Chapter 9

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THE EFFECT OF THERMAL TRANSFORMATIONS ON THE MELT MASS-FLOW RATE AND THE MELT VOLUME-FLOW RATE OF ABS

Abstract: The melt mass-flow rate and the melt volume-flow rate determine the processing conditions for thermosetting plastics, and in recycled materials, they are indicators of the susceptibility of polymers to recycling and its frequency. This paper investigates the melt mass-flow rate and the volume-flow rate of ABS subject to the number of thermal transformations, including transitions to plastic state, liquid state and solid state induced by cooling. The results were subjected to mathematical analysis. The examined melt flow rates change very slowly, therefore, polymer materials can be processed repeatedly.

Key words: polymers, melt mass-flow rate, melt volume-flow rate, recycling.

9.1. Introduction

Melt mass-flow rate and melt volume-flow rate are the key process indicators in the production of polymers by injection molding. Flow rate values are directly related to material viscosity which, in turn, is determined by the length of the polymer chain and its branches. A sound knowledge of the above indicators is essential in the process of injecting recycled compounds. It supports optimal setting of operating parameters in an injection molding machine and, in extreme cases, it prompts the operator to select an alternative recycling method. Changes in melt flow rate values are determined mainly by the structure and crystallinity of

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a polymer chain. Different changes are observed in materials with amorphous structure, crystalline or partially crystalline structure (ŻUCHOWSKA D. 2000, SZLEZYNGIER W. 1998, BŁĘDZKI A.K. 1997, MAZUR P., JASIUKIEWICZ D. 2010, MAZUR P., SMOLEŃSKI P. 2010)

The key methods of ABS production are (ŻUCHOWSKA D. 2000, SZLEZYNGIER W. 1998):

- mechanical mixing of polybutadiene (or butadiene/styrene copolymer) with the S/AN copolymer and grafting of the styrene/acrylonitrile copolymer onto polybutadiene as the polymer matrix,
- double-stage process involving butadiene polymerization and copolymerization.

The first method involves mechanical mixing of the S/AN copolymer with polybutadiene (or butadiene/acrylonitrile rubber) at plastic-state temperature on hot rollers and screw extruders (ŻUCHOWSKA D. 2000, SZLEZYNGIER W. 1998). The second method is a two-stage processes. The first stage involves radical polymerization of butadiene to produce butadiene in the form of rubber latex. In the second stage, acrylonitrile is copolymerized with styrene (to produce S/AN), and the resulting S/AN copolymer is grafted onto polybutadiene (ŻUCHOWSKA D. 2000, SZLEZYNGIER W. 1998).

ABS (acrylonitrile-butadiene-styrene), a thermosetting polymer with amorphous structure, is highly valued for its usable properties, including (ŻUCHOWSKA D. 2000, SZLEZYNGIER W. 1998):

- high rigidity,
- high notched impact strength,
- resistance to stress corrosion cracking.

ABS plastics can be used in a wide temperature range of -40ºC to 80ºC. ABS copolymers are characterized by significant density, high levels of chemical resistance and creep resistance (SIKORA R. 1995, ŻUCHOWSKA D. 2000).

Other characteristic features of ABS include (SIKORA R. 1995, ŻUCHOWSKA D. 2000):

- moderate hardness,

- glossy surface finish (80 – 90% light reflection),
- ease of processing and very high mold quality,
- low solubility,
- low fatigue strength,
- low resistance to UV radiation,
- maximum continuous service temperature of around 70^0C.

There are various types of ABS plastics for injection molding, extruding and special applications. ABS is more hygroscopic than polystyrene (it absorbs up to 3% of atmospheric humidity in 24 h), therefore, it has to be dried thoroughly before processing. The discussed material may produce smoke when overheated ($250 \div 260^0$C). Higher pressure and shorter injection times are commonly used to prevent the above. The following processing parameters are applied in injection molding of ABS (SIKORA R. 1995, ŻUCHOWSKA D. 2000, SZLEZYNGIER W. 1998):

- cylinder temperature – $220 \div 275^0$C,
- mold temperature – $40 \div 95^0$C,
- injection pressure – $70 \div 180$ MPa.

Precise determination of viscosity curves illustrating the correlation between material viscosity and share rate is a costly and time-consuming process. For this reason, MFR and MVR indicators are used to determine the plasticity of polymers in processing machines. MFR and MVR values indicate the mass and volume of material extruded in the course of 10 minutes through a nozzle with a given diameter, under specific load and temperature. The melt flow index is determined by measuring average melt flow at given values of key processing parameters. The melt flow index is a measure of a material's flowability, which is the reverse of viscosity. It represents a point on the viscosity curve of the analyzed material, determined at the temperature of measurement. The melt flow index does not unanimously characterize the examined material, and it may be identical for plastics with different viscosity values (PIELICHOWSKI J., PUSZYŃSKI A. 1998). Testing requirements (ISO 1133, PN-93/C-89069) are imposed on capillary and piston geometry, piston load, time and temperature of measurement. Measurement results are stated in g/10min (MFR) and cm^3/10min (MVR). The melt mass-flow rate and volume-flow rate are determined by plastifying a sample in a heated cylinder, extruding the plastified material through a nozzle in the lower part of the cylinder, measuring the quantity of extruded matter and piston displacement.

