above effects were observed in early attempts to create EXPLORE® CT structures with PP.

Two-layer Systems for Polypropylene

Following extensive research, several structures comprising an impact modified PP backed by a flexible modified polyolefin material (MPO) have been developed that can withstand significant impact and can retain structural integrity.

Figure 3 compares the impact performance at room temperature conditions. The enhanced performance of the EXPLORE® CT structure can be observed, especially at increased wall thickness. Even at 6 mm thickness, the impact strength is far in excess of the market-derived target of 30J.

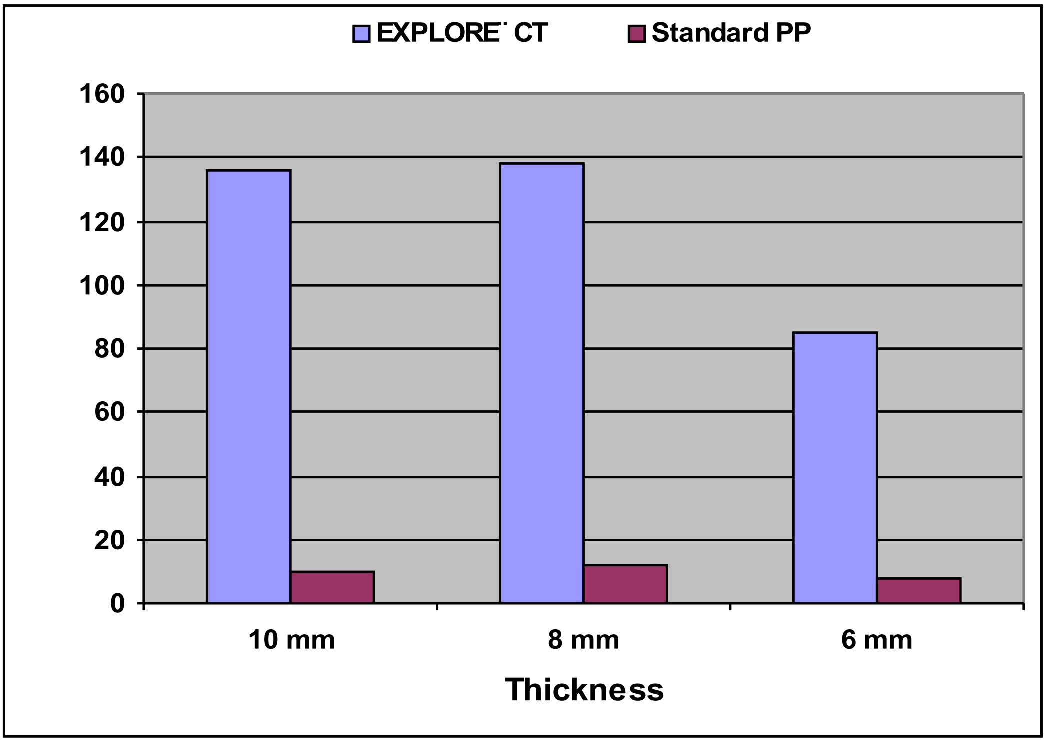

Figure 3: Improved Impact Strength using Two-Layer Structure

Long term testing of this optimised double layer structure is now underway to validate its resistance to high operating temperatures. Initial results look promising; the structure retains the high temperature resistance, stiffness and exterior scratch resistance of PP whilst exhibiting excellent low temperature resistance and toughness. In effect, the PP acts as an ecto-skeleton to the inside layer.

Figure 4 shows the high temperature test rig that has been built to carry out these evaluations. Hot oil (or other thermal fluid) is pumped around a circuit that includes the specimen tank, in order to maintain a constant pre-set internal temperature.

Full-scale industrial molding and life-in-service service trials are also underway at a number of European molding customers.

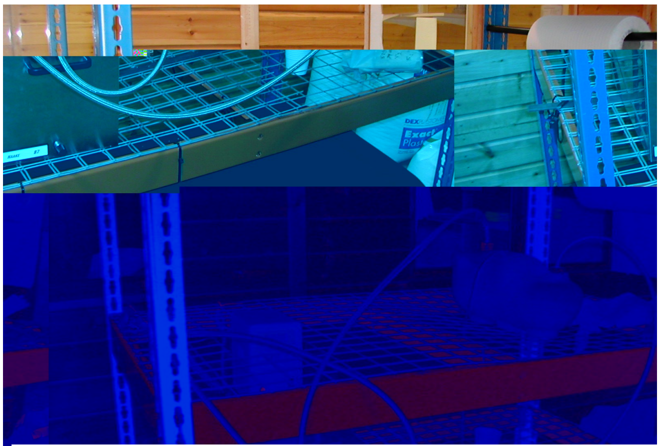

Figure 4: High Temperature Test Rig

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Conclusions

There is a clear need for new rotomolding materials that will sustain the growth of the rotomolding market. Polypropylene appears to hold potential as a material that could contribute to the future or rotomolding, provided that its impact strength can be improved.

Impact modification of polypropylene, as practised for injection molding grades, can improve the impact strength but at the cost of a reduction in other desirable properties. More investigation is required to establish whether it is possible to achieve a satisfactory balance between properties.

Two-layer systems, using an exterior "ecto-skeleton" of polypropylene with an inner layer of a more flexible material, hold considerable promise as an immediate solution to the needs of the rotomolding market. Further optimisation of such structures is proceeding.