JAN RYBNICEK
Czech Technical University in Prague
Innovation Centre for Diagnostics and Application of Materials (ICDAM)
Karlovo nam. 13, 121 35 Prague 2, Czech Republic
e-mail: jan.rybnicek@fs.cvut.cz

Recycling of automotive lighting — effect of UV cured coating contaminants on polycarbonate toughness

Summary — This work presents studies on the impact of the coating on reprocessed polycarbonate (PC) in order to evaluate changes in the fracture behavior and toughness of polycarbonate. The comparison of instrumented and non-instrumented impact testing methods is given. The fracture mechanics parameters such as dynamic strain energy release rate (G_{Id}), and fracture toughness (K_{Id}) where determined. The coating creates non-homogeneously dispersed particles, which act as stress concentrators facilitating multiple crazing and causing embrittlement of the material. The fracture toughness was diminished only slightly and was accompanied with the rise of dynamic yield stress (σ_d) and dynamic flexural modulus (E_d). The heat deflection temperature (HDT), melt volume flow rate (MVR) and density were affected only marginally in comparison to recycled polycarbonate without coating contaminants.
Keywords: polycarbonate, reprocessing, silicon-modified polyurethane acrylate coating, fracture toughness, dynamic strain energy release rate.

RECYKLING ELEMENTÓW OŚWIETLENIA SAMOCHODOWEGO — WPŁYW ZANIECZYSZ-CZEŃ POCHODZĄCYCH OD POWŁOK UTWARDZANYCH PROMIENIAMI UV NA WY-TRZYMAŁOŚĆ UZYSKIWANEGO POLIWĘGLANU
Streszczenie — Z poliwęglanu (PC) wykonano metodą formowania wtryskowego soczewki, na które następnie nanoszono utwardzaną promieniami UV powłokę. Później materiał przetwarzano poprzez rozdrabnianie i formowanie próbek do badań wytrzymałości. Materiał przetwarzano jednokrotnie (próbka PC1) lub dwukrotnie w taki sam sposób (próbka PC2). Zbadano wytrzyma-łość przygotowanych próbek, a dodatkowo, w celu porównania badano również nieprzetwarzaną próbkę (próbka PC0) oraz próbkę uzyskaną przez przetworzenie złomu technologicznego PC (próbka PC1C) (tabela 1). Pomiary odporności na pękanie uzyskanych materiałów wykonano metodami instrumentalnymi (Charpy'ego) i nieinstrumentalnymi (Izoda). Określano wartości dynamicznego współczynnika uwalniania energii (G_{Id}) (rys. 5) i odporności na kruche pękanie (K_{Id}) (rys. 6). Pozostałość powłok w materiałach przetwarzanych powoduje powstanie niejedno-rodnie zdyspergowanych cząstek, które ułatwiają wielokrotne spękania i zwiększają kruchość materiału. Odporność na kruche pękanie zmniejszała się jednak tylko nieznacznie i towarzyszył temu wzrost dynamicznej granicy plastyczności (σ_d) i dynamicznego modułu sprężystości przy zginaniu (E_d) (rys. 6). Współczynnik odkształcalności termicznej (HDT) (rys. 2), objętościowy wskaźnik szybkości płynięcia (MVR) i gęstość (rys. 1) badanych próbek zmieniała się w niewiel-kim stopniu w porównaniu z wartościami charakteryzującymi próbkę PC0, nie zawierającą zanie-czyszczeń pochodzących z powłok.
Słowa kluczowe: poliwęglan, przetwarzanie, powłoka poliuretanowo-akrylowa modyfikowana krzemem, odporność na kruche pękanie, dynamiczny współczynnik uwalniania energii.

New design possibilities, better performance and weight decrease lead to the choice of plastics to be used as car parts. This is the case of headlight lenses, where poly-carbonate (PC) has been used as a substitute for glass since 1995. PC enables new design and decreases production costs. It is lighter and 250 times stiffer than glass, but has lower hardness and resistance to the environment. The lenses are therefore coated with thermally or UV curable hardcoat. From the recycling point of view the coating can strongly affect the otherwise high toughness of the material

and the question can be raised whether to utilize costly filtration devices [1] and separate the coating from the PC.

