DEFECTS IN POLYMER MATERIALS AS DESIGN PROCESS CONSEQUENCE

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1. Introduction
Consumer interest is always focused on properties of some materials or final articles. There is an eternal need for better materials and better products. But, the properties of any material or product are a response of its structure to external conditions. Properties of polymers are processing-sensitive. Thermoplastic polymers form their final structure and morphological order after their processing. Thermosetting polymer processing includes always a chemical reaction as the final stage of polymerisation. Furthermore, thermoset resins are very rigid, inflexible and brittle, so they have to be reinforced. Most of these materials are composites.
In both cases, the final product properties are strongly affected by structure designing (processing) and product design.
The paper deals with investigation of the structure of commercial materials and products in an attempt to explain their failure in use.

2. Thermoplastic polymers
By their structure polymers, even the crystalline ones, are heterogeneous. This fact is very important, because the crystallinity of a material has a significant influence on its properties and cannot be neglected. Primarily the amorphous mediate the mechanical response of the material. To detect possible defects resulting from processing, the polybutene pipe was analysed by optical polarizing microscope. Polybutene is the commercial name of the semi crystalline thermoplastic resin based on high-molecular isotactic poly(1-butene) homopolymer and copolymer. Due to polybutene properties, specifically its excellent flexibility and resistance to creep, environmental stress cracking, chemicals and wet abrasion, the pipe was its first important application and remains to this day its dominant end-use.
Depending upon conditions five crystalline forms of poly (1-butene) have been reported [Rubin, 1990]. In conventional melt processing, crystallisation of the resin initially produces the metastable form II, which transforms to the stable form I over a period of 5 to 7 days at the ambient temperature and pressure. During the transformation, density, crystallinity, hardness, rigidity, stiffness and tensile yield strength all increase to values characteristic for form I. After fabrication and transformation to form I, these resins show crystallinity of 48 % to 55 % and density of 0,93 to 0,94 g/cm³.
This polymorphic transformation after melt processing could be one of potential disadvantages of polybutene. As the consequence of fabrication conditions or defects, inadequate local distributions of crystalline and amorphous regions may occur. This leads to a different mechanical response of these
regions in the tested pipe. Using the optical polarizing microscope the morphology of polybutene pipe was analysed to explain failure of pipes.

![Figure 1. Different distribution of morphological order in polybutene pipe (polarizing optical microscope, magnification 400x)](image)

**Figure 1. Different distribution of morphological order in polybutene pipe**

- left: higher morphological order (tough failure)
- right: lower morphological order (brittle failure)

Figure 1 shows different distribution of morphological order of the observed pipe. This local microstructural disorder affected strongly the behavior such as transition of tough to brittle failure. In the higher ordered regions (fig.1, left), due to stronger inter- and intramolecular forces, propagation of defects (crazes, cracks) in submolecular interfaces occurs. This leads to a higher plastic deformation before failure and eventually to a tough crack. However, the increase of amorphous region (fig.1 right) influences widely transition of tough to brittle failure.

### 3. Polymer composites

Even more complex are polymer composites. By definition, the composites generally are complex materials made of minimum two components [ISO 472, 1999]. Composite properties differ from those of basic components (matrix and fibres), but depend strongly on components composition and structure, as well as on their interaction. It is increasingly being recognised that the interface region between fibre and matrix and the fibre distribution play an important role in defining composite properties. The fibre distribution very strong indicates mechanical response of composite.

![Figure 2. GR PBT connector A- analysed area](image)
Processing of various components to the final composite article can affect strongly its properties. Therefore, one critical section of glass-reinforced poly(buthylene therephtalate) (GR PBT) (fig. 2) connector, was investigated by using the optical polarizing microscope to determine short glass reinforcement distribution due to manufacturing conditions. In fig. 2, the “bleaching” of mechanically loaded connector section surface is visible, that indicates a considerable plastic deformation. Upon unloading, no elastic return is possible, that is essential feature for this connector section functioning. To obtain necessary information, the adequate microtomic cross-sections have been prepared.

Figure 3.a     Figure 3.b

**Figure 3. Morphological order of GR PBT connector**
**(polarizing optical microscope, magnification 400)**

Two reasons for failure were detected. The first one is the consequence of improper structure design. Figures 3.a and 3.b show very narrow area with only few fibers perpendicular to cross-section plane. Going from the connector edge there are more and more fibers that follow connector contour. On figure 3.b fibers discontinuities are visible which could be starting points for deformation and/or crazing and finally cracking. This wide edge area with unfavorable fiber orientation and very low fiber content is not reinforced properly. This can be explained by the fact that because of flowing during injection moulding (the process used to make this connector) as a rule the short glass fibers are oriented perpendicularly to the flow direction. In addition, the fiber orientation depends upon the shape of product, its wall thickness, process conditions, etc. In the connector subsurface layer the fiber orientation perpendicular to the observation plane has been noticed. It means that in the area loaded most during the connector exploitation, the reinforcement practically is not in function. Consequently, if the subsurface layer is thicker, the mechanical properties will be weaker, namely plastic deformation, crazings and eventually crack widening inside the investigated connector part will occur. The second one is connected with an inadequate shape design of the investigated part. The radius of the notch in all cases of failure has been found to be too small or not rounded at all.

