

**CL-19**  
**THERMAL DESORPTION –**  
**PROGRESSIVE WAY OF ANALYTICAL CHEMISTRY**  
**ON PLASTICS AND RUBBERS**

**FRANKY PUYPE** and **JIŘÍ SAMSONEK**

*Institute for Testing and Certification – Zlín, Třída T. Bati  
 299, CZ-764 21 Zlín-Louky  
 fpuype@itezlin.cz*

## 1. Introduction

Thermal desorption (TD) is the last decade a sampling technology in evolution. The main applications are supporting the automotive and building material industry as well the environmental sector.

This evolution goes simultaneously with the complaints about odors and emissions of volatile organic compounds from plastic/rubber material causing a major problem for indoor air quality. This paper describes briefly the analytical approach of analyzing a broad range of plastic/rubber materials with thermal desorption gas chromatography coupled with mass spectrometry (TD-GC-MS).

Thermal desorption is defined as a sampling technology that utilizes heat to increase the volatility of analytes such that they can be removed (separated) from the solid matrix (plastics, wood, textile, extracts, foam, hair, gel, paint, etc.). Thermal desorption allows analysis of almost all sorts of materials including insoluble materials and complex materials at trace levels without any pretreatment of samples.

TD-GC-MS is used since short time in many applications due to the many advantages compared to conventional solvent-based sample preparation methods like solvent extraction, solvent exchange and steam distillation. Advantages of thermal desorption are mainly:

- 1000 fold improvement of the sensitivity because there is no solvent needed which is diluting the interested analyte. A good sensitivity is needed when looking for ultra-trace compounds
- Automation: vapours or test materials are collected/weighted into sample tubes or cups and directly introduced on the thermal desorber unit.
- There is no additional sample preparation required. This is saving time and costs. Conventional analytical methods like gas chromatography, thin layer chromatography (TLC) and liquid chromatography (HPLC) require a time consuming liquid extraction.
- Nearly no sample contamination is possible due to reduced manual preparation.
- There is selective focus on compounds of interests without interferences like water.
- There is no contamination from solvent peaks. The chromatographical data is coming from the sample itself.
- The adsorbent tubes are reusable, the solvent consumption is lead to a minimum. It eliminates the environmental health and safety issues.

There are 2 basic possibilities for sampling. The first possibility is the easiest. The sample is direct desorbed as it

was placed into a sample tube or cup used for TD-GC-MS. The second possibility is the purge and trapping of air or vapours from a solid sample on sorbent tubes followed by TD-GC-MS.

This purge and trapping process is mostly done by off-line process (emission chamber technique and on-site air quality measurement). The on-line trapping process is practically done by refocusing thermal desorption instruments (chapter 2.2). The sorbent has to be chosen according to the analyte which is required. There are on the market lots of sorbent materials available that for each application there exists a sorbent however nowadays there are more universal trapping materials used like carbon absorbent material (carbotrap) and polymeric adsorbents (TENAX TA). They can according to the application be used as mixed combinations (TENAX GR). All of them have a low affinity for water and methanol.

The thermal desorption range varies from very volatiles (Bp 0 °C) till the “heavies” from the semi-volatile class (Bp 400 °C, MW approx. 1000 g mol<sup>-1</sup>). The use of temperatures higher than 400 °C will lead to a C-C bound cleavage. This is not favored due to the pyrolysis process of the analyte and the polymer matrix as well.

## 2. Available systems

Below are given the commercial systems available for thermal desorption at this moment. They are divided according the injection technique however all are based on the same processes: desorbing, separating and detecting.

### 2.1. Direct thermal desorption

The easiest commercial thermal desorption systems are direct thermal desorption systems. The sample is transported to a furnace and at certain temperature heated. The evolved gasses are going immediately to the beginning of the analytical column and the analysis starts. Direct thermal desorption is mainly used for fast screening or quantitative analysis of high mol weight compounds (up till 1000 g mol<sup>-1</sup>). The main application with direct thermal desorption are the identification of antioxidants/brominated flame retardants in plastic materials and accelerators/stabilisers in rubbers. Fig. 1 shows a schematic presentation of direct thermal desorption system.

There are a number of considerations to be made for this analysis. Firstly the sample needs to be very small (max. 10 mg) and therefore the sample should be sufficiently homogeneous. The sample needs to have a relatively high surface area. This surface area is needed to have an optimum diffusion process from inside the polymer/rubber to the gas stream.

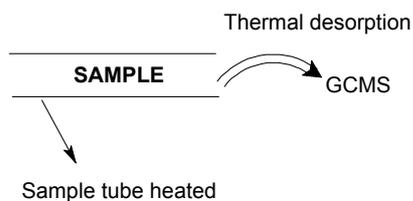


Fig. 1. Schematic presentation of direct thermal desorption system

## 2.2. Refocusing thermal desorption (cold trap)

A more complex thermal desorption system is refocusing thermal desorption. The sample is transported into a furnace and the evolved gasses are refocussed on a cooled adsorption tube with TENAX TA. Refocusing is a collection technique. A volume of several liters of gas is pulled over an adsorption tube. Permanent gasses pass the tube while molecules with higher molecular weight remains on the adsorbent in the sample tube. Refocusing is done by cooling. The injection exists of fast heating of this TENAX TA trap and evaporating the analytes towards the analytical column.

Refocusing thermal desorption has the advantage that the analytical peaks are far sharper and the sensitivity is bigger. The TENAX TA trapping material has a high capacity and it is possible to refocus the analytes for a longer time. This longer trapping time is required for quantitative analysis.

The thermal desorption unit used for this paper was a TD-20 system (Shimadzu) with Peltier cooling/programmable temperature vaporising injector. The advantage of the TD-20 systems is that they have a reverse sample path. The sample leaves the TENAX TA tube in opposite direction than it was trapped (Fig. 2).

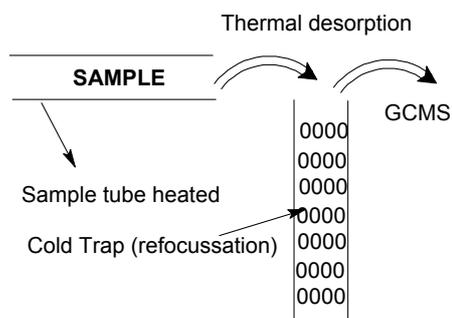


Fig. 2. Schematic presentation of a refocusing thermal desorption system

## 2.3. Emission chamber-TD-GC-MS

The test chamber method followed by thermal desorption is an analysis which is associated with the “sick building syndrome” for building materials but can also applied for testing of car materials and air quality measurements. Sick building syndrome (SBS) is a combination of ailments associated with an individual's place of work (office building) or residence. A 1984 World Health Organization report into the syndrome suggested up to 30 % of new and remodelled buildings worldwide may be linked to symptoms of SBS. Most of the sick building syndrome is related to poor indoor air quality.

The principle of the emission chamber can be explained that the sample is staying at certain conditions (temperature and humidity) in an emission chamber. The most influencing factor is the air exchange rate. It is possible to regulate the flow and change the air by continue stream. The air can flow over an adsorbent tube filled with an appropriate trapping material (Fig. 3). The emissions can be measured by perform-

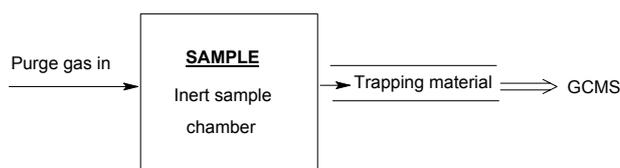


Fig. 3. Schematic presentation of a test chamber system

ing refocusing TD-GC-MS analysis of the adsorbent tube. The main application with this chamber is the ISO 16000 emission chamber test for building material. However the automotive industry needs a similar testing for characterizing air quality in car interiors.

The emission chamber can predict long term emissions for real areas like car interior or rooms. The mass spectrometry detection can not only detect the real emissions and odor but also give understanding of the reaction mechanism between emissions. It is known that carpets and water based adhesives might cause a reaction between the hydrolysed phenoxypropanol and the inorganic bromine from the latex textile covering. This is resulting in formation of smelling bromophenols.

## 2.4. Evolved-Gas-Analysis (EGA)

Evolved gas analysis is a thermal analysis which determines evolved products at certain temperature. The polymer sample is placed in a desorption unit and the evolved gasses are immediately detected by GC-MS. This analysis doesn't need chromatographical separation due to the quick gas flow in the system. The analysis result is a graph with in abscissa the desorption temperatures and in ordinate the identified volatile and its intensity. Evolved gas analysis is comparable with thermal gravimetrical analysis but has the advantage to give the exact compound identification due to the mass spectrometrical detection (Fig. 4).

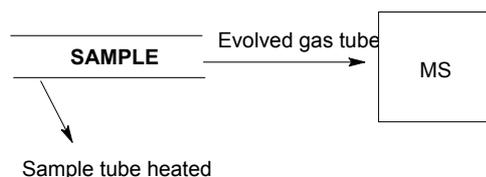


Fig. 4. Schematic presentation of a the EGA analysis

This method is mostly used to optimize the production process temperatures. Sometimes during polymer preparing processes some unexpected thermal reactions might occur or component loss. A simulation of the production process can learn a lot about the behavior of the blended compounds. This is applicable for rubber blends as well for polyolefin/condensed polymers.

### 3. Potential applications for automotive industry

#### 3.1. Additives from plastic material and rubber

The trend observed in plastic technology is that the additives are far higher mol weight molecules. This is needed to get them more stable and slow down the migration in the plastic material. To get an identification report of the additives classical liquid extraction might be applied. The quick thermal desorption is again a great alternative. This method can be used to check the raw materials or defects from the supplier. The automotive business requires certain quick analytical methods like this.

