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Recovery of mechanical properties of aged polystyrene after reprocessing

RAPID COMMUNICATION

Summary — A combined procedure of thermal ageing followed by injection molding has been applied for ten times to simulate the repeated recycling. The processability of the recycled material was somewhat improved and the mechanical parameters were rather retained. Regular oscillations in strength characteristics of the successively aged and recycled samples have been registered. Namely, stress at break was repeatedly decreased and restored again after ageing and reprocessing steps, respectively. The very similar zig-zag pattern has been observed for elongation at break. Similarly, impact strength of the remolded samples shows on average better values than those of the aged samples. On the contrary, z-average molecular weight and melt flow rate were changed rather monotonically — a decrease and on increase, respectively. Considering the above, the observed phenomenon of alternating deterioration and recovery of the strength parameters has been attributed to material homogenization under the reprocessing steps.
Key words: polystyrene, simulated recycling, multiple reprocessing, tensile test, molecular weight, melt flow rate.

POPRAWA WŁAŚCIWOŚCI MECHANICZNYCH STARZONEGO POLISTYRENU PODDANEGO RECYKLINGOWI

Streszczenie — Badano właściwości polistyrenu poddanego symulowanej recyrkulacji materiałowej. W badaniach zastosowano kombinowaną procedurę złożoną z kolejnych cykli starzenia termicznego i następującego po nich wtryskiwania. Sprzyjający przetwarzalności recyklatów wzrost wartości wskaźnika szybkości płynięcia (MFR) (rys. 2) oraz spadek temperatury płynięcia (rys. 1) spowodowane są stopniowym zmniejszaniem się z-średniego ciężaru cząsteczkowego (rys. 3). Stwierdzono regularne cykliczne zmiany wytrzymałości na zerwanie, wydłużenia przy zerwaniu oraz udarności. Badane właściwości mechaniczne otrzymanych metodą wtryskiwania próbek ulegają pogorszeniu po kolejnym cyklu wygrzewania i wykazują poprawę po następującym po nim cyklu wtryskiwania (rys. 4—7).
Słowa kluczowe: polistyren, symulowany recykling, wielokrotna regeneracja, próba rozciągania, ciężar cząsteczkowy, wskaźnik szybkości płynięcia.

Polymer recycling is beneficial for both economical and environmental topics [1, 2]. For that reason numerous investigations are performed on the recyclate processing and application [3—15]. The ability of a polymer to be recycled is usually estimated by means of multiple reprocessing steps [12—15]. On the other hand, properties of postconsumer material are affected by various oxidative reactions, taking place during service life of a polymer article [16—17] and resulting in macromolecule scission [18]. For that reason more adequate approach includes also artificial ageing steps to simulate degradation during the use [8—10]. The improved simulated recycling procedure consists of alternating thermal ageing and reprocessing steps, and results in far more pronounced deterioration of polymer properties than either thermal ageing or repeated processing steps performed separately [8, 9]. The most probable cause is fast thermal decomposition of hydroperoxides with formation of macroradicals causing accelerated oxidation of the polymer matter [10].

In the present study the simulated recycling procedure has been applied to polystyrene with the objective

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to estimate the processability and properties of the recycled material.

EXPERIMENTAL

Material

The virgin material was polystyrene STYRON type PS 678 E7 Clear (Dow Europe GmbH, Switzerland), characterized by producer's technical data: density — 1050 kg/m^3, MFR (200 ^{o}C/5 kG) — 10.5 g/10 min, hardness by ball indentation method — 150 MPa, elongation at break — 1—3 %, stress at break — 43 MPa.

Simulation of recycling

Simulated recycling included ten repeated cycles. Each cycle consisted of two steps: injection molding and thermal ageing. The injection molding has been performed using Wh 80Ap machine (Metalchem, Poland). The following parameters were applied: temperature profile was 190–200–225 ^{o}C, injection time 2 s, cooling time 50 s, injection pressure 12 MPa. The accelerated ageing step has been performed in an air-circulating oven at 80 ^{o}C for 72 hours. Before each reprocessing step the aged material has been ground using a laboratory mill.