9.2. Aim

The aim of this study was to determine correlations between the number of thermal transformations and the melt mass-flow rate and volume-flow rate of ABS for injection molding.

9.3. Materials and Methods

The tested material was ABS, a polymer which is widely used in aviation, motor, electrical engineering and electronic industries as well as in the production of household equipment. Granulated ABS for injection molding was used (Fig. 9.1). The experiments were carried out in accordance with standard ISO 1133 (PN-93/C-89069). Measurements were performed with the use of the REO-100 plastometer (Fig. 9.3). .

Piston load and measuring temperature were set in view of the type of analyzed material and its properties. The results were given in g/10min (MFR) and cm^3/10min (MVR). Prior to measurements, the cylinder and the piston of the plastometer were heated to the temperature of 220ºC which was maintained with a tolerance margin of $\pm 0.5^0$C for 15 minutes before and during the test. Measurements were performed with the use of the REO-100 plastometer at the temperature of 220ºC and under the load of 2160 g. The tested ABS had the density of $\rho = 1.06 g/cm^3$.

Fig. 9.1. Granulated ABS.

Source: own study.

The REO-100 plastometer has the following parameters:

- max. heater power - 1050 W,
- temperature range - 30-300^{0}C,
- temperature stabilization - ± 0.2^{0}C,
- time measurement accuracy - 10 ms,
- route measurement accuracy – 5 μm,
- route measurement - 100 mm.

The tested substance was granulated ABS. After the experiment, the material was mechanically cut into fractions with the length of 4 mm (Fig.9.7). The resulting regranulate (Fig.9.2) was tested in the plastometer. The first ten MFR and MVR measurements were performed after every heat transformation, and successive measurements – after every 5 transformations, i.e. after 15, 20, 25...100 transformations. Ten MFR and 10 MVR measurements were performed for each transformation.

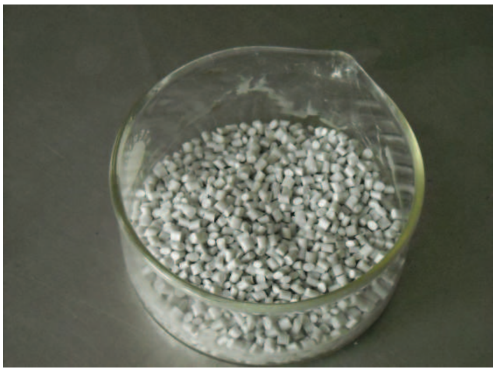

Fig. 9.2. Regranulate.

Source: own study.

9.4. Results

The resulting melt mass-flow rates are shown in Figure 9.8. The curve presenting changes in melt mass-flow rates is described by equation (9.1):

$$y = -0.0016x^2 + 0.449x + 48.858 \quad (9.1)$$

for which $R^2 = 0.9358$.

The curve presenting changes in melt mass-flow rates is shown in Figure 9.9, and its mathematical form is described by equation (9.2):

$$y = -0.0017x^2 + 0.4435x + 45.726 \quad (9.2)$$

for which $R^2 = 0.9382$.

The values of MFR and MVR increase with every thermal transformation. The above changes take place very slowly, which is why the analyzed polymer can be recycled many times. After the 100^{th} transformation, the value of MFR changes by 47%, and the value of MVR – by 54%. The viscosity of ABS decreases with every transformation. The above results from degradation and destruction of the studied polymer (chain shortening) due to the effects of processing temperature and mechanical processing (recycling). MFR and MVR are closely related, as demonstrated by the similarities in regression curves and equations.

Fig. 9.3. REO - 100 plastometer.

Source: own study.

Fig. 9.4. Parameter setting in the REO – 100 plastometer.

Source: own study.

Fig. 9.5. MFR measurements in the REO – 100 plastometer.

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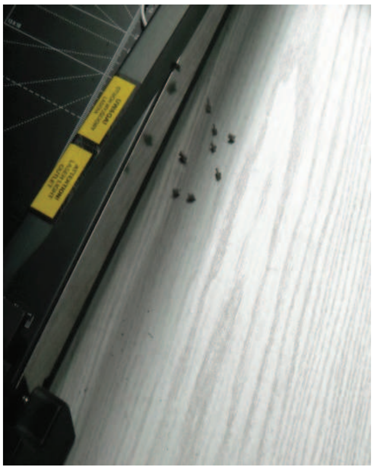

Fig. 9.7. Material cutting after plastometer measurements.