In Fig. 5 is seen that all the additives are separated from the matrix peaks. The polycarbonate was stabilized against oxidation by irgafos 168 and irganox 1076. While the sample also was stabilized against UV by tinuvin 350 and uvinul 3027.

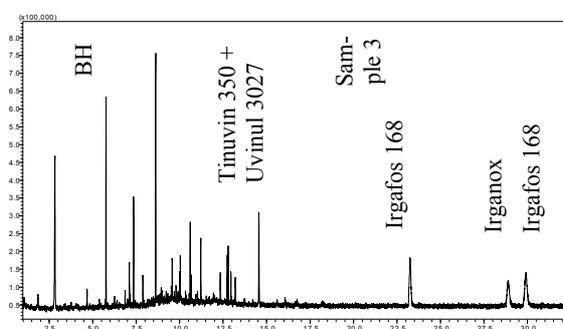


Fig. 5. Additive screening by TD-GC-MS of polycarbonate based coating

#### 3.2. Volatile organic compounds (VOC/SVOC)

VDA is the German Quality Management System (QMS) for the automobile industry (Verband der Automobilindustrie). Their VDA 278 norm describes the emission from plastic materials intended to use in automotive industry. This analysis exists into two parts:

- The first part describes the volatile organic compound analysis (VOC) with thermal desorption at 90 °C for 30 minutes. The peaks are calibrated with and compared to a toluene standard.
- The second part describes the semi-volatile organic compound analysis (FOG) with thermal desorption at 120 °C for 60 minutes. The peaks are calibrated with and compared to a hexadecane standard.

The example in Fig. 6 shows a chromatogram overlay of VOC analysis. 3 polyethylene samples were measured and were taken from different batches. This method proved that the lowest 2 chromatograms (sample 1 and 2) have a VOC value of 360  $\mu\text{g g}^{-1}$  toluene equivalent. The sample 3 (highest chromatogram) gives the highest VOC emission of 500  $\mu\text{g g}^{-1}$

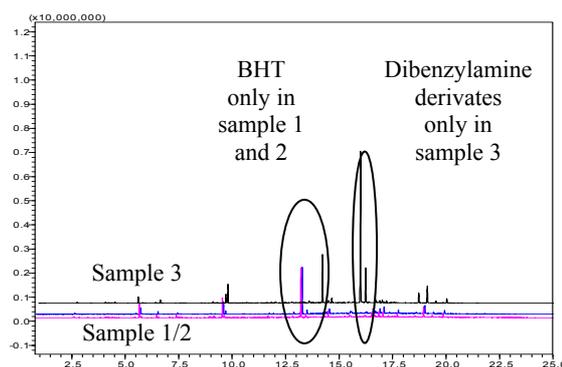


Fig. 6. VOC analysis of 3 polyethylene samples by refocusing GC-MS

toluene equivalent. The VOC analysis shows that the material is based on the same due to the presence of similar matrix related emissions. The used additives are different. Sample 1 and 2 contains butylated hydroxyl toluene (BHT) at retention time 13,2 min while sample 3 contains dibenzylamine derivates at retention time 16 minutes.

This VDA 278 analysis gives information about the additives and their emission value. The power of this method is that the emission of a single compound can be calculated and the formulation can be adjusted by reverse engineering.

#### 3.3. Defect analysis

Thermal desorption is a perfect tool for the explanation of many defects on surfaces and raw materials for automotive industry. Defects can either be surface defects like blooming, cracking, discoloring or smelling but also physical defects like cracking, weakening, etc.

The rubber production process is one by complex handlings after each other like mixing, extrusion, calendering, vulcanization but also storage. This happens all under certain conditions like temperature and mixing speed but also by adding a complex mixture of chemicals. Not only the rubber industry but the automotive polymer industry in common is more and more faced by short delivery times and high production speed. This all can lead to defects in production and storage due to the lack of good storage conditions. Rubber for instance is still vulcanising during storage. As the rubber product arrives to the customer it sometimes happens that the defect is noticed after selling the final product.

The chromatogram below in Fig. 7 shows a defect from a polypropylene production plant. The lower chromatogram gives the reference sample which has no defect at all. The paint was adhesive to the polypropylene profile. The upper chromatogram shows the defect sample where the paint could not stay on the polypropylene profile. A simple screening by direct thermal desorption proved the presence of wax in the defect sample.

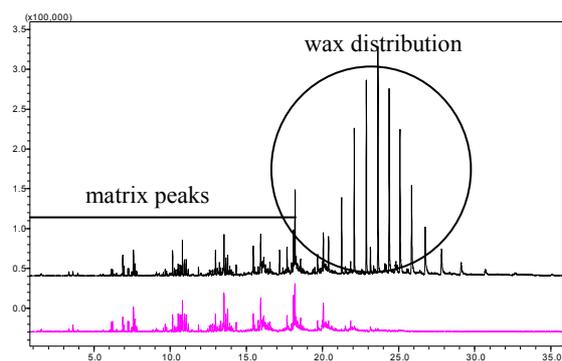


Fig. 7. Determination of differences between polypropylene samples can lead to a solution for defects in the production

### 3.4. Liquid injections/extracts/washes

To omit the large volume injections in liquid chromatography large volume injections can also be done easily by thermal desorption. An amount of 100  $\mu\text{l}$  can be added to a tenax tube if the solvent is methanol. Other solvents can be used if the analyte is much heavier than the solvent. The solvent can evaporate and the analyte remains in the sample cup or tube. This residue can be oil or a thin film which is excellent for using thermal desorption.

Applications are mainly surface related problems of car parts like dashboards, rubber, leather, tires, driving wheel, carpets, paint, adhesives, etc.

Blooming is a recently more and more appearing defect which implements the migration of additives, accelerators towards the surface or a synthetic polymer. The surface gets affected by a flower field shaped structure and even a snow white layer can be seen if the sample is blooming for long time.

This blooming process is depending on the polarity of the analyte, its volatility, concentration, migration time and storage conditions. The following example is the analysis of a blooming door panel. The white smear on the surface is making a flowerfield structure on the surface of the sample (Fig. 8).



Fig. 8. Detailed picture of a blooming defect on a car door panel

Thermal desorption after surface washing proved that the bloom was caused by the toxic hexabromocyclododecane (Fig. 9). This is a commonly used flame retardant for automotive applications. On the surface of the blooming panel was seen such a high concentration of hexabromocyclododecane that there was surely a mistake in the production line of the manufacturer.

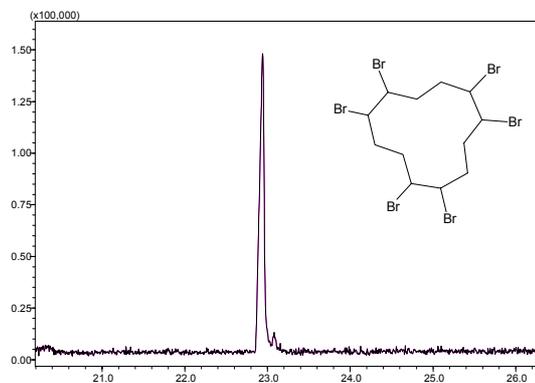


Fig. 9. Chromatogram after TD-GC-MS of a surface wash for blooming analysis

## 4. Conclusion

The new trends in modern analytical chemistry are based on quickness, trueness and quality. The automotive/rubber sector requires the same assessments and both sections are fully cooperating with labs nearby. To fulfill the needs of the industry thermal desorption can save lots of time and money compared to the classical wet chemistry or instrumental chemistry.

Its applications range from quality control to defect analysis. The importance of this technique is still not well understood by customers from analytical laboratories. However the huge number applications with this technique are proving their need.

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## CL-20 EMISSION BEHAVIOUR OF NON-METALLIC PARTS, INTENDED INTO A CAR INTERIOR

**JIRI SAMSONEK and FRANKY PUYPE**

*Institute for testing and certification, a.s. Tř. T. Bati 299,  
764 72 Zlín, Czech Republic  
analyt@itczlin.cz*

### Introduction

Almost all car manufacturers take care about environment inside the car having regards the passenger's health, comfort or protection. Modern car interiors are loaded by many non-metallic components (plastics, rubbers, textiles, varnishes, lubricants or adhesives) so the study of their influence on the car environment is vital. The approach of each car manufacturer varies, but generally they are based on similar principles. Material is tested under the conditions that simulate real conditions in a car environment.

Testing is based on establishing of the balance between solid phase (tested sample) and vapour phase (ambient air or generally gaseous phase). Then the vapour phase (or substances, that are emitted to the gaseous phase) are subjected to the analysis. Standards are aimed on testing of odour, total organic compounds, selective organic substance emission and transport behaviour of certain substances.

Examples<sup>1</sup> of volatile organic substance (VOCs) and semi-volatile organic substances (SVOCs) are:

VOCs – alkanes, alkenes, aromatic hydrocarbons, carbonyl compounds, alcohols, esters, ethers, aldehydes, halogenated hydrocarbons, terpenes, nitrogen and sulphur compounds  
SVOCs – high boiling point substances such as paraffins, glycols, higher fatty acid and their esters, phenols, phthalates, adipates (generally plasticisers), organophosphorous substances, organobromine substances (flame retardants), organosilicon substances (silicon oil), amines (catalysts from PU foams) etc.