The effect of several contaminants of amorphous and semicrystalline polymers and organic coatings on PC properties was described in [2]. For example, the influence of the thermally curable siloxan coating on PC (Macrolon 2805) was reported. The coating does not react with PC and forms non-thermoplastic particles in a PC matrix. These particles, which act as a stress concentrator, reduce the elongation at break. A small proportion of the coating (1 %) does not impair unnotched impact strength tested even at -20 °C (the resistance to crack formation was still very high). On the other hand, the notched impact strength (according to ISO 180/4A standard) at room temperature was reduced to a brittle fracture level (a decrease of 20 %). Moreover, the siloxan decreases the injection pressure by up to 5 %, the melt volume flow rate (*MVR*, 300 °C/1.2 kg) by 5 to 10 % and the intrinsic melt volume flow rate (*IMVR*, 300 °C/1.2 kg, 20 min) by 10 to 20 %. The optical properties were assessed on the basis of the yellowness index and transmission. Both quantities deteriorated by more than 20 %. Further, a uniform dulling of the surface was observed on the surface of the colored test plaques. Finally, like all other contaminants studied in the mentioned work [2], siloxan lowered the stress cracking resistance of PC. It is obvious that contamination with siloxan is crucial to PC properties.

The effect of reprocessing on PC was described for example in works [3—10]. Liu *et al.* [3] concentrate on the physical background of variations in PC performance with repeated processing, and show the possibility of using certain physical properties (molecular weight, specific volume, free volume) for estimating the mechanical, rheological and optical properties of reprocessed moldings. Abbas [4] carries out measurements of reinforced and un-reinforced PC and closely studies the effect of processing temperature. Bernardo [5] developed mathematical models based on experimental data according to which the variation of properties can be predicted. Furthermore, these models help to find the maximum proportion of regrind in a mixture with original material that will not exceed the allowed decrease in property level. Repeated injection molding has a major effect on material degradation. At high temperatures and high shear rates, a polymer may suffer thermal, thermo-oxidative as well as mechanical and chemical degradation [6]. The main degradation mechanism is chain scission: the breaking of an in chain chemical bond in a polymer molecule, thus producing two new molecules of lower molecular weight. All studies agree that chain scission, resulting in molecular weight reduction, prevails over other degradation mechanisms. Chain scission becomes more important in further cycles, especially during the second to fourth cycle. For example, Abbas [4] did not observe any chain scission in the first cycle.

From the results of Fourier transform infrared spectroscopy (FT-IR) analysis Liu *et al.* [3] found that the initial controlling degradation mechanism may be a release of phenol and CO_2. Further, in agreement with other works, he claimed that reprocessing did not change the intrinsic structure of the macromolecules. Authors also proposed another possible thermal degradation mechanism taking place during processing as the Davis-Golden mechanism (*i.e.* simultaneous occurrence of condensation and branching reactions), non-random chain scission and homolysis. On the other hand, according to Bernardo *et al.* [6], mechanisms that may increase molecular weight are crosslinking, formation of unsaturations and cyclization of side reactions. Mantia [7] claimed that apart from the temperature, mechanical (shear) stress also played an important role in degradation mechanisms. When material was processed in a mixer under different thermal conditions he observed that the viscosity decreased with increasing temperature and mixing time. Mantia deduced that mechanical stress enhances the amount of degradation and then acts as a catalyst for thermal degradation. On the other hand, Abass [4] referred to his earlier works and reported that an increase in shear stress did not raise the extent of degradation. However, he considered similarly that high shear rates brought about viscous heating, which degraded the material.

Liu *et al.* [3] observed even growing impact strength which started to decrease after the 5 cycle. He attributed this puzzling result to the combined effect of molecular weight, free volume, chemical nature and molecular orientation. Bernardo and co-workers [5—6] reported that the PC studied in his work is highly sensitive to recycling, which was documented by enormous elevation of melt flow and a substantial decrease in impact strength. PC with trade name Makrolon 2805, as it was shown in [4, 8] seems to well withstand the degradation process. It can be seen from the relatively low decrement of impact strength and melt flow in the first and second cycle. An interesting question is whether the degradation rate is dependent on the molecular weight. A comparison of the decrease in melt flow for Lexan 123R and Makrolon 2805 shows that materials with higher molecular weight (Makrolon 2805) can deteriorate easily. Certainly, this idea would have to be verified. In general, the literature [4—8] reports that the deformation behavior of recycled polycarbonates under a tensile stress exhibits: a decrease in breaking stress (σ), a decrease in elongation at break (ε_b) and no change or a moderate decrease in Young's modulus (*E*).