3.1 Void content

By their heterogeneous nature (the heterogeneity due to chemical diversity of components) the polymer composites, even advanced ones, have voids that can be reduced only to a minimum. Voids are the result of polymer composite designing process. The increased interest in the use of composite materials in primary structural applications has resulted in attention being focused also on the role of defects, in particular voids, on the decrease of performance of these composites. In fibre-reinforced polymer composites these voids have been shown to reduce mechanical properties such as interlaminar shear strength, longitudinal and transverse strength and modulus, and fatigue resistance [Thomason, 1995]. Voids can be found in the composites in a variety of shapes and sizes (figure 4).
There are two principal causes for initial void formation [Thomason, 1995]. The first is the air entrapment in the composite during the initial manufacturing stage, due either to air bubbles being trapped in viscous resin during their preparation or to poor wetting of the fibres. Secondly, voids may be formed by volatile components or contaminants, which vaporize during the high-temperature part of the composite curing cycle.

Figure 4. Voids in tested composites (optical polarizing microscope, magnification 400 x)

Therefore, control and measurement of the void content have an important role in predicting the composite behaviour, because of its great influence on composite mechanical and water-absorption properties. In order to estimate void content, two composite materials based on the same polymer matrix with different type of glass reinforcement (mat, mat/roving) were investigated [Španiček, 1998].

Composite A: 34.13 % wt mat glass-reinforcement
Composite B: 45.38 % wt mat/roving glass-reinforcement
Matrix: unsaturated polyester resin based on orthopthalic acid type Colpoly 7725, cured for 28 minute at 20°C with styrene and 1.5 % catalyst MEK P 50, and then tempered for 16 hours at 40°C

<table>
<thead>
<tr>
<th>Table 1. Void content and mechanical properties of tested composites</th>
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<tr>
<td>Void content</td>
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<tr>
<td>Vv %</td>
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<tr>
<td>composite A</td>
</tr>
<tr>
<td>2.05</td>
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<tr>
<td>after wetting</td>
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<tr>
<td>composite B</td>
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<tr>
<td>1.25</td>
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<td>after wetting</td>
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The void content was obtained on dry and wet composite. The void content measurement requires the determination of the fibre density ρf, the composite density ρc, the resin density ρm, the weight of the sample wc and the weight of fibres in the sample wt. The density measurements were carried out by the standard density method to ASTM D-2734 using a minimum of five samples from each composite. Mechanical testing was carried out by standard method (ISO 178-1993 for bending strength and modulus, and BS 2 782 for interlaminar shear strength). The results are given in table 1. Differences obtained for mechanical properties are certainly, in first approximation, due to different type and quantity of reinforcement. The void content strongly affected all mechanical properties,
because voids can act as stress concentrators, which weaken the composite. Furthermore, voids reduce
the interlaminar shear strength because at such points bonding is lacking.
As voids affect strongly absorption of any media, the mechanical properties were determined after
immersion in distillate water at room temperatures for 28 days. The action of water must always be
taken into account, because of permanent presence of moisture due to the humidity of the atmosphere.
Immersing samples in water is the worst possible moisture attack. Leaving specimens in the humid air
results in lower moisture content. As expected due to void content, the composite A has absorbed
larger amount of water (0,82 %) than the composite B (0,58 %)(figure 5).

![Figure 5. Water absorption of tested composites
Immersion in water for 28 days at the room temperature](image)

Water absorption takes place because of microcapillary areas in interfacial regions as the result of an
inadequate matrix-fibres bonding or delamination [Španiček, 1998]. But, the major factor influencing
water uptake in tested composites was found to be void content. The literature data [Thomason, 1995]
suggest that the voids could have diffusivity 15 times higher then that of polymer matrix (for the
epoxy resin matrix, that has higher chemical resistance than the polyester resin). Enclosed voids will
provide sites for storage of water at much higher concentration then in the resin. Therefore, the
composite water content cannot be compared directly with the resin water content, since the fibres do
not absorb water and the absorbed water is concentrated within matrix phase.

4. Conclusions
The structure of both, the polymer and the polymer composites, being generally processing-depending,
their properties are affected strongly by structure and shape design. Consequently, the occurrence of
possible defects in final products always must be taken into account. By carefully selected processing
conditions, especially melt flow and cooling, proper morphological order in thermoplastic polymer can
be achieved. To reduce the void content of polymer composites to minimum, selection of composite
components as well as the curing pressure during processing have significant role.

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