### Emission kinetics

The process of vaporisation of volatile or semi-volatile organic substance (low molecular substances) from solid material (plastic, rubber, textile) can be described from thermodynamical point of view by many equations. The basic is vapour pressure equilibrium. All liquids and solids have a tendency to evaporate to a gaseous form, and all gases have a tendency to condense back into their original form (either liquid or solid). The equilibrium is dependent on the temperature, molecular weight, interaction between substance and the solid matrix and interactions between each volatile substance.

Presence of volatile and semivolatile compounds in the car environment can be described by following balance diagram:

The main process that occurs is vaporisation and subse-

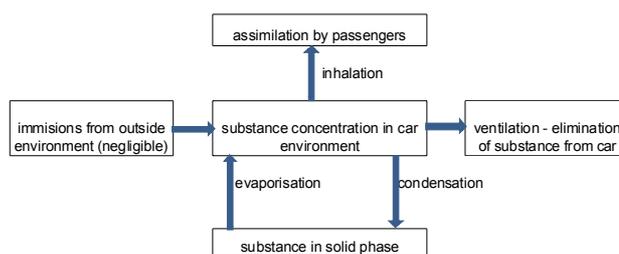


Fig. 1. Emission diagram

quent condensation. The imissions from outside are source of different substances (like exhaust fumes, dust etc.). They have no relation to the emission behaviour of car material. Comparing to the concentration levels of organic pollutants inside the car it can be named as a “diluting or clean” air. Over a long period of non-usage of a car the vaporisation and condensation reach equilibrium so the air is saturated by volatile and semi-volatile substances. All the process depends on a temperature, the higher the quicker the equilibrium is reached and higher is the final concentration level of each substance. Passengers are exposed to this equilibrium emission concentration immediately after they sit into the car. As they run a car and the air exchange dilutes the ambient environment the concentration of chemicals start to decrease. The opposite process can be increasing the emission flow by heating of interior caused by car-heating system. Transport of the pollutant inside the car is complex process. Evaporation and condensation can occur on different surfaces so one material can emit semi-volatile substance and on another material the condensation can occur. A typical phenomenon is fogging of phthalic acid esters. This plasticisers can be emitted to the car environment mainly when it is heated and then strong condensation on the cold front glass result in light scattering thin film on the inside of the windshield<sup>1,2</sup> fogging.

### Typical tests of emission behaviour

There are several very often used tests for evaluation of emission behaviour of non-metallic materials in far interiors. Some of them are non-selective, describing complex behaviour of sample, others are selective, focusing on certain substance.

#### Emissions of total organic carbon

This test evaluates total amount of organic substances emitted under certain temperature and time (typically 120 °C, 5 hours) from the material. The quantification is done by recalculation of all quantifiable substances expressed as an acetone organic carbon. This test can characterise samples capability to emit mainly volatile substances that remains in the sample like residual solvents, monomers, dimmers, volatile and semivolatile additives etc. Semivolatile substances con-

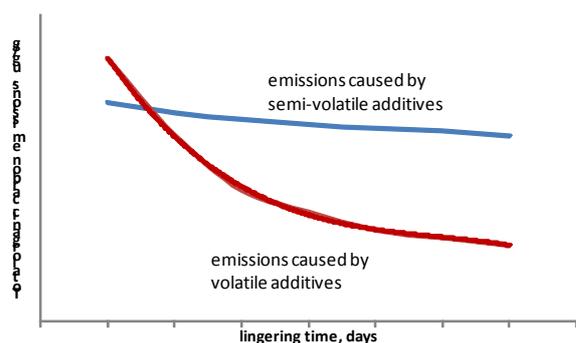


Fig. 2. Decreasing of TVOC on the lingering time

tribute to the total emission lower than those of lower boiling point. Excessive results of total organic carbon can be caused by many factors, like high residual monomer content, high dosing of volatile or semi-volatile additives, like plasticisers, lubricants, stabilisers, or residual solvents in the surface treatments. Total organic carbon emissions (TVOC) arising from polymer additives are difficult to omit as even after leaving the part to linger after manufacturing for a longer time almost the same vapour phase equilibrium during the test is reached again. Excessive organic carbon emissions caused by residual high volatile substances like varnish solvents, monomers etc. have a tendency to decrease easily (approximately 20 % per week, with the stabilisation after 6 month<sup>1</sup>) so the total TVOC in the time fall depends mainly on the ratio between high volatile and semivolatile substances in the sample. Higher emission of organic substance does not necessary lead to the worse odour of the material as many of the organics are not sensorial important than others.

Special care is placed on the emission of formaldehyde. Although its emission is included into a total organic carbon these substance is controlled separately<sup>5</sup> due to its enormous influence on the human health. Formaldehyde is classified as a positional carcinogenic substance class 2A.

#### Fogging behaviour

Mainly presence of semi-volatile substances in the non-metallic car interior parts can lead to the phenomena, named "fogging". Substances with higher boiling point that have vapour pressure which enable them to vaporise during heating can condensate on colder parts of car interiors (windshield). Typical substance that can concern in fogging are phthalic acid esters (phthalates), commonly used as a plasticiser. Also flame retardants of plastics and rubbers can increase the fogging<sup>1</sup> as they show similar behaviour as phthalates because molecular weight and the boiling point of both groups of chemicals are comparable. Fogging-supporting chemicals are generally those that have similar physical/chemical properties like plasticisers or flame retardants. They can be residual catalysts<sup>3</sup>, by-products of polymerisation, carriers of colour batches, oils, waxes etc.

Lingering of sample in the storage before testing or assembling cannot decrease significantly fogging characteris-

tics. High loading of car parts by fogging-supporting chemicals supports the fogging effect for a long period of time regardless the number of heating/cooling cycles. To avoid fogging of non-metallic parts the manufacturer has to change the composition of the whole materials.

Special tests are concerning to the direct measurement of light beam reflection<sup>6</sup>. The sample is heated on 100 °C and above it the glass plate, cooled on 20 °C is kept. Then the light beam reflection is measured and compared the clean glass surface reflection.

#### Odour

Sensorial perception of car interior air is heavily influence by non-metallic parts properties. Regardless the other parameters human smell can detect certain substances on the levels difficult to quantify by common analytical techniques. Samples are tested under defined conditions and raised odour evaluated by group of trained evaluators by use of rating scale. Some car manufacturers have set more detailed standards for describing of the smell<sup>7</sup>. Main substances that can influence the final smell are amine or sulphur-based organics, aldehydes, ketons, organic acids, esters, phenolic substances, products of microbiological proceses etc.

#### The whole car testing

Another approach can be also applied to the evaluation of emission behaviour. While above mentioned tests are describing each material the summary test of final car can be also applied. Either sensorial tests or analysis of ambient car can be performed or testing of ambient air quality by adsorbing of the air on the sorbents (charcoal tubes, TENAX<sup>®</sup> sorbents). with this type of analysis we can better understand the real behaviour of VOCs in the real car interior an. Also analysis of fogging film on the windows can give information about real transport of SVOCs in the car interior.

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## CL-21 PLASTICS PARTS DESIGN SUPPORTED BY REVERSE ENGINEERING AND RAPID PROTOTYPING

**MICHAL STANEK, MIROSLAV MANAS, DAVID  
MANAS, and STEPAN SANDA**

*Tomas Bata University in Zlin, Faculty of Technology, Department of Production Engineering, TGM 275, 762 72 Zlin, Czech Republic, stanek@ft.tub.cz*

### Abstract

Rapid prototyping technologies for easy production of prototype, parts and tools are new methods which are developing unbelievably quickly. The main objective of this article is to give the basic introduction to this problem.

### 1. Introduction

Successful product development means developing a product of high quality, at lowest cost, in the shortest time, in at a reasonable price<sup>1</sup>. The development of the part and its introduction to market is time consumption process. But „time is money“ and therefore could be said that money saving is greatest when time to market is minimalized utmost.

On principle, the conventional model making processes based on two-dimensional (2D) drawings. The rapid prototyping process is based on complete 3D models. The 3D geometric information from the CAD is split into layer information and the layers are gradually build directly with the aid of the computer. The advantage of the rapid prototyping technologies is the part building possibility using 3D CAD data only.

All process by which 3D models and components are produced additively, that is, by fitting or mounting volume elements together (voxels or layers) are called generative production process. Rapid prototyping describes the technology of generative production processes. The application of rapid prototyping technology lays in solid imagining and functional prototyping. Prototypes are made from plastics (mainly ABS, PVC or special resins, metals or other materials that simulate one or more mechanical or technological functionalities of the final serial component.

Often use word Rapid tooling describes a principles and technologies for tools and molds preparation. This prototypes

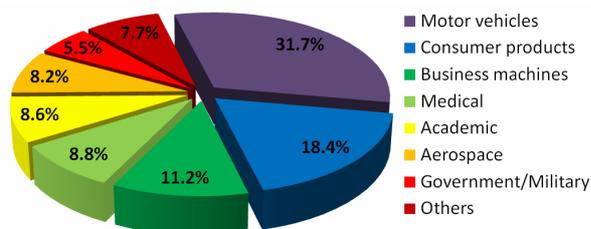


Fig. 1. Percentage use of rapid prototyping worldwide

are used for production of prototypes and preseries products. The rapid tooling uses the same processes as those used in rapid prototyping. Rapid manufacturing represent such a rapid prototyping applications that produce products with serial character. For these purposes can be used most of rapid prototyping methods. But the mechanical and other properties of materials used for the rapid prototyping do not reach mostly the characteristics of the serial products.