The current literature provides a very broad description of the effect of reprocessing on the degradation behavior of PC. However, little information exists about the role of contaminants on the quality of the reprocessed material, knowledge of which belongs to the key aspects of designing products for increased recyclability [11, 12]. Automotive lighting industry widely used polyurethane based coatings to protect PC lenses.

The aim of this work was to investigate the impact of the coating on fracture behavior and toughness of repro-

cessed PC. Comparison of instrumented and non-instrumented impact testing methods will be given. Contaminated material will be compared with recycled material to eliminate the effect of reprocessing on toughness.

<div align="center">EXPERIMENTAL</div>

Materials

Lexan LS2 (GE Plastics), a medium viscosity polycarbonate, was used for lens production. In Table 1 there are listed the important, from a point of view of this work, properties of Lexan LS2.

Polyurethane acrylate UV curable silicon-modified coating (trade name UVHC 3000, GE Silicones) was also applied as hard coating for PC.

The technological scrap (gating system, defective moldings) and the defective coated lenses were used as a source of PC recovered from waste.

Samples preparation

The lens of Lexan LS2 was injection molded using Engel ES 3500/750k equipment. The melt and mould temperature were kept at 300 and 90 °C, respectively. The pressure reached 18 MPa. The lenses weighed 600 g on average. A hard coating of UVHC 3000, polyurethane acrylate silicon-modified coating was applied by flow and cured with UV lamps. The cured layer was 8 to 12 μm thick.

T a b l e 1. Specimen designation

Specimen designation	PC0	PC1	PC1C*)	PC2
Number of reprocessing cycles	0	1	1	2

*) PC1C stands for recycled polycarbonate with coating concentrations.

The technological scrap of the polycarbonate Lexan LS2 generated during production of car lighting (gating system, defective uncoated lenses; further referred to as PC1) and the defective coated lenses (further refered to as PC1C) were ground separately in a PH TRIA 47-30/CN granulator with three cutting knives. The regrind was dedusted in an Allgaier dust separator with 2 mm scanning equipment and cleaned of metal particles in a Mesurtronic magnetic separator. The PC1 was again reprocessed (grounded and injection molded) under the same conditions and using the same equipment, so twice reprocessed polycarbonate sample without coating contamination was generated (PC2). The original granulate of Lexan LS2, as received from supplier, was also used for investigation and was referred to as PC0. The material of all samples was injection molded into ISO 527 specimens. The modes of reprocessing and designation of samples are summarized in Table 1.

Methods of testing

The melt volume flow rate (*MVR*) and the density of original granulate and ground materials were tested according to ISO 1133 (300 °C, load 1.2 kg) and ISO 1183 standards, respectively.

Heat deflection temperature (*HDT)* was determined according to ISO 75-2 using CEAST HDT instrument.

Thermogravimetric analysis (TGA) were performed with the help of DSC NETSH STA thermogravimetry device.

The measurement of non-instrumented Izod notched impact strength (a_{iN}) was carried out according to the ISO 180/1A standard using Izod impact testing machine. All instrumented Charpy impact tests and determination of fracture mechanics parameters was carried out according to the procedures described in detail in literature [13—15]. The methods enable to record load-displacement diagrams and determine the initiation energy (E_i), the maximum force (F_{max}) and the displacement at the onset of unstable crack propagation (f_{max}). Based on E_i data parameter named dynamic strain energy release rate (G_{Id}) can be determined as slope of the plot of E_i versus value of product $B \cdot W \cdot \Phi$, where: B, W are the specimen thickness and the width, respectively, Φ is the energy calibration factor depending on the specimen crack length (a). The slope value is expressed by formula:

$$G_{Id} = \frac{\Delta E_i}{\Delta(B \cdot W \cdot \Phi)} \qquad (1)$$

Dynamic fracture toughness (K_{Id}) can be estimated using F_{max}:

$$K_{Id} = \frac{F_{max} \cdot s}{B \cdot W^{3/2}} \cdot f\left(\frac{a}{W}\right) \qquad (2)$$

where: s — *the distance between supports.*

Dynamic modulus (E_d) and dynamic yield stress (σ_d) were calculated according to equations:

$$E_d = \frac{F_{gy}s^3}{4BW^3 f_{gy}} \qquad (3)$$

$$\sigma_d = \frac{3F_{gy}s}{2BW^2} \qquad (4)$$

where: F_{gy}, f_{gy} — *the force and the displacement at yield point of an un-notched specimen, respectively.*

Fracture surfaces were observed by using JEOL JSM-540 scanning electron microscope (SEM).

