# POSSIBILITY TO DETECT DEGRADED RECYCLED MATERIAL IN THE MOULDED PARTS FROM PP

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In the frame of injection moulding production process not all raw material creates the final products and a waste material is generated (defective and rejected products, cold runners, etc.). This technological waste is very often reused in production, which reduces the final production costs, however, this regrind or regranulated material affects the final properties of the part. The negative impact of recycled material presence depends on the degree of chain cleavage of the polymer macromolecules caused by high temperature load. The deterioration of the product end-use properties does not have to be demonstrated immediately (or in a short time period) after the removal of the part from injection mould. However, the product service life can be dramatically reduced which is simulated in the technical practice as exposure of the product to elevated temperature for prolonged time periods. This paper is focused on experimental methods for detection of heat-damaged recycled material incorporated to the non-filled moulded parts made of polypropylene. For the purpose of the analyses the multipurpose test specimens type A (specified by ISO 3167 standard) were prepared under the conditions defined in ISO 1873-2 and ISO 294-1 standard (melt temperature, mould temperature, injection rate, holding time, cycle time, etc.). Subsequently, the melt was overheated within the injection unit which caused the heat-induced macromolecule cleavage. This material was used for production another specimens that were then grinded and added to the original (virgin) raw material in the wide range of concentrations (from 10 to 100 wt%). These final specimens were analyzed using the physical methods modified for engineering practice to determine morphological, rheological, thermal and physical-mechanical properties of the moulded parts.

**KEYWORDS**

*recycled material, polypropylene, rheological properties, mechanical properties, differential scanning calorimetry, induction oxidation time*

## 1 INTRODUCTION

During the processing of polymer are formed by technological waste that can be recycled and re-processed even with minimal negative effects on parts quality. Polypropylene is one of the most widely used polymers across industrial applications. When the technological parameters are not kept during the processing of polypropylenes, the macromolecules can be subjected to high temperatures and shear stresses and thermal or thermal-oxidation degradation mechanism could be activated [Dobransky 2007]. The degradation processes of polypropylene macromolecules depend on the length of the polymer chain and are particularly fast and dangerous [Bertin 2010]. Polypropylene is very prone to all types of degradation because of its chemical structure - specifically the presence of a labile tertiary carbon atom in the main chain. This phenomenon results in chain scission, reduction of molecular weight, build-up of hydroxyl and carbonyl compounds, and loss of tensile strength. Defective products and process waste are not suitable for re-processing by mechanical (material) recycling. Otherwise (without a good stabilization) the desired product quality cannot be achieved. Applicability of selected methods for the detection of thermally damaged recycled polypropylene added to the virgin material is the main aim of this paper [Crompton 2006].

There are different experimental techniques to determine the chemical changes within the polymer structure. The Melt Flow Index (MFI) measures the fluidity of a polymer melt going through a cylinder. The polymer melt is exposed to specific temperature and load. The results as other rheological characteristics of polymers are strongly influenced by the molecular weight [Drabek 2015].

The chemical and molecular weight variations can affect the thermal transitions of the polymer, and thus, the final mechanical and physical material properties. The transitions can be determined e.g. by means of Differential Scanning Calorimetry (DSC). DSC measurement also provides information about the crystallization behaviour and the content of organised regions within the semi-crystalline polymers [Běhálek 2016].

With respect to the mechanical properties, tensile is the most popular test allowing the analysis of differences in mechanical properties such as Young modulus and stiffness, yield strength and ductility [Senkerik 2014].

The fracture toughness as a material parameter, that implies stiffness, strength and strain to failure, is of basic importance for application fields in which recycled plastic are subjected to impact and severe safety requirements have to be met by the designer. Fracture properties are strongly influenced by two principal areas. Firstly, the external conditions, e.g. temperature, strain rate, presence of geometrical discontinuities as cracks, type of loading and environment. Secondly, these properties are influenced by the microstructural parameters, which include crystalline structure, degree of crystallinity, supermolecular structure or skin-core configuration [Moeller 2018].