### 2. Principles of Rapid prototyping

Rapid prototyping belong to the additive production processes. In contrast to abrasive processes such a milling, drilling, grinding eroding etc. in which the form is shaped by material removing, in rapid prototyping the part is formed by joining volume elements. Most of used rapid prototyping processes work with layers where single layers are produced and joined to a final geometry. On principle, rapid prototyping processes are two and half D processes, that is tacked up 2D contours with constant thickness. But for layer creation 3D model is necessary. Rapid prototyping as the generative manufacturing processes are divided among two fundamental process steps:

- generation of the mathematical layer information,
- generation of the physical layer model.

The principle is given in the Fig. 2.

Industrially are used many types of rapid prototyping systems working on different physical principles:

- solidification of liquid materials (polymerization process),
- generation from the solid phase:
  - cutting from foils or paper (LOM),
  - binder of powder or granules,
  - powder sintering,
- generation form the pasty phase.

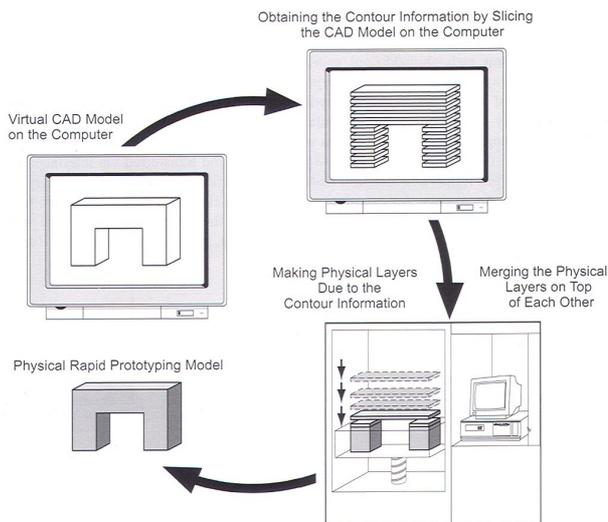


Fig. 2. Rapid prototyping principle

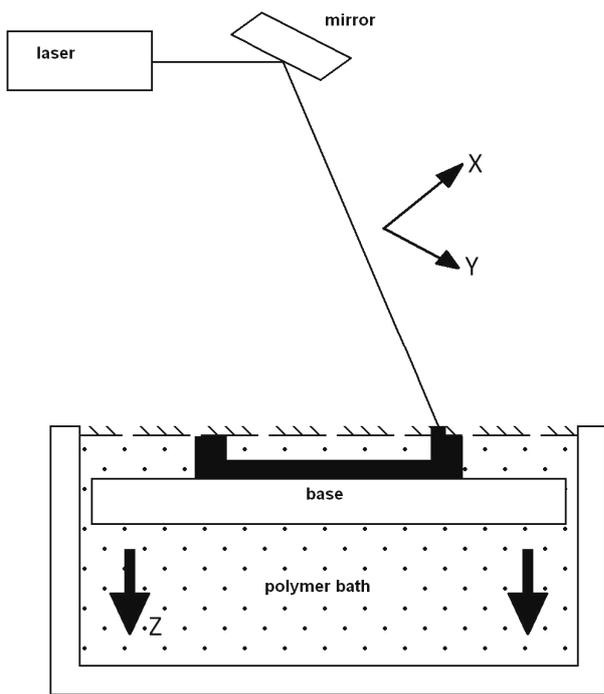


Fig. 3. Principle of Stereolithography

Solidification of liquid materials (Photopolymerization) represents stereolithography. Stereolithography use a viscous monomer. Exposed to ultraviolet radiation or laser beam set off a spontaneous polymerization and the liquid monomer changes to solid polymer (Fig. 3).

Laser sintering (LS) is most important principle from the group of RP technologies which use the product generation from the solid phase. LS works with the powder (polymers, metals, etc) which is sintered by the laser beam and form a layer usually in the thickness of the powder particles size (Fig. 4).

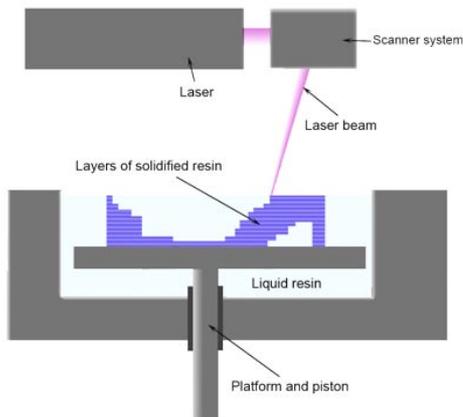


Fig. 4. Principle of Laser Sintering

Laminated Object Manufacturing is the most simple method producing 3D models. Models are produced from 2D countered layers cutted out from the foils or paper by the help of knife or laser beam and than to assembled them into 3D models (Fig. 5).

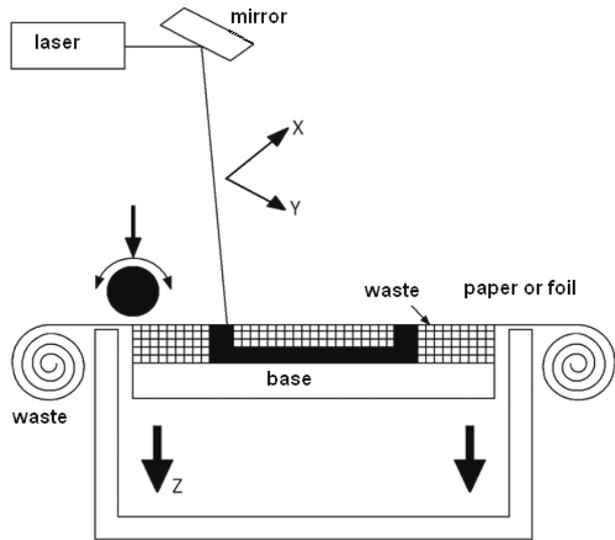


Fig. 5. Principle of Laminated Object Manufacturing

Extrusion process is based on melted polymer which is extruded from nozzle system (extrusion die) and deposited geometrically defined onto a structure. As building materials are used different types of polymers (Fig. 6).

3D printing is very often used rapid prototyping method. The principle is very similar to 2D printing process of inkjet printer. The injected material is a polymer which after cooling form the required layer or binder which bonds

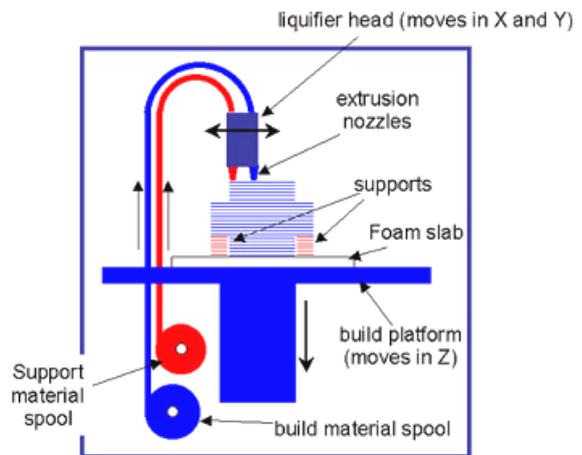


Fig. 6. Principle of Fused Deposition Modeling



Fig. 7. Examples of parts from FDM

### 3. Reverse engineering

Reverse Engineering allows stacking already existing product. For this reason the entire surface needs to be able measured and recorded and returned to the CAD system.

The measurement produces an enormous number of data that are also known as clouds of points. Reverse engineering enables these clouds of points to be defined as surface elements, thereby facilitate their further processing in the CAD system.

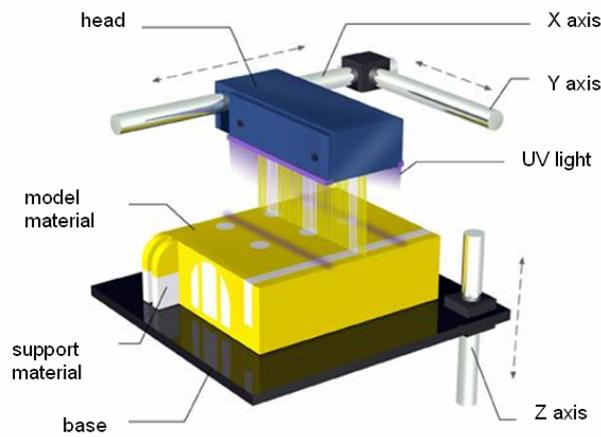


Fig. 8. Principle of 3D printing

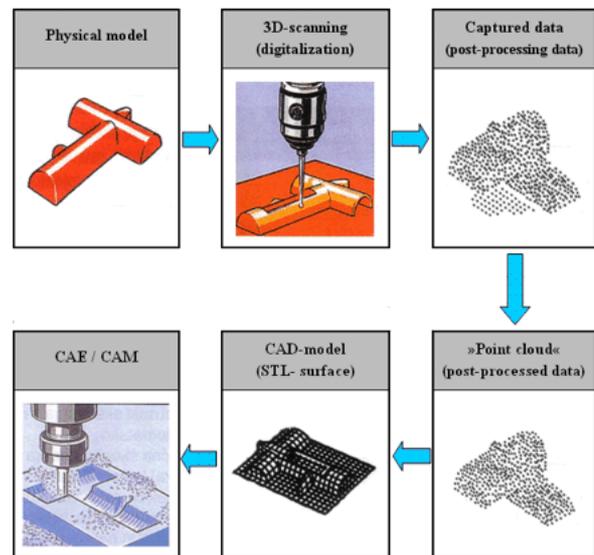


Fig. 10. Principle of Reverse Engineering

a powder particles. As in case of the inject printer, also 3D printer makes print the multicolor parts possible (Fig. 8).