<div align="center">RESULTS AND DISCUSSIONS</div>

As follows from literature the chain scission takes place during reprocessing which leads to lower molecular weight and subsequently lower viscosity of the polymer. *MVR* and density values for reprocessed samples of PC are shown in Figure 1 together with values determined for original Lexan LS2 (PC0, for which these and other properties are listed in Table 2). These results show
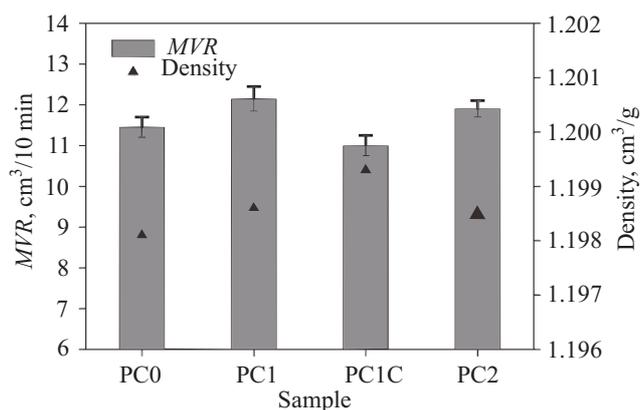
Fig. 1. Melt volume flow rate (MVR) and density values of original material and reprocessed PC

Fig. 3. The results of thermogravimetric analysis of original material and reprocessed PC (heating rate 10 deg/min)

that the reprocessing raised the melt flow of PC1 and PC2 samples. The exception is PC1C sample, which contains ground particles of PUR coating (hardened by UV light during the production process). At some places the agglomeration of particles is visible, the material is less transparent and locally turns to yellow. Subsequently, the density of contaminated material PC1C rises. In general, the presence of inorganic particles deteriorates flow properties of polymer melts. As a result, the *MVR* value of PC1C lies below the original material PC0.

presented in Figure 3. No differences between recycled and contaminated samples were observed.

The Izod notched impact strength (a_{iN}) results are presented in Figure 4. It can be stated that a_{iN} of the reprocessed PC1 and PC2 samples was decreased as an effect of the reprocessing cycles. It can be expected that the toughness will deteriorate upon further processing steps, however depending on the molecular weight reduction (chain scission mechanisms). There is a substantial drop of the toughness of PC1C (about 60 %) compared to the

T a b l e 2. Reference properties of Lexan LS2 designated as PC0

a_{iN}, kJ/m^2	HDT, °C	Vicat hard-ness, °C	MVR cm^3/10 min	Density g/cm^3
14.2	125.7	143.9	11.5	1.2

In Figure 2 the results of *HDT* for reprocessed materials are shown. The *HDT* value of PC1C is reduced by about 2 deg in comparison to the unprocessed sample. The reduction of *HDT* for other materials was smaller. The thermo-oxidative stability expressed by percentage sample weight reduction with increasing temperature is

Fig. 4. Izod notched impact strength (a_{iN}) values of original maerials

original polycarbonate PC0. In a similar manner, the reprocessing gradually decreases the fracture energy (G_{Id}) values, which are showed in Figure 5. But the G_{Id} of reprocessed polycarbonate with the coating contaminants PC1C does not differ much from its equivalent without coating PC1. It is important to note that in contrast to the non-instrumental Izod impact testing the concept of G_{Id} counts only with the energy associated with the crack initiation and not the crack propagation. So it can be stated that contaminated material exhibits good resistance against unstable fracture as the non-contaminated recycled polycarbonates PC1 and PC2. This is in agreement