## 2 EXPERIMENTAL PROCEDURE

Polypropylene was used for experimental measurements, respectively poly (propylene-co-ethylene) Sabic CX02-82 with Melt Volume-flow Rate (MVR) 19 $cm^3 \cdot 10min^{-1}$. This material is optimised by emission exposure and is a part of high crystalline copolymers family. It is the alternative to conventional talc-filled copolymers and is typically used for automotive interior applications.

In accordance with ISO 1873-2 (Polypropylene moulding and extrusion materials – preparation of test specimens and determination of properties) the specimens were moulded (acc. to ISO 294-1). The optimal melt temperature was 200 °C. Subsequently, the melt temperature was increased up to 300 °C which simulated together with increased back pressure the degradation processes of the virgin material. The scission of macromolecules chains induced the increase in MVR index to the value of 50 $cm^3 \cdot 10min^{-1}$ (if the MVR increases by more than 1,5 times comparing to the virgin polypropylene the injection moulding evoked the molecular breakdown, see ISO 1873-2). The specimens produced under the conditions having strong impact on the macromolecular length were ground using the knife mill and the regrind was added to the virgin material at

the ratio of 10:90, 20:80, 30:70, 50:50 and 100:0. From these mixtures the final specimens were produced again under the optimal technological conditions (melt temperature 200 °C, mould temperature 40 °C, average injection rate 200 mm·s⁻¹, holding time 40 sec. and overall cycle time 60 sec).

Different experimental techniques have been used to determine structure variations, as well as fracture mechanics parameters:

- MVR index measurements for determining the molecular structure (acc. to ISO 1133-1) ;
- Calorimetry techniques for melting and crystallization behaviour and for oxidation stability evaluation (acc. to ISO 11357-1/3/6);
- Non-instrumented Charpy impact tests for impact properties determination (acc. to ISO 179-1);
- Tensile and flexural tests for mechanical parameters determination (acc. to ISO 527-1/2 and ISO 178).

### 2.1 Melt volume-flow rate index (MVR)

The melt flow rate indicates the viscosity of polymer melt. The melt volume-flow rate (MVR) is defined as the volume of polymer in cubic centimetre flowing per 10 minutes through a capillary of specific diameter (2.095 mm) and length (8.00 mm) by a pressure applied via a range of standard weights at specified temperature. The final value is not universal and corresponds to the conditions of the test. The fact must be taken into account that the viscosity of any polymer material depends on the applied forces [Han 2007].

This simple test is very useful for fast identification of the polymer viscosity. Furthermore, the MVR index provides the basic information about the average molecular weight of the analysed polymer. Higher melt flow rate corresponds to low molecular weight.

The melt volume-flow rate was determined according to ISO 1183-1 at the specific temperature of 230 °C and under the load of 2.16 kg. The resulting values of MVR index depending on the amount of recycled material that is thermally degraded are shown in Fig. 1. With the increasing proportion of recycled material in the mixture with original PP the overall decrease in the molecular weight can be identified. With 10 wt% of recycled thermally degraded material incorporated into the virgin material the value of MVR increased approximately by 14 %, respectively by 24 % (with 20 wt% of recycled material), by 39 % (with 30 wt% of recycled material) and by 65 % (with 50 wt% of recycled material). During the analysis of thermally degraded material the final MVR index reached the values 2,5 times higher (lower viscosity) comparing to the values reached by the virgin material.
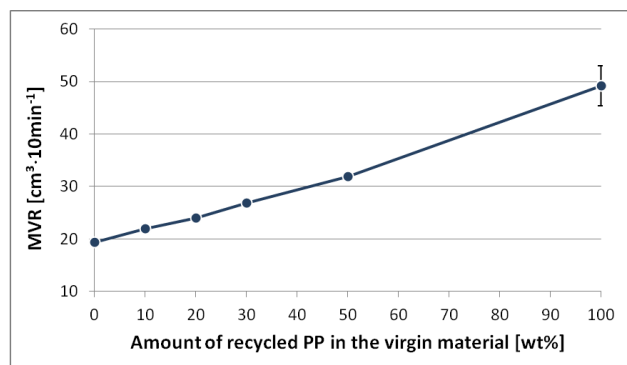


**Figure 1.** Melt flow index depending on the amount of thermally degradated polypropylene in the virgin material

### 2.2 Melting and crystallization behaviour

Polypropylene's melting and crystallization behaviour influenced by the amount of recycled material in the virgin polypropylene was investigated using a regular differential scanning calorimetry (DSC) according to ISO 11357-1/3.