Method of testing

Melt flow temperature has been determined by measurements of the deformation under load upon temperature. Melt Flow Rate (*MFR*) has been measured according to PN-EN ISO 1133, using the die with the specified dimensions L/D = 8/2 mm, and applying 5 kG load during 10 min at temperature 195 ^{o}C. Each result is an average of three measurements.

Stress-strain testing has been performed according to PN-EN ISO 527 using oar-shaped specimens and TIRA test 2200 machine at tensile rate 10 mm/min. The reported values are averages of three tensile tests. Charpy impact strength has been measured according to PN-EN ISO 179-1, based on averages of three measurements. Hardness by ball indentation method has been measured according to PN-EN ISO 2039 using 5 mm steel ball under 358 N force during 60 s. Average molecular weights have been determined by means of size exclusion chromatography (L6200 A MERCK Hitachi, tetrahydrofurane, 1.5 mL/min, 40 ^{o}C) using three-column system (two 1110-6504 PLgel 5 μm, Mixed-D, 300 · 7.5 mm plus one 1100-6520 PLgel 5 μm, 100 A, 300 · 7.5 mm).

RESULTS AND DISCUSSION

Processability

Processability of the recycled polystyrene has been characterized by means of melt flow temperature and melt flow rate. Melt flow temperature decreased for approximately 10 ^{o}C during ten full recycling steps as it is shown in Fig. 1.

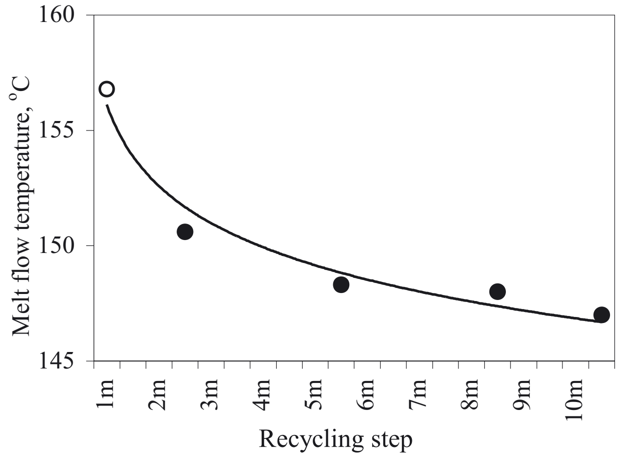

Fig. 1. Melt flow temperature changes under simulated recycling; empty circle correspond to molding steps and solid circle correspond to ageing steps