Source: own study.

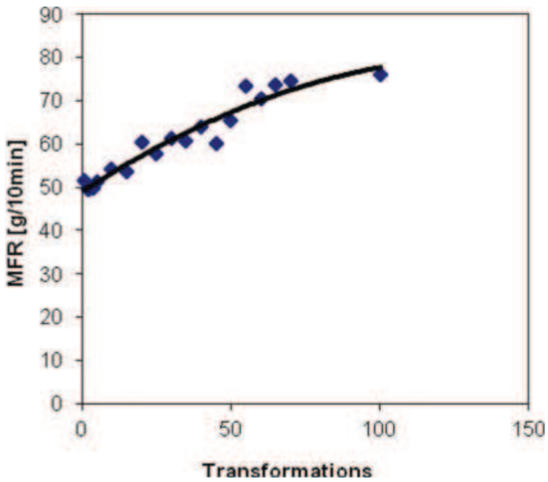

Fig. 9.8. Changes in melt mass-flow rates subject to the number of thermal transformations.

Source: own study.

The quality of ABS surfaces deteriorated after the 20th transformation. The surface was deprived of its glossy appearance, it became matte and rough. On account of esthetic considerations, ABS should not be recycled more than 20 times. After the 20th change, ABS can be only used as an additive in primary production to lower production costs.

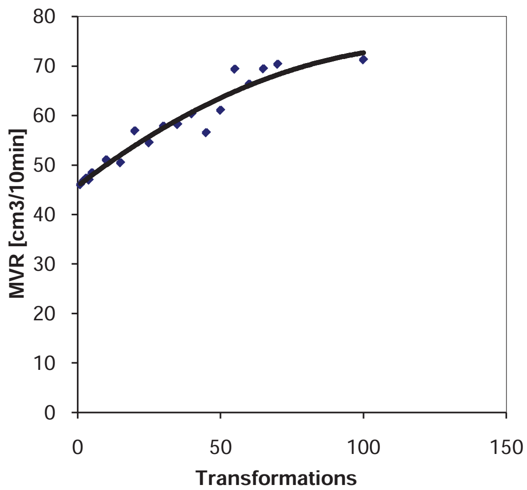

Fig. 9.9. Changes in melt-volume flow rates subject to the number of thermal transformations.

Source: own study.

9.5. Conclusions

In this experiment, similar changes were observed in the value of MFR and MVR. The analyzed indicators increased with every recycling process. After the 100th transformation, the value of MFR was determined at 75.955 g/10 (initial value of 51.415/10 min) and the value of MVR – 71.215 cm^3/10 min (initial value of 46.03 cm^3/10 min). The noted changes in the value of the examined indicators suggest that ABS can be recycled an unlimited number of times.

PPS and PC were subjected to identical tests. The results reveal completely different changes in the analyzed indicators (MFR and MVR) subject to the number of heat transformations. The curve presenting changes in the melt mass-flow rate can be described by the following equation (9.3) (MAZUR P., SMOLEŃSKI P. 2010):

$$y = 0.0002x^3 - 0.0142x^2 - 0.5386x + 47.838 \quad (9.3)$$

for which $R^2 = 0.8747$.
The curve presenting changes in the melt volume-flow rate can be described by equation (X.4):

$$y = -0.0026x^2 - 0.4968x + 35.477 \quad (9.4)$$

for which $R^2 = 0.8801$.
For PC, the curve presenting changes in the melt mass-flow rate can be described by equation (X.5) (MAZUR P., JASIUKIEWICZ D. 2010):

$$y = 14.587e^{0.6927x} \quad (9.5)$$

for which $R^2 = 0.9589$.
The curve presenting changes in the melt volume-flow rate can be described by equation (X.6):

$$y = 12.381e^{0.6883x} \quad (9.6)$$

for which $R^2 = 0.9601$.

A comparison of the test results reported for the three analyzed polymers indicates that PC is the least stable polymer due to the effect of heat transformations on MFR and MVR values which increased rapidly and which could be determined up to the fourth transformation. Successive transformations led to uncontrolled flow without loading in plastometer measurements. In PPS, MFR and MVR values changed significantly more slowly and show a decreasing trend. The changes in the examined indicators were analyzed up to the 40^{th} transformation. Recycling after the 40^{th} transformation significantly increases energy consumption in injection molding due to a considerable drop in MFR and MVR values in comparison with the original material. ABS is the most stable polymer due to very slow changes in the analyzed indicators (increasing trend), and it can be recycled even after the 100th transformation.

Further experiments will be carried out to determine changes in the mechanical properties of ABS which are induced by thermal transformations.

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