Study of melting and crystallization behaviour of polypropylene with the addition of recycled material was carried out using the DSC1/700 Mettler Toledo which was calibrated against the indium and zinc standard. An empty aluminium crucible was the reference sample. Test samples (10 ± 0.3 mg) were exposed to two heating cycles (linear heating rate: 10 °C·min⁻¹) in flowing atmospheres of nitrogen at flow rate 50 ml·min⁻¹. Results from first cycle reflected initial state of samples (as a result of thermal history induced by the processing steps). The limit temperature was 200 °C (over the melting temperature) when the material achieved equilibrium state. The second measurement was carried out after the cooling of sample at defined cooling rate of 10 °C·min⁻¹ to complete removal of previous thermal history and to compare the material properties of individual samples. Principally, the sample and the reference were maintained at the same temperature. All the energy divergences (indicating the sample transitions) are recorded in the DSC diagrams as a rate of dQ/dt against a temperature or a time.
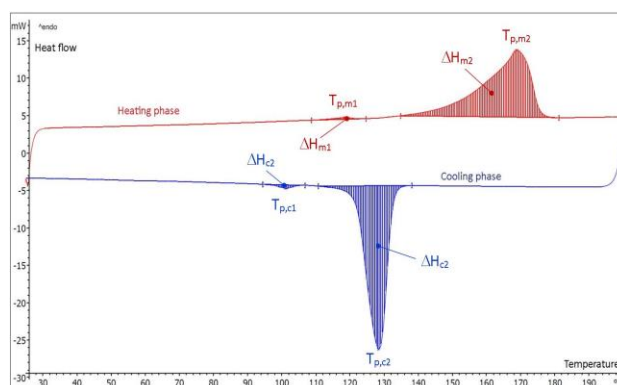


**Figure 2.** DSC thermogram of virgin polypropylene copolymer

From the DSC thermograms (see Fig. 2) the impact of the addition the recycled material on melting and crystallization behaviour of polypropylene is evident. Thermal properties such as endothermic melting temperature peak ($T_{p,m}$), melt crystallization temperature peak ($T_{p,c}$), fusion enthalpy ($\Delta H_m$) and melt crystallization enthalpy ($\Delta H_C$) are shown in Table 1 and Table 2.

**Table 1.** Melting behaviour of test samples

| Amount of recycled PP [wt%] | $T_{p,m1}$ [°C] | $\Delta H_{m1}$ [J·g⁻¹] | $T_{p,m2}$ [°C] | $\Delta H_{m2}$ [J·g⁻¹] |
|---|---|---|---|---|
| 0 (virgin) | 118.3 | 0.9 | 168.2 | 87.5 |
| 10 | 118.1 | 0.9 | 167.8 | 87.2 |
| 20 | 118.8 | 1.0 | 167.6 | 86.4 |
| 30 | 118.3 | 0.9 | 167.6 | 86.7 |
| 50 | 118.8 | 0.9 | 167.4 | 84.9 |
| 100 | 119.5 | 1.2 | 168.0 | 83.6 |

Based on the results of the DSC analysis the fact can be stated that the addition of thermally degraded regrind to the virgin material did not evoke perceptible changes of the thermal properties during melting and crystallization transition phases of the polymers. With increasing content of the recycled material, however, a decline in the value of the enthalpy of

fusion ($\Delta H_{m2}$) was observed, which is related to the crystalline regions formed by regular arrangement of propylene units in the macromolecules chains. Decline in the fusion enthalpy indicated lower degree of crystallinity and thus lower rigidity and strength of the material. These changes were obvious for the mixtures with higher content of recycled regrind than 50 wt%.