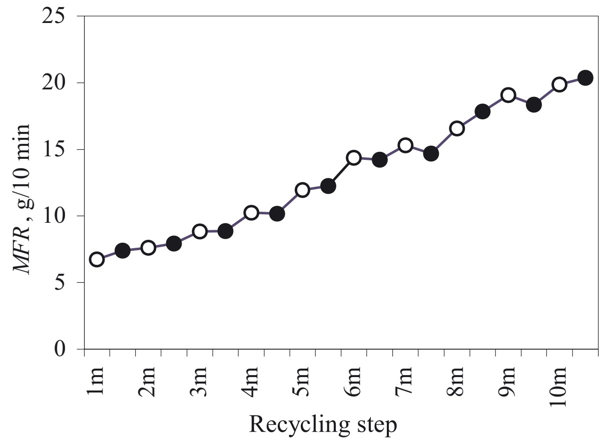

Fig. 2. MFR changes under simulated recycling; meaning of symbols as in Fig. 1

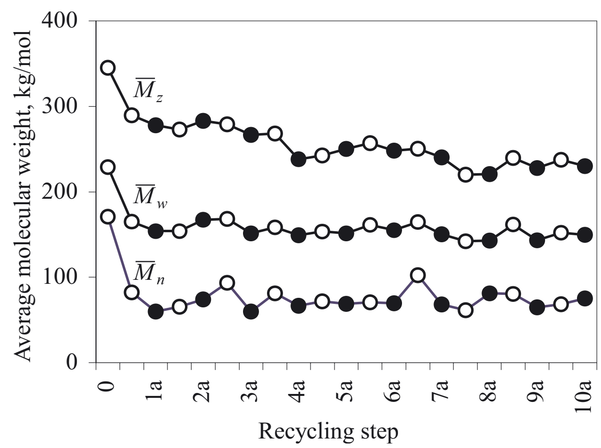

Fig. 3. Changes of average molecular weights ($\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$) under simulated recycling; meaning of symbols as in Fig. 1

The observed trend is rather fortunate allowing broadening temperature window for polystyrene reprocessing. The *MFR* values proved to be steady increased (from 6 to 20 g/10 min) with the number of recycling steps (Fig. 2). The observed substantial change of melt viscosity suggests that partial degradation of polystyrene macromolecules may take place.

In order to elucidate possible degradation processes, number-average molecular weight ($\overline{M}_n$), weight-average molecular weight ($\overline{M}_w$) and z-average molecular weight ($\overline{M}_z$) of the recycled polystyrene samples have been measured (Fig. 3). One can clearly see that all the values have considerably dropped after the first processing step. Under the next recycling steps the values of both $\overline{M}_n$ and $\overline{M}_w$ proved to have random fluctuations and rather no trend to decrease. On the other hand, marked trend to decrease is observed for $\overline{M}_z$, suggesting that partial degradation of the high-molecular fractions takes place. Apparently, the quite high shear stress during injection molding results in partial scission of the longest macromolecular chains. Such an inference is also confirmed by the *MFR* data (Fig. 2).

Strength parameters

The strength parameters of the recycled polystyrene proved to have substantial fluctuations. That is usually characteristic for the mechanical testing data. As it is shown in Fig. 4 the hardness values tend rather to increase. On the other hand, impact strength plotted in Fig. 5 decreases, especially after six full cycles. The presented data indicate clearly that recycled polystyrene becomes more brittle.

The stress at break (Fig. 6) and the elongation at break (Fig. 7) have a general trend to decrease indicating that gradual deterioration of mechanical toughness takes place. Both tensile testing parameters are strongly correlated and demonstrate quite similar dependences upon recycling step. The very interesting regular repeating oscillations of the mechanical strength characteristics upon the step number are observed. It is evident, that the tensile strength characteristics of the samples after thermal ageing step (solid circles) are obviously inferior to those of the samples after molding step (empty circles). Simi-

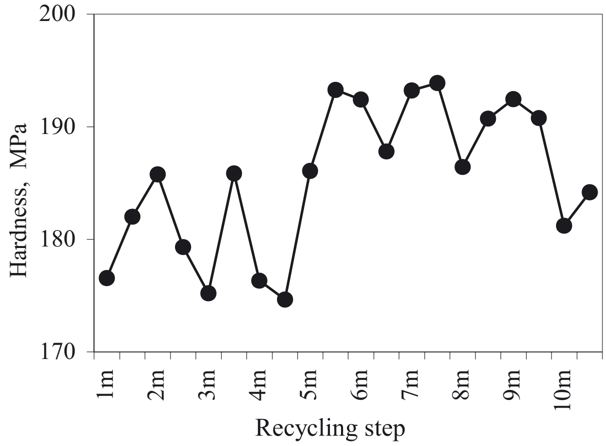

Fig. 4. Hardness changes under simulated recycling; meaning of symbols as in Fig. 1