Fig. 2. Heat deflection temperature (HDT) values of investigated samples
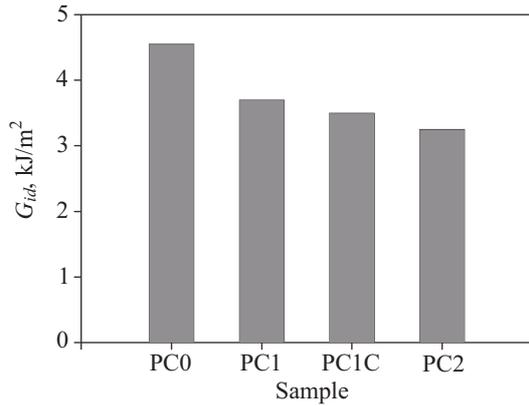
Fig. 5. Dynamic strain energy release rate (G_{Id}) values of original material and reprocessed PC
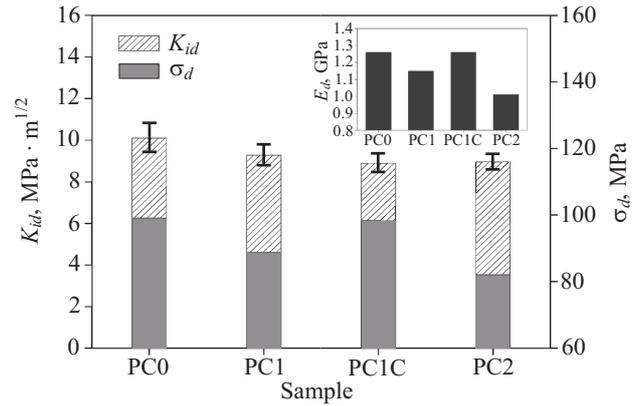
Fig. 6. Fracture toughness (K_{Id}), dynamic yield stress (σ_d) and dynamic modulus (E_d) (inserted graph) for investigated samples
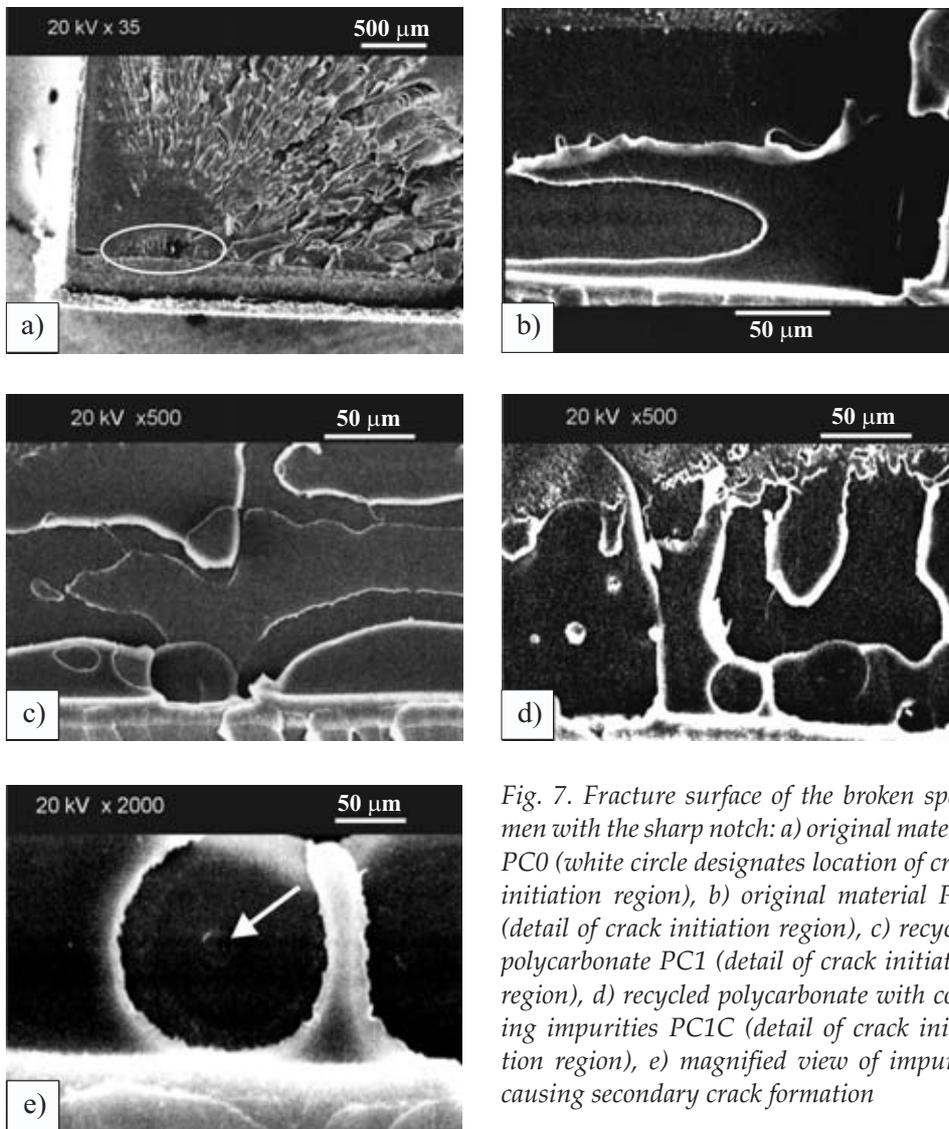
Fig. 7. Fracture surface of the broken specimen with the sharp notch: a) original material PC0 (white circle designates location of crack initiation region), b) original material PC0 (detail of crack initiation region), c) recycled polycarbonate PC1 (detail of crack initiation region), d) recycled polycarbonate with coating impurities PC1C (detail of crack initiation region), e) magnified view of impurity causing secondary crack formation