**Table 2.** Crystallization behaviour of test samples

| Amount of recycled PP [wt%] | $T_{p,c1}$ [°C] | $\Delta H_{c1}$ [J·g$^{-1}$] | $T_{p,c2}$ [°C] | $\Delta H_{c2}$ [J·g$^{-1}$] |
|---|---|---|---|---|
| 0 (virgin) | 129.5 | -88.8 | 101.4 | -1.3 |
| 10 | 129.6 | -88.5 | 101.7 | -1.3 |
| 20 | 129.0 | -88.0 | 101.5 | -1.4 |
| 30 | 129.3 | -87.9 | 102.0 | -1.3 |
| 50 | 128.9 | -84.9 | 102.2 | -1.3 |
| 100 | 129.2 | -84.9 | 102.7 | -1.5 |

### 2.3 Oxidation induction time (isothermal OIT)

The oxidation stability was determined via the Oxidation Induction Time (OIT) by means of differential scanning calorimetry in standardized procedures acc. to ISO 11357-6. In practice, two different methods are used: dynamic and isothermal oxidation induction time tests [McKeen 2014]. In isothermal OIT tests, the materials to be investigated are first heated under a protective gas, then held at a constant temperature for several minutes to establish equilibrium state and subsequently exposed to an atmosphere of oxygen or air. The time interval from the first contact with oxygen until the beginning of oxidation is called the oxidation inductive time. For polypropylene, a longer OIT time means that the oxidation stability is better and the lifetime therefore longer.
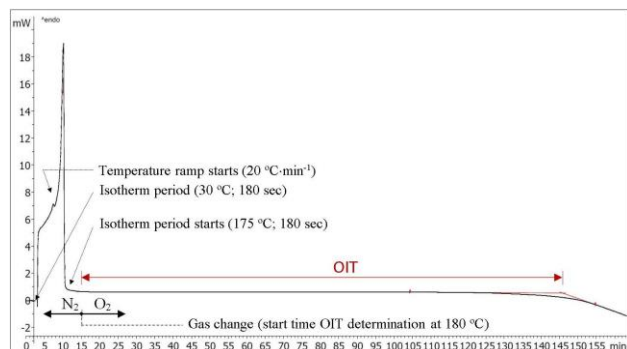


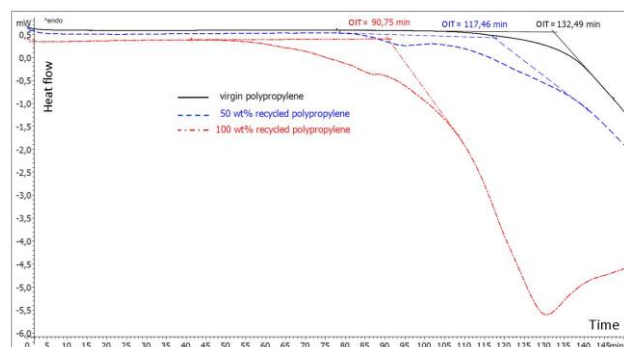**Figure 3.** DSC thermogram of virgin copolymer polypropylene during OIT analysis



**Figure 4.** OIT curve of test samples measured in a DSC

The sample was heated in an open DSC pan under the atmosphere of nitrogen gas from 30 °C to a test temperature 175 °C at a fast heating rate: 20 °C·min$^{-1}$. The instrument was

then switched to isothermal mode and the sample was exposed to an oxygen atmosphere by switching the pure gas. The OIT was expressed as the elapsed time from the test samples exposure to an oxidizing gas (oxygen) to the onset of oxidation at the isothermal test temperature. The time interval was determined from the DSC curve as the time-distance between the admission of oxygen and the point of intersection of the "tangent" to the oxidation exotherm and the "baseline" as shown in Fig. 3. The isothermal test temperature is usually selected to procedure OIT values in the range 15-150 min. OIT curve of test samples measured by DSC is shown in Fig. 4 and OIT results are summarised in Table 3.