Fig. 9. Examples of printed parts



Fig. 11. Reverse engineering system with the laser scanner Copy Mate

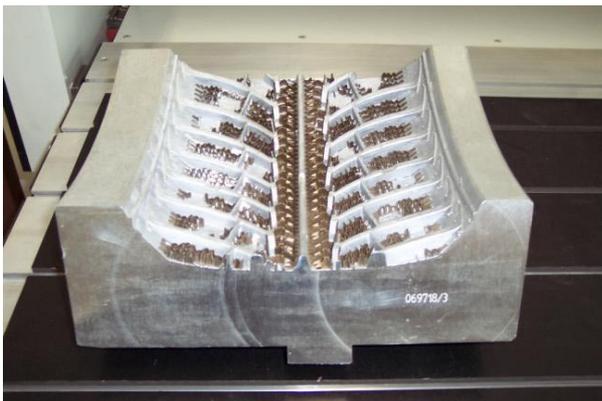


Fig. 12. Part before scanning

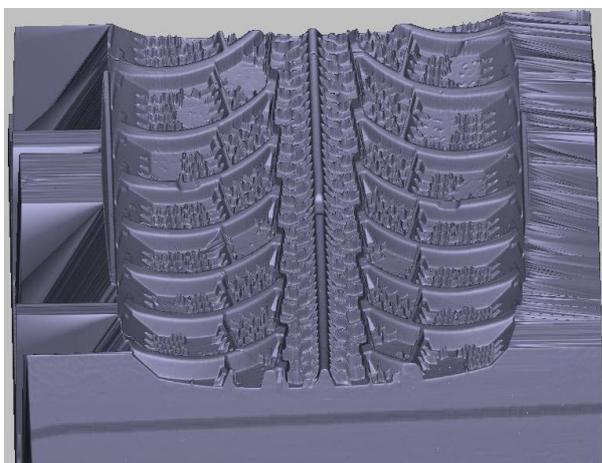


Fig. 13. Scanned part

#### 4. Conclusion

Rapid prototyping and reverse engineering are very useful tools which can accelerate the way of product from the idea to market. Generative principle of rapid prototyping methods enables to produce parts of any geometry. These processes are practically unlimited in their ability to form complex shapes, they can produce both positives (parts) and negatives (dies and molds).

*This article is financially supported by the Czech Ministry of Education, Youth and Sports in the R&D project under the title 'Modelling and Control of Processing Procedures of Natural and Synthetic Polymers', No. MSM 7088352102.*

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#### CL-22

#### INFLUENCE OF SURFACE ROUGHNESS ON FLUIDITY OF THERMOPLASTICS MATERIALS

**MICHAL STANEK, MIROSLAV MANAS, DAVID MANAS, and STEPAN SANDA**

*Tomas Bata University in Zlin, Faculty of Technology, Department of Production Engineering, TGM 275, 762 72 Zlin, Czech Republic  
stanek@ft.tub.cz*

#### Introduction

Polymer injection molding is the most used technology of polymer processing nowadays. It enables the manufacture of final products, which do not require any further operations. The tools used for their production – the injection molds – are very complicated machines that are made using several technologies. Working of shaping cavities is the major problem involving not only the cavity of the mold itself, giving the shape and dimensions of the future product, but also the runners leading the polymer melt to the separate cavities. The runners may be very complex and in most cases takes up to 40 % volume of the product itself (shape cavity). In practice, high quality of runner surface is still very often required. Hence surface polishing for perfect conditions for melt flow is demanded. The stated finishing operations are very time and money consuming leading to high costs of the tool production. This work gives the results of studying the influence of the quality of flow pathway surface and influences of other technological parameters on the polymer melt flow.

Results of the experiments carried out with selected types of thermoplastics proved a minimal influence of surface roughness of the flow channels on the polymer melt flow. This considers excluding (if the conditions allow it) the very complex and expensive finishing operations from the technological process as the influence of the surface roughness on the flow characteristics does not seem to play as important role as was previously thought.

Regressive models created on the basis of experiment results enable to predict the flow behaviour of the polymers quite precisely with regard to the surface quality and the parameters of the process injection molding itself. Application of the measurement results may have significant influence on the production of shaping parts of the injection molds especially in changing the so far used processes and substituting them by less costly production processes which might increase the competitiveness of the tool producers and shorten the time between product plan and its implementation.

## Injection molding

Injection molding is one of the most used and the most popular manufacturing technologies. The main phase of injection molding is the transport of polymer melt to the mold, where the polymer solidifies and shapes into the required product. Injection proceeds at non-isothermal conditions, when the process of melt solidifying gets influenced by a number of rheological polymeric properties.

### Process of polymer material injection

Injection molding is a way of shaping polymeric materials, during which the molded material is filled at high rate (injected) into a closed cavity of a tempered mold. It produces high quality and precise products (shots) from a wide range of plastics. Injection molding has some other advantages. For instance, precise mold design might eliminate other working. Cold runner molds in case of thermoplastics can be crushed and reused, decreasing the polymer waste to minimum. The injection molding process is quite fast and can be well automated. In order to get a shot with good physical properties and good surface, the filling of the mold must be controlled so that the melt would not flow into the form in one flow front but gradually. A plastic nucleus is formed by this way of laminar flow, which enables the compression of the melt in the mold and consecutive creeping. A constant flowing rate given by the axial movement of the screw is chosen for most of the flows. During filling the mold cavity the plastic material does not slide along the mold surface but it is rolled over. This type of laminar flow is usually described as a “fountain flow” (Fig. 1).

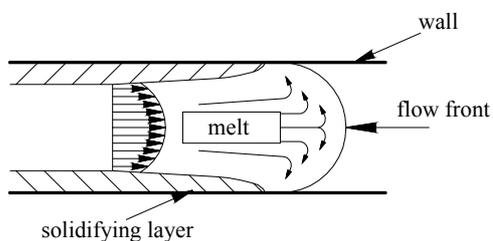


Fig. 1. Fountain flow

## Injection mold for samples

The injection mold was designed for the easiest possible manipulation both with the mold itself and during injection while changing the testing plates, size of the mold gate etc. The injection mold is inserted into a universal frame. Its description and reasons for use are stated below.

### Universal frame

The frame was designed for use with many different injection molds that fit the size of the frame. This makes the change of the separate injection molds easier, because the

frame remains clamped to the injection molding machine and only the shaping and ejection parts of the molds are changed. Attaching right and left sides of the frame to fixed and moving plates of the injection machine is done using four clamps on each side.

### Cavity parts of the injection mold for thermoplastics

The shaping part of the injection mold is composed of right and left sides, see Fig. 2. The most important parts of the injection mold concerning the measurements are: testing plate 2, cavity plate 3 and a special sprue puller insert 8.

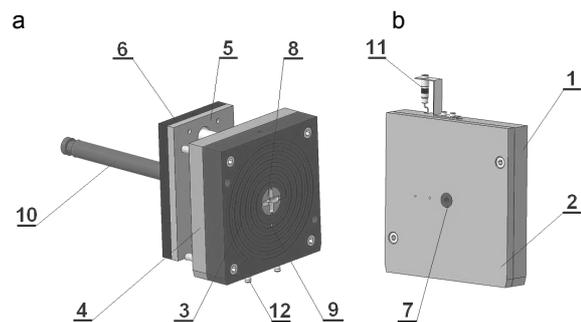


Fig. 2. Cavity parts of the injection mold for thermoplastics a) left side, b) right side; 1 – clamping plate, 2 – testing plate, 3 – cavity plate, 4 – plate, 5 – anchor plate, 6 – ejector plate, 7 – sprue puller insert, 8 – special sprue puller, 9 – ejector, 10 – ejector rod, 11 – pressure sensor, 12 – cooling end

### Special sprue puller insert

The sprue puller insert is used for changing the gate size. It is composed of four different gates (1, 2, 4 a 6 mm). Turning the sprue puller changes the size of the gate, the position of the sprue puller is secured by a stopping bushing.

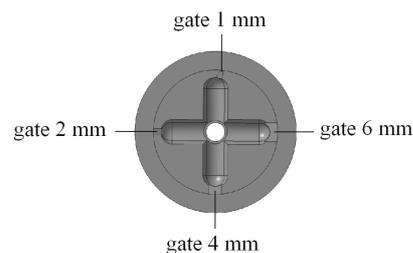


Fig. 3. Special sprue puller

### Cavity plate

The cavity of injection mold is in a shape of a spiral with the length of 2000 mm. The cavity is created when the injection mold is closed, i.e. when shaping plate seals the testing plate. The dimensions of cavity are indicated on Fig. 4.

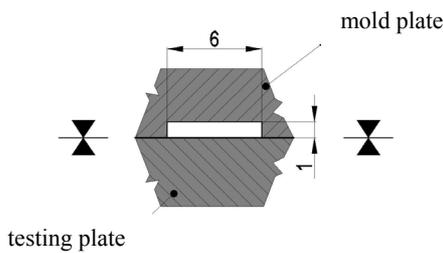


Fig. 4. Cross section of mold cavity

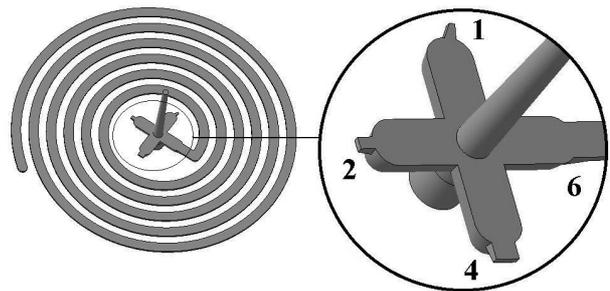


Fig. 5. Testing sample

Testing plates

The injection mold can operate with 5 exchangeable testing plates with different surface roughness. The surface of the plates was machined by four different technologies, which are most commonly used to work down the cavities of molds and runners. These technologies are polishing, grinding, milling and electro-spark erosion. The testing plates are used for changing the surface of the mold cavity.