with the results of K_{Id} (presented in Figure 6), the concept of which is based on determining the critical value of the stress field at the moving crack tip (the moment of instability and the onset of the unstable crack growth is considered to appear at the maximum force F_{max} at the

recorded load displacement diagrams). The decrease in the K_{Id} of PC1C was accompanied with the rise of σ_d and E_d values (Fig. 6, see inserted graph), which is common fracture behavior of rigid particle filled materials without optimum strength of the matrix/filler interface. In other

words, the hard coating particles strengthen the material but at the cost of toughness.

The results of SEM investigation are shown in Figure 7. Fracture surface of polycarbonate PC0 after instrumented Charpy impact test is shown in Figure 7a, where the crack initiation region can be seen (designated by a white circle in the image). Magnified view of crack initiation region of the original PC0 and recycled materials PC1 and PC1C give the following information:

— a homogeneous craze and plastically deformed fibrils are formed during crack initiation of the original polycarbonate PC0 (Fig. 7b);

— the area of the initiation region of PC1 slightly decreases with reprocessing and the fibrillation is less common, the craze surface is more broken and the crack generates in several planes (by multiple crazing) (Fig. 7c);

— the initiation region of PC1C contains several round regions of secondary crack formation — a magnified view of one region reveals a small impurity at its cen-

ter (very likely the coating particle, diameter of about 3 μm) (Fig. 7e).

Fracture surfaces after non-instrumented Izod impact test of PC0, PC1 and PC1C are shown in Figure 8. The crack growth can be divided in three subsequent phases —designated by numbers (see Fig. 8a): 1 — stable crack growth at the notch tip (around 50 μm wide), 2 — crack initiation and 3 — unstable crack propagation. The stable crack part and crack initiation region is decreasing upon reprocessing (compare Figs. 8a, 8b and 8c) and the coating contamination of PC1C (compare Figs. 8b with 8c). Moreover, the conchoidal shape of crack propagation area appears to flatten with the number of reprocessing cycles and the coating contamination (easier crack propagation).