**Table 3.** Oxidation induction time of test samples

| Amount of recycled PP [wt%] | OIT [min] | Amount of recycled PP [wt%] | OIT [min] |
|---|---|---|---|
| 0 | 132,5 | 30 | 121,6 |
| 10 | 129,2 | 50 | 117,5 |
| 20 | 125,1 | 100 | 90,8 |

The first significant differences in the behaviour of a material during the OIT analyses were detected from 30 wt% of thermally damaged regrind in virgin polypropylene. The oxidation stability decreased by approximately 8 % comparing to pure material. OIT values dropped by almost 32 % when analysed the specimens made only from the regrind.

### 2.4 Mechanical properties

Study of mechanical properties was performed under static loading in tension and also bending and dynamic impact stress (Charpy method). Testing samples were conditioned and tested in the standard environment 23/50 acc. to ISO 291 and ISO 1873-2.

Tensile properties were determinate using the multipurpose test specimens of type 1A acc. to ISO 527-1/2: tensile modulus ($E_t$) deformed by testing rate of 1 mm·min$^{-1}$, tensile strength ($\sigma_m$) and tensile strain at break ($\varepsilon_b$) deformed by testing rate of 50 mm·min$^{-1}$ acc. to ISO 1873-2. Changes of polypropylene tensile properties, depending on the amount of recycled polypropylene in virgin material are obvious from the Fig. 5, 6, 7 and 8.

Changes in tensile properties were negligible considering the degree of results repeatability for the mixtures containing less than 50 wt% of thermally damaged material. Material ductility, respectively tensile strain at break, was unchanged considering the variances of measured values. In the case of specimens made only from thermally damaged material the tensile modulus decreased by 6 %, tensile strength by 4 % and the tensile strength increased by 24 %.
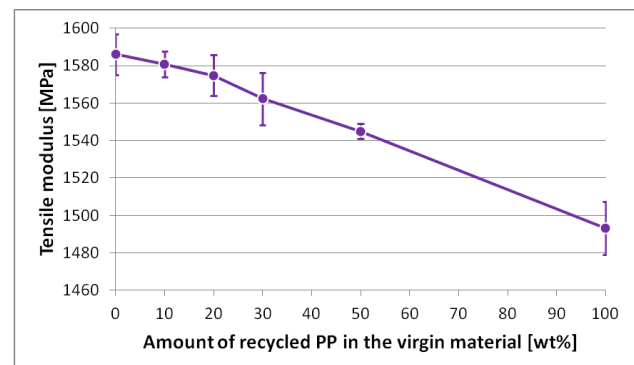


**Figure 5.** Tensile modulus depending on the amount of recycled polypropylene in the virgin material
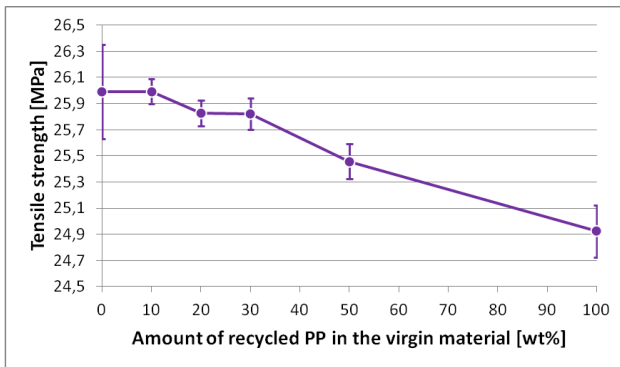
**Figure 6.** Tensile strength depending on the amount of recycled polypropylene in the virgin material
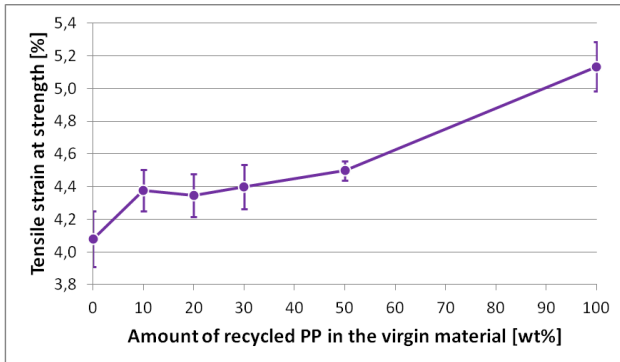