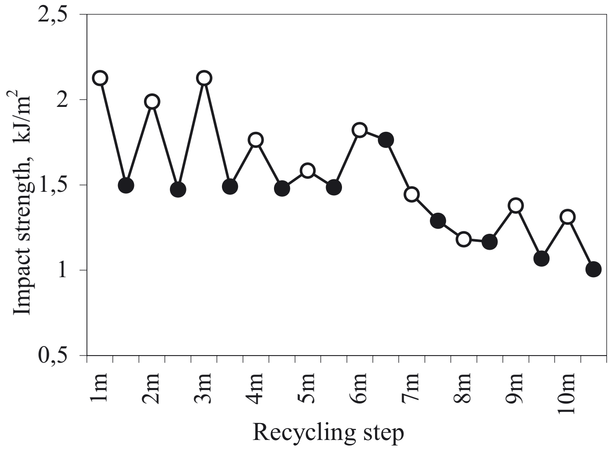

Fig. 5. Impact strength changes under simulated recycling; meaning of symbols as in Fig. 1

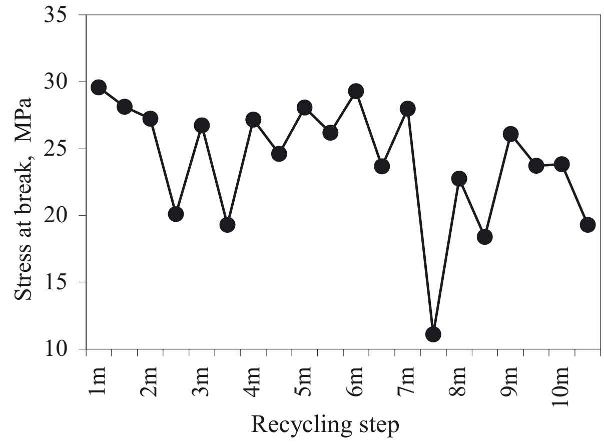

Fig. 6. Stress at break changes under simulated recycling; meaning of symbols as in Fig. 1

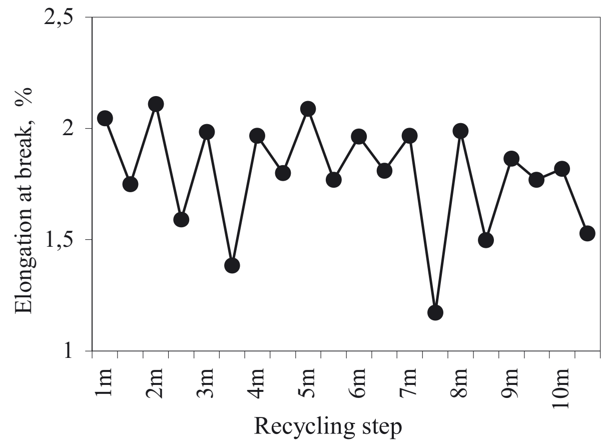

Fig. 7. Elongation at break changes under simulated recycling; meaning of symbols as in Fig. 1

larly, impact strength shows on average worse values for the aged samples than those for the remolded samples. In fact, the alternating deterioration and restoration of mechanical strength during alternating thermal ageing and reprocessing, respectively, have been clearly observed. There are the same zig-zag patterns that have been registered under the simulated recycling of acrylonitrile-butadiene-styrene terpolymer (ABS) [8] and polypropylene [9, 10]. Recovery of the mechanical properties has been also reported in the study on reprocessing of photooxidized polyethylene films [13]. The observed regularity may be attributed to homogenization of degraded polymer material [10, 13]. It is well known that the surface layer undergoes far more pronounced degradation than the internal layers [13—16]. The brittle surface matter give rise the microcracks and promote the sample breakage. All the surface microcracks are eliminated under reprocessing and for that reason the mechanical strength is improved.

CONCLUSION

Polystyrene may be recycled at least ten times without substantial deterioration of main properties. The mechanical parameters such as tensile strength, impact strength and hardness are retained at a satisfactory level. The processability characteristics (melt flow temperature and melt flow rate) are improved. An obvious regularity of alternating zig-zag changes of the tensile strength characteristics has been registered. As a matter of fact, both elongation at break and stress at break are deteriorated after thermal ageing, and both the characteristics are again restored after injection molding.

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