Injected materials

Representatives of thermoplastics with varying flow properties were chosen for the experiment with the other decisive criteria being representation of almost all kinds of materials that are commonly used in injection molding. These are: LDPE (Bralen VA 20-60), ABS (Polylac PA 757), PP (Mosten GB 003), PP filled by 10 % talk (Keltan TP 7603), PP filled by 20 % talk (Taboren PH 89 T20).

Table I  
Surface of testing plates

Technology	Photo	Surface roughness
Polishing		Ra = 0,102 μm
Grinding		Ra = 0,172 μm
Electro – spark machining (fine design)		Ra = 4,055 μm
Milling		Ra = 4,499 μm
Electro – spark machining (rough design)		Ra = 9,566 μm

Injection molding machine DEMAG ERGOtech 50-200 with oil tempering unit Regloplas 250 KL were used to prepare samples (Fig. 6).

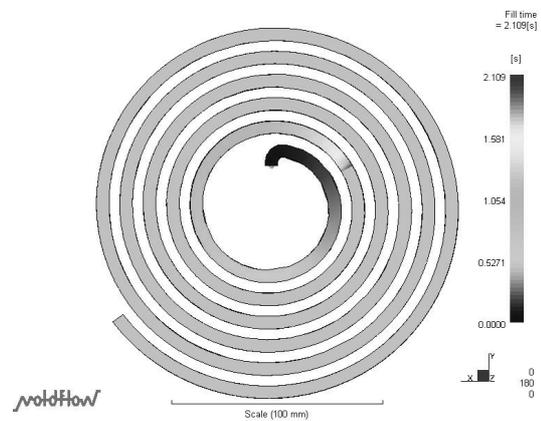


Fig. 6. Simulation of the flow length

Injection molding process simulation

A simulation of the injection molding process in SW Mouldflow 6.1 was carried out for comparison with the reality. The same conditions were set as during the actual injection molding. The flow length in the mould cavity of the polymers was observed.

Discussion

The effect of material and surface roughness of the plate on the flow length

The aim of the measurements was to find out the influence of separate technological parameters, especially the quality of the injection mold cavity surface, on the flow length of the injected materials.

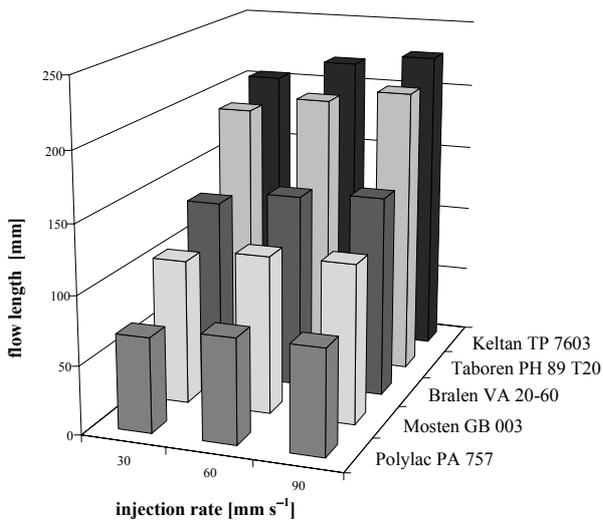


Fig. 7. Dependence of the flow length on the injected material and injection rate; plate with fine design, injection rate  $30 \text{ mm s}^{-1}$ , size of gate  $2 \text{ mm}$

The observed influences on filling the injection mold cavity (the flow length respectively) in the thermoplastics were injection pressure, injection rate, size of the gate and the surface roughness of the testing plates.

### Statistical evaluation of the measured data

The final statistical evaluation of the measured data was done by SW STATISTICA 7. The aim of the statistical evaluation was to determine the influence of separate parameters on filling the mold cavity by material. Due to the influence of more factors (some independent variables) on the change of the observed feature (dependent variables), multiple

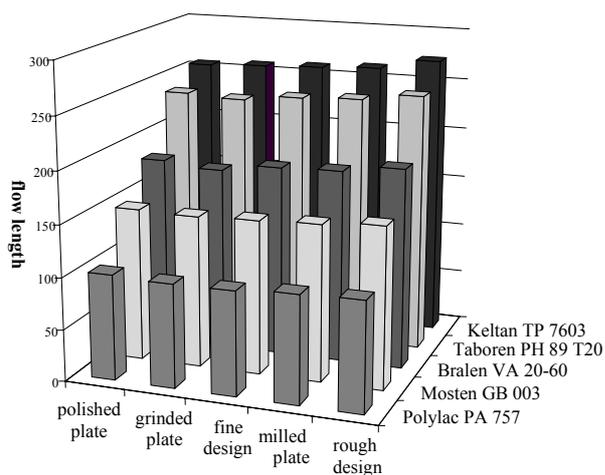


Fig. 8. Dependence of the flow length on the injected material; injection rate  $60 \text{ mm s}^{-1}$ , injection pressure  $8 \text{ MPa}$ , size of gate  $6 \text{ mm}$

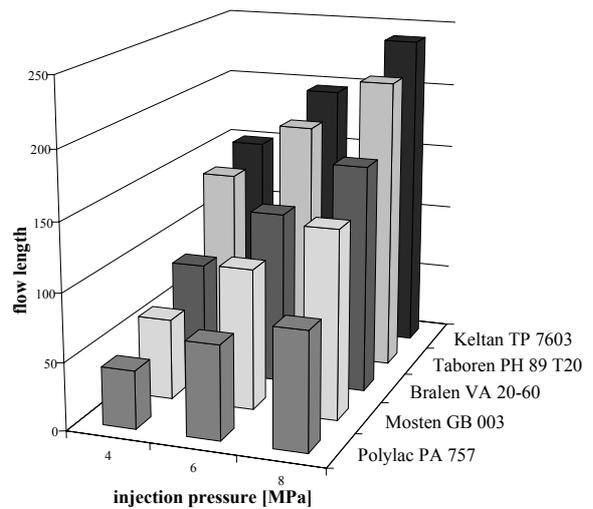


Fig. 9. Dependence of the flow length on the injected material and injection pressure; plate with rough design, injection pressure  $6 \text{ MPa}$ , size of gate  $2 \text{ mm}$

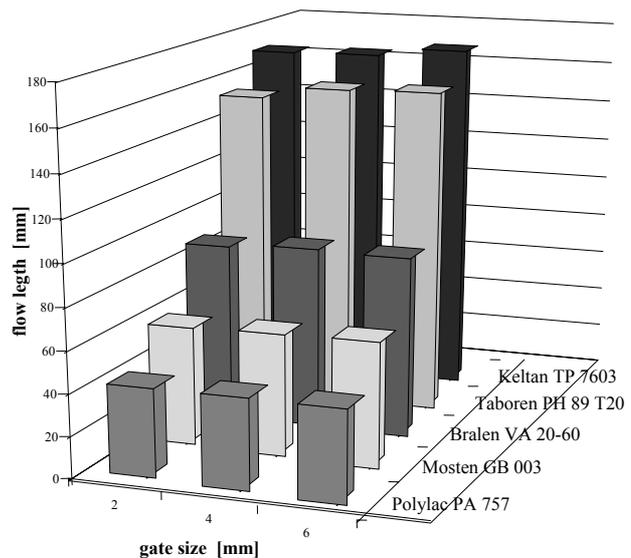


Fig. 10. Dependence of the flow length on the injected material and gate size; polished plate, injection rate  $90 \text{ mm s}^{-1}$ , injection pressure  $4 \text{ MPa}$

regression was chosen for the description. The result of the regressive analysis is the regressive model used to predict the value of dependent variable at a given value of independent variable. The dependent variable is the flow length. We observe the influence of five independent variables (injection pressure, injection rate, size of the gate, surface roughness of the testing plates and Melt Flow Index of the materials) on the flow length. To find out the impact of the factors on flow length, the dispersion analysis was carried out. The resulting

p-values are stated in Table II. The values under  $p < 0,05$  are statistically relevant.

The following regressive model was found out using the mul-

Table II  
p-values of observed factors

Factor	p-value
Injection rate	0,000001
Injection pressure	0,000000
Size of gate	0,000000
Surface roughness of testing plate	0,291675
Melt flow index	0,000000

tiple regression.

$$R^2 = 0,943915$$

$$y_i = 0,025286X_1 + 0,692656X_2 - 0,041169X_3 - 0,003387X_4 + 0,351107X_5 + \varepsilon_i$$

where  $y_i$  – flow length,  $X_1$  – injection rate,  $X_2$  – injection pressure,  $X_3$  – size of gate,  $X_4$  – surface roughness of testing plate,  $X_5$  – melt flow index,  $\varepsilon_i$  – incidental values

## Conclusion

This research looked into the influence of technological parameters on filling the injection mold cavity and the flow length respectively. The parameters observed during the experiments were injection pressure, injection rate, size of the gate, surface roughness of the testing plates and injected material. All stated parameters, especially injection pressure and injection rate, showed influence on the flow length of all three groups of materials; the influence of surface roughness on the flow length of thermoplastic materials was not so significant. The differences in flow lengths at the plates were very small, rather higher in case of rougher surfaces. The measurement shows that surface roughness of the injection mold cavity or runners have no substantial influence on the length of flow. This can be directly put into practice. It also suggests that working and machining (e.g. grinding and polishing) of some parts of the mold, especially the runners, are not necessary.