**Figure 7.** Tensile strain at strength depending on the amount of recycled polypropylene in the virgin material
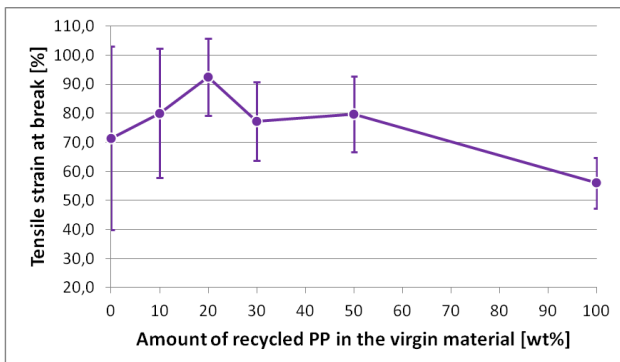


**Figure 8.** Tensile strain at break depending on the amount of recycled polypropylene in the virgin material
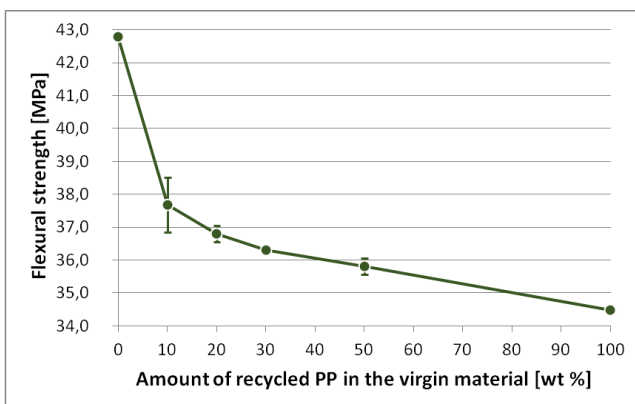


**Figure 9.** Flexural strength depending on the amount of recycled polypropylene in the virgin material

Flexural properties: flexural strength ($\sigma_{fM}$) and flexural modulus ($E_f$) were determinate acc. to ISO 178 with testing rate 2 mm·min$^{-1}$ on specimens with dimensions of 80 x 10 x 4 mm und with the distance between the supports 64 mm. Changes of

polypropylene flexural properties depending on the amount of recycled polypropylene in virgin material are obvious from the Fig. 9 and Fig. 10.
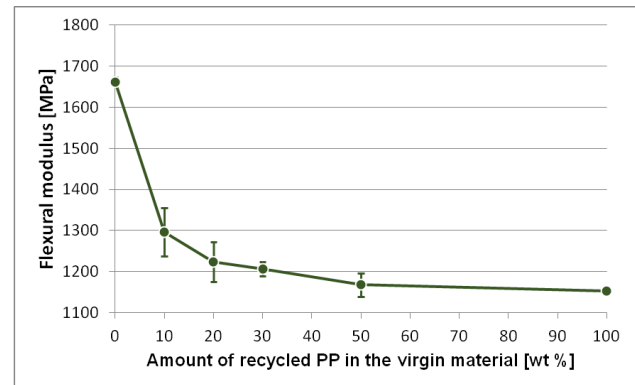


**Figure 10.** Flexural modulus depending on the amount of recycled polypropylene in the virgin material

Even a small amount of thermally degraded regrind in virgin material (10 wt %) significantly affected the bending properties of the specimens. The flexural strength decreased by 12 % with the presence of 10 wt% of regrind and flexural modulus dropped by 22 %. The flexular properties measured on specimens produced only from the thermally degraded material decreased by 19 % and flexural modulus decreased by 30 %.

The Charpy impact tests were performed on specimens with dimensions of 80 x 10 x 4 mm. The specimens had V-notch - type A with notch base radius 0.25 mm. The tests were carried out on the impact tester Resil 5.5 Ceast with energy scale from 0.5 J to 2 J so that no less than 10 % but no more than 80 % of stored energy was exerted on specimen fracture. The distance between the supports was 62 mm and the specimens had edgewise orientation (method ISO 179-1/1eA).
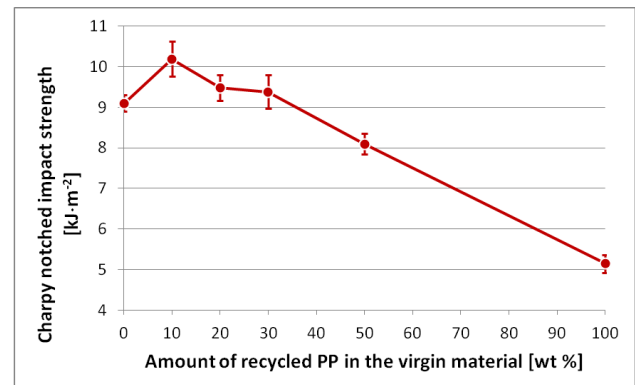


**Figure 11.** Charpy notched impact strength depending on the amount of recycled polypropylene in the virgin material

In the case of Charpy notched impact strength (see Fig. 11) the addition of thermally degraded regrind to the virgin material affected the measured values from the content higher than 50 wt%, which induced the decrease in the Charpy notched impact strength by approximately 11 %. The specimens produced from thermally degraded material reached only 66 % of Charpy impact strength comparing to virgin material.

## 3   CONCLUSIONS

This contribution deals with the feasible detection techniques developed for determination of thermal decomposition of recycled regrind incorporated into the virgin polymer matrix

based on polypropylene, respectively poly (propylene-co-ethylene). In the frame of this study standard experimental techniques were compared that are widely used in the industrial practice. These methods generally provide the information about the melt flow properties, material oxidation stability and also the thermal and physical properties.

Based on the results the fact can be clearly stated that the melt-flow index acc. to ISO 1183 is the most reliable method for detection of thermally damaged material (regrind) within polypropylene. The MVR index increased by 14 % with adding 10 wt % of regrind, by 24 % with 20 wt % of recycled material. The thermally degraded material induced changes in the molecular structure of the material, respectively the reduction of final molecular weight.

Bending test manifested the most predicative results among the mechanical properties tests for detection of the recycled material presence. Similarly as MVR method the bending tests revealed the obvious decrease in mechanical properties even for minimal analysed content of thermally degraded material. The bending strength was reduced by approximately 12 % and the flexural modulus dropped by 22 % with 10 wt% of regrind in the original polypropylene (the mixture with 20 wt% of recycled material reached the flexural strength lower by 14 % and modulus of elasticity by 26 %). The other techniques based on the mechanical properties measurement did not allow unambiguous detection of thermally degraded material up to the content of 20 wt %. Changes in tensile properties among the analysed samples can be considered as negligible with respect to low degree of repeatability in the frame of unfilled polypropylene and detectable changes in Charpy impact toughness were observed only when the proportion of recycled material in the original polypropylene was more than 50 wt %.

Differential scanning calorimetry provided the information about thermal behaviour of the material, which reflects the morphology. DSC analyses are also used for determination of the oxidation induction time under constant temperature load in oxygen atmosphere. Based on the findings the fact can be stated that OIT method is more feasible for determination of recycled material presence, respectively thermally degraded regrind. Conventional DSC diagrams showed transition temperatures and enthalpy of the transitions (melting and crystallization processes). Decrease in the enthalpy of fusion, which indicated lower degree of crystallinity, was evident for mixtures with minimal regrind content of 50 wt %. On the other hand the OIT analyses detected the presence of recycled material in mixtures containing the 30 wt % of the regrind.

## ACKNOWLEDGEMENT

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