*This article is financially supported by the Czech Ministry of Education, Youth and Sports in the R&D project under the title 'Modelling and Control of Processing Procedures of Natural and Synthetic Polymers', No. MSM 7088352102.*

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## CL-23

### STRUCTURE AND PROPERTIES OF FIBRES PREPARED FROM METALLOCENE AND ZIEGLER-NATTA POLYPROPYLENE

**ANNA UJHELÝIOVÁ<sup>a</sup>, PETER MICHLÍK<sup>b</sup>, and JOZEF RYBA<sup>a</sup>**

<sup>a</sup> *Department of Fibres and Textile Chemistry, Institute of Polymer Materials, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava,* <sup>b</sup> *Research Institute for Man-Made Fibres, a.s., Šturova 2, 059 21 Svit, Slovak Republic*  
anna.ujhelyiova@stuba.sk

The fiber-forming properties of polypropylene (PP) prepared by Ziegler-Natta (ZN) catalysts for over five decades had started an interest in its application in all areas of fibre and textile industries. The high molecular weight as well as wide molecular distribution caused the problems at the fibre preparation.

The introduction of chemical degradation enabled to prepare the PP with the lower molecular weight and narrower molecular distribution, what had led to an improvement of processability and increase of evenness of PP fibres. Today, the fibres prepared from ZN-PP are applied in the many engineering areas such as human and household goods, various electronic, building and medical products, automotive parts, etc.<sup>1</sup>.

After several years since the industrial application of ZN-PP there were generated the metallocene catalysts for the polymerisation of polyolefine polymers with narrower molecular weight distribution, lower melting temperature, tacticity etc.<sup>2-5</sup>.

mPP has the narrower molecular weight distribution  $M_w/M_n \approx 2-2.5$ , lower portion of high molecular fraction, lower rheological index polydispersity  $PI \approx 2.0$  (ref.<sup>7</sup>), lower elasticity of melt, low atacticity portion ( $< 0.5\%$ ) and index isotacticity above 99% (ref.<sup>1,6</sup>), lower melting temperature about 15 °C, crystallization temperature about 2–3 °C and melting enthalpy about 3–11 J g<sup>-1</sup> (ref.<sup>10,11</sup>). These properties of m-PP provide to use the higher take-up speed at the spinning with the lower rate of PP melt in the wide range of sheared rates. The application of direct deformation at the spinning and drawing of fibres from m-PP with the presented properties leads to their better drawingability, higher orientation and tenacity in comparison with the fibres prepared from ZN-PP. It is able to prepare the fibres from mPP with the lower linear density, higher tenacity, lower elongation and higher Young's modulus<sup>1,8,9</sup>.

This paper deals with the evaluation of structure, thermal and mechanical properties of drawn fibres formed from mPP and ZN-PP at the same prepared conditions.

The undrawn mPP and ZN-PP fibres prepared from the metallocene polypropylene HM562N (mPP, Lyondell Basell Co., Italy) and Ziegler-Natta polypropylene Tatrex HG1007 (ZN-PP, Slovnaft, a.s. Bratislava, Slovak Republic) with MFI = 27 g/10 min of the both polymers by classical procedure using laboratory pilot plant with the twin screw  $\phi = 16$  mm with the take-up speed at the spinning from 8.33 to 18.33 m s<sup>-1</sup>. The prepared undrawn fibres were drawn on the drawn ratio of 3.0

with the final linear density from 4.7 to 2.3 dtex.

Melting ( $\Delta H_m$ ) enthalpies of mPP and ZN-PP fibres were measured using DSC 7 Perkin Elmer and evaluated from thermograms of 1<sup>st</sup> heating. All measurements were carried out under nitrogen.

The birefringence represents the anisotropy of oriented polymer system and expresses the full orientation of macromolecular chains in fibres. The full orientation of m-PP and ZN-PP fibres was estimated on the basis of measurements of birefringence using polarization microscope DNP 714BI.

The average orientation of macromolecular chains in the surface layers of fibre has been estimated on the basis of the different speed sound between particles of variously oriented systems. The supermolecular structure of drawn mPP and ZN-PP fibres was determined on the basis of the measurement of sound speed in fibres using equipment of PND 129-126-06.

The Instron equipment was used for evaluation of the mechanical properties (tenacity and elongation at break, Young's modulus) of the mPP and ZN-PP fibres.

The mainly aim of this work is the comparison of the supermolecular structure and properties of fibres prepared from mPP and ZN-PP at the same spinning and drawing conditions. There were observed the effects the take-up of spinning on parameters of the supermolecular structure, thermal and mechanical properties of these fibres.

The melting enthalpies were estimated for the drawn mPP and ZNPP fibres from the endotherms measured at the 1<sup>st</sup> heating (Fig. 1). The conditions used at the spinning and drawing of fibres from polymers induce the form of their supermolecular structure which is different than the supermolecular structure of un-oriented polymers. The melting temperatures of fibres from both m-PP and ZN-PP are different and the melting temperatures of mPP fibres are lower about 8–10° than the ZN-PP fibres.

The melting enthalpies of drawn ZN-PP fibres are higher than the drawn mPP fibres in the full observed area of take-up spinning (Fig. 1). The mPP has the lower ability of crystallization, which goes out from their molecular structure<sup>11</sup>.

The direct deformation of undrawn fibres in process of their preparation on the drawn ratio = 3.0, excepted the fibres from mPP at the take-up spinning used of 15.83 and 18.83 m s<sup>-1</sup>, where the drawn ratios were of 2.7 and 2.5 increases the orientation of their macromolecular chains. It is represented by the growing of average orientation estimated on basis of the

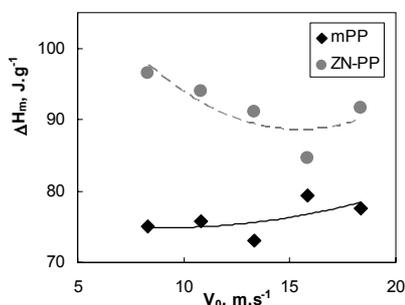


Fig. 1. The dependencies of melting enthalpy obtained from 1<sup>st</sup> heating of drawn mPP and ZN-PP fibres on take-up speed used

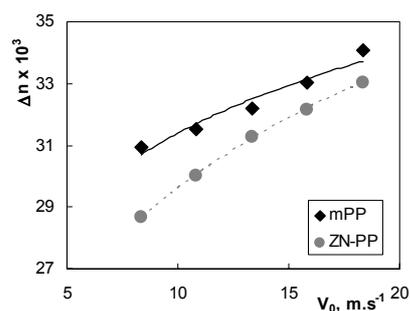


Fig. 2. The dependencies of birefringence on the take-up speed of drawn mPP and ZN-PP fibres

measured birefringence (Fig. 2). The birefringence of fibres from mPP as well as ZN-PP increases with the growing of take-up speeds at the spinning at the same drawn ratio, but the increase of birefringence of mPP is lower than the increase of fibre birefringence from ZN-PP. But, the absolutely values of birefringence of m-PP fibres are higher than the values of ZN-PP fibres. The both dependencies have the direct proportional in the observed areas of take-up speeds at the spinning without achievement of equilibrium state.

The similar dependence was obtained at the evaluation of average orientation estimated on the basis of measurements of sound speed of drawn m-PP and ZN-PP fibres (Fig. 3).

The better ability of deformation can support also the improvement of mechanical properties, mainly higher tenacity at break and Young's modulus and lower elongation at the break.

The previous positive results of structured parameters of mPP as well as ZN-PP fibres confirm the results obtained at the evaluation of the mechanical properties (tenacity at the break) (Fig. 4). The higher take-up speeds used at the spinning at the same drawn ratio of mPP and ZN-PP fibres induce proportionally the higher tenacity. But the tenacity of m-PP fibres is higher than the ZN-PP one (Fig. 4) and the increase of tenacity and Young's modulus is more rapid and elongation is slower than the increase of ZN-PP fibres. It is in the accordance with the formed supermolecular structure of drawn mPP.

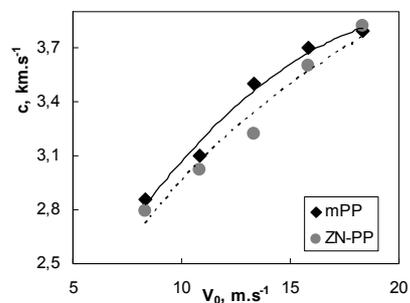


Fig. 3. The dependencies of sound speed on the take-up speed of drawn mPP and ZN-PP fibres

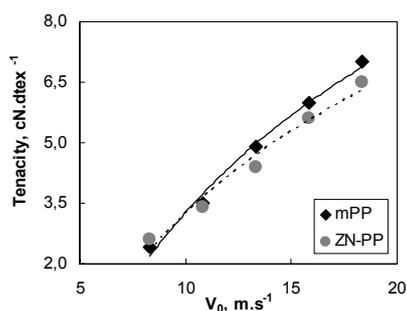


Fig. 4. The dependencies of tenacity on the take-up speed of drawn mPP and ZN-PP fibres

## Conclusion

- The melting enthalpies of mPP fibres are lower than the ZN-PP fibres prepared at the same spinning and drawing conditions.
- The lower level structural arrangement of undrawn mPP fibres ensures their better deformation at the same deformation (the same drawn ratio) with the improvement of structured parameters (the better orientation of macromolecular chains estimated on the basis of measurements of birefringence) of drawn mPP fibres.
- The better orientation of mPP fibres induces the improved mechanical properties in comparison with ZNPP fibres.

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0226-06.

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## CL-24 CRYSTAL STRUCTURE OF A 4,4'-BIPHENYLENE BASED POLYKETONE WITHOUT ETHER LINKAGES

ZULKIFLI AHMAD<sup>a</sup> and HOWARD M. COLQUHOUN<sup>b</sup>

<sup>a</sup> School of Material and Mineral Resources, Universiti Sains Malaysia, Transkrian, 14300, Pulau Pinang Malaysia, <sup>b</sup> The University of Reading, Whiteknight, Reading, Berkshire, RG6 6AH, UK

[zulkifli@eng.usm.my](mailto:zulkifli@eng.usm.my)

## Abstract

A wholly aromatic ketone polymer and its crystalline structure of the polymer was elucidated using powder XRD and electron diffraction method and interfaced with molecular mechanic force-field computational modeling. It was found that the polymer adopted an orthorhombic system in Pbcn having 2 chains per unit cell of dimensions  $a = 7.55$ ,  $b = 6.28$  and  $c = 17.88$  Å. The biaryl unit of the aromatic ring is coplanar with the ketone bridge torsion angle of ca. 30°. Reitveld refinement of final structure yield an agreement factor (Rwp) of 9.16 %. The simulated electron diffraction of the proposed structure corresponded well with that of the experimental.

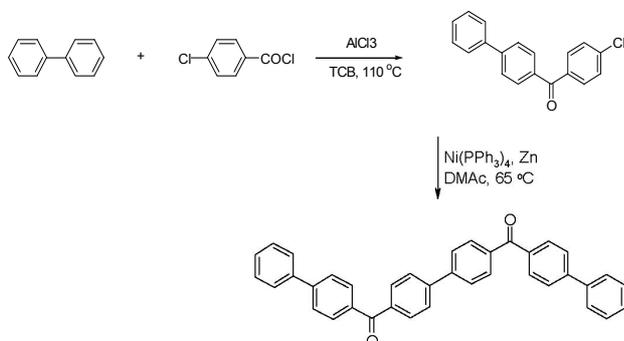
## Introduction

Aromatic polyketone is a high performance polymer widely used in automotive industry due to their ability to withstand high pressures, chemical resistant and high temperatures. This is due mostly to their highly crystalline nature. Several efforts were geared in elucidating and understanding the polymer crystal system. However, it is this very nature which hinder the production of high molecular weight polyketone which is indispensable for a good x-ray diffraction data. Numerous structural studies have been reported for aromatic polyketone series, mostly containing ether bond<sup>1-10</sup>. They display a consistent basic crystal structure with minor dimensional changes<sup>1-5</sup>, by adopting a space group of Pbcn with two chain orthorhombic cell. It has also been shown that the ether and ketone groups are crystallographically equivalent. Similarly, the substitution of biphenylene unit at each alternate phenyl position found in a homologous PEEK result in a crystal structure closely related to that of parent PEK and PEEK<sup>8</sup>. Interestingly, the simulated biphenylene unit displayed coplanarity despite this being an unfavorable conformation in gas phase<sup>9,10</sup>. To the best of authors knowledge, no structural study has previously been reported for wholly aromatic polyketones without ether linkages.

In the present work, poly(4,4'-biphenyleneketone), a biphenylene polyketone without ether linkages, were synthesized. Its crystal structure was elucidated using XRD powder data followed by computer modeling and simulation of its crystal structure whose structural parameters were based on synthesized six-ring all-ketone analogous oligomer, 4,4'-bis(4''-biphenylcarbonyl)biphenyl and other analogous oligomers previously studied.

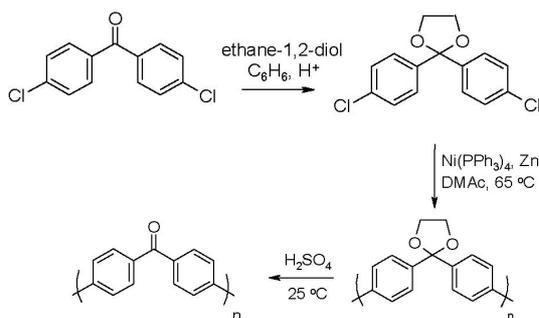
## Experimental Section

A six rings aromatic polyketone 4,4'-bis(4"-biphenylcarbonyl)biphenyl was firstly synthesized based on the reaction scheme 1 as shown below.



Scheme 1.

The polyketone, poly(4,4'-biphenyleneketone) was then synthesized based on the reaction scheme 2 as shown below



Scheme 2.

Table I  
Selected bond, angles and torsion angles for 1,4-polybiphenyleneketone

Bond	Distance(Å)	Bond	Angle(°)	Bond	Angle(°)
O-C9	1.240	C3-C8-C7	118.5	C7-C6-C5-C4	1.4
C1-C2	1.394	C1-C2-C3	120.6	C3-C4-C5-C6	-178.0
C6-C9	1.470	C3-C4-C5	118.0	C1-C2-C3-C4	0.1
C2-C3	1.492	O-C9-C10	119.6	C5-C6-C9-C10	-29.7
		C6-C9-C10	120.0		

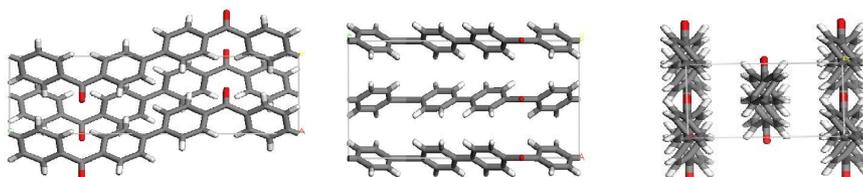


Fig. 1. Crystal structure of poly(4,4'-biphenyleneketone) in various; projections:(a) *bc* plane, (b) *ac* plane, (c) *ab* plane

## Crystallographic and modeling method

X-ray powder diffraction data were collected on a Bruker D5000 X-Ray powder diffractometer (The University of Reading). Computational modeling was performed using software package *Cerius2* (v.3.5). The model-building and energy-minimisation was derived from molecular mechanics Dreiding 2.21 Force-field. Rietveld refinement was performed in Rietveld Refinement module of *Material Studio* (v.2.0).

## Result and discussion

FTIR, H-NMR, C-NMR, DSC, elemental analysis and GCMS analysis confirm the right six ring oligomer as synthesized. It shows a melting point of 355 °CC (DSC) and a molar mass of 514.19 (*MS-CI*). The polyketone polymer was successfully synthesized by polycondensation of a ketal-protected monomer to give an amorphous polyketal, followed by hydrolysis to reform the ketone function (Scheme 2). FTIR spectrum corresponded well with the anticipated structure of the polymer. It is insoluble in most solvents which precluded NMR analysis. It showed a glass transition temperature of 322 °C and crystal melting range of 440–480 °C, the first ever reported thermal properties for this polymer. No other thermal transitions occurred up to 500 °C.

Modelling was initially performed by constructing a repeat unit of the polymer whose structural parameters were derived from the analogous six rings oligomers as well other related structures from past works<sup>11,12,13</sup>. This structure was energy minimized using Dreiding Force Field resulting an almost linear zig-zag chain conformation. An arbitrary unit cell of dimension 20.0 × 20.0 × 18.0 Å was created comprising of 2 minimised chains structure, one along the centre of the unit cell and the other passing through the origin with both parallel to *c*-axis. Successive optimization of the system was performed so as to give a simulated x-ray diffraction pattern comparable with the experimental. This operation finally led to a final structure with two diagonally-related chains, generated by *b*-glide symmetry, one passing along the *c*-axis and

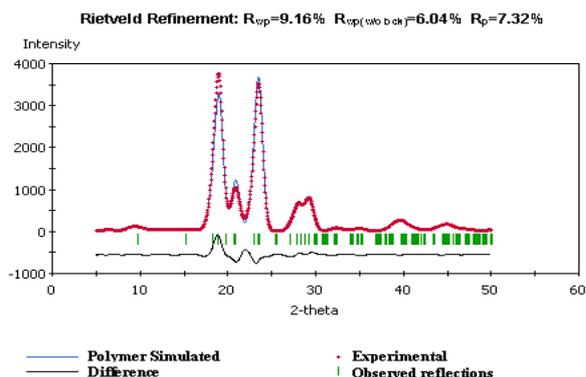


Fig. 2. Rietveld Refinement plot for poly(4,4'-biphenylene ketone)

the other, parallel to this, at the centre of the unit cell, with the carbonyl groups in register between the chains. The unit cell was orthorhombic in space group  $Pbcn$  with dimensions  $a = 7.56$ ,  $b = 6.384$  and  $c = 18.000$  Å. Rietveld Refinement was performed on the minimized crystal system which finally led to a  $R_{wp}$  value of 0.092. Selected chain conformation was given in Table I and the crystal structures viewed from various projections were shown in Fig. 1. Rietveld refinement plot was shown in Fig. 2. The aromatic rings in the biaryl unit are co-planar, with the C–C bond connecting the two rings set at 1.48 Å, whilst the C–O<sub>carbonyl</sub> distance is 1.23 Å. The space group of the polyketone found here is similar to the analogous polymer, poly(4,4'-biphenylene ether)<sup>14</sup> substantiating further the proposal that aromatic carbonyl and ether groups are crystallographically interchangeable.

## Conclusion

An aromatic polyketone without ether linkage was successfully synthesized and its crystal structure elucidated. The polymer adopt space group of  $Pbcn$  with unit cell dimension a

= 7.56,  $b = 6.384$  and  $c = 18.000$  Å. The biphenylene unit adopted a coplanar conformation with the carbonyl linkage torsional angle of ca. 37°. This work substantiate further that ether and carbonyl linkages are crystallographically equivalent.

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