To better understand the difference between the significant drop of the Izod results compared to the fracture mechanics results (G_{Id}), the instrumented Charpy impact testing of the original polycarbonate PC0 and PC1C (the PC1C material was this time from a different recycled lot, but the results are similar) was carried out. The samples were produced with a blunt notch (r = 0.25 mm, according ISO 179 standard) and a sharp notch (r = 0.01 mm, fracture mechanics standard to assure plain strain deformation). Results of these investigations are presented in Figure 9. First of all, it is well known that PC is highly sensitive to the notch radius. The maximum force F_{max} of the original polycarbonate PC0 decreased from 600 N (blunt notch) to 350 N (sharp notch). Similarly, the initiation energy (the energy absorbed until the maximum force) of the original PC0 decreased from 14.7 kJ/m^2 (blunt notch) to 4.8 kJ/m^2 (sharp notch). We can notice that when sharp notches were used the load-displacement diagrams of PC0 and recycled and contaminated PC1C are similar yielding the same initiation energies for PC0 (4.8 kJ/m^2) and for PC1C (4.2 kJ/m^2) — compare with G_{Id} results
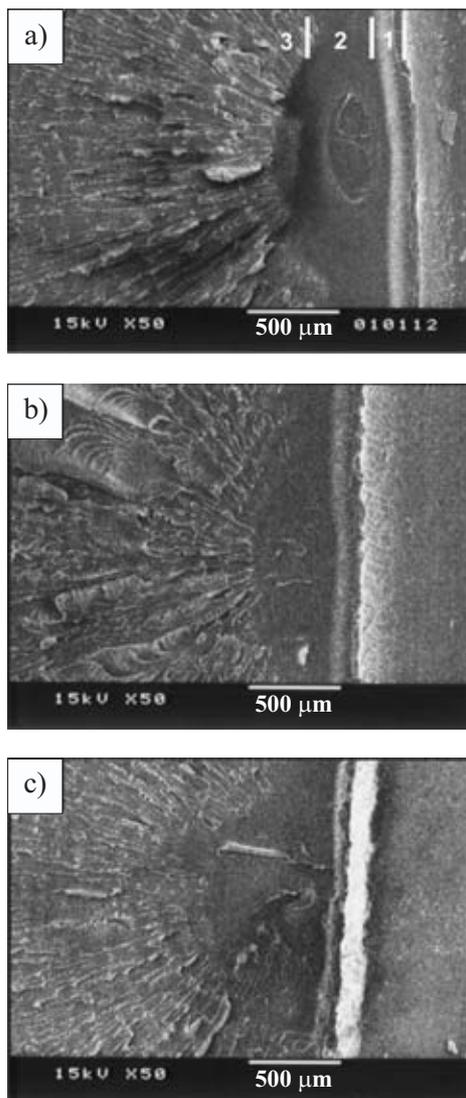
Fig. 8. Fracture surface of the broken specimen with the blunt notch: a) PC0, b) PC1, c) PC1C
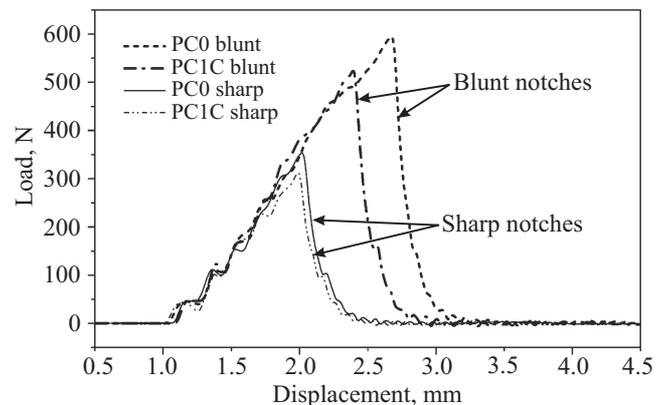
Fig. 9. Load-displacement diagrams recorded by instrument Charpy impact test of original polycarbonate PC0 and recycled and contaminated PC1C; test carried out with blunt (r = 0.25 mm, initiation energy 14.7 and 10.1 kJ/m² for PC0 and PC1C, respectively) and sharp (r = 0.01 mm, initiation energy 4.8 and 4.2 kJ/m² for PC0 and PC1C, respectively) nothing of samples
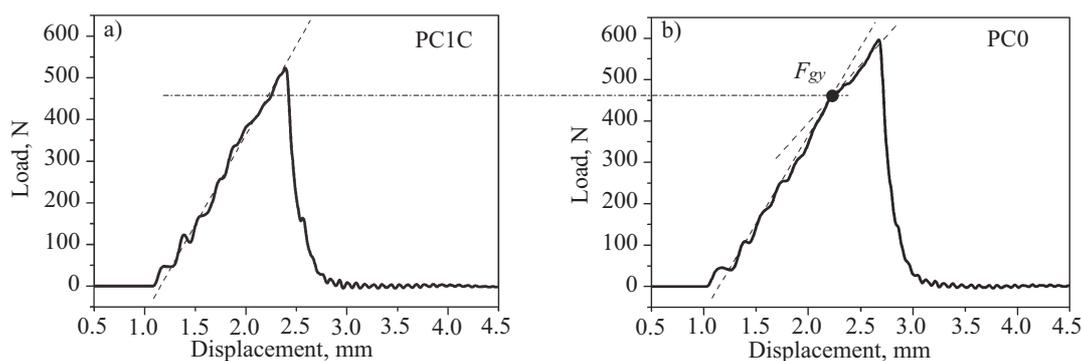
Fig. 10. Load-displacement diagrams of PC1C (a) and PC0 (b) when blunt notching of samples was used

(Fig. 5). However, there is a significant difference when blunt notches were used: PC0 (14.7 kJ/m^2) and PC1C (10.1 kJ/m^2). Looking closely to load-displacement diagrams of tested polycarbonates PC1C and PC0, presented in Figure 10, a linear elastic deformation behavior can be seen but in case of PC0 (Fig. 10b) it is followed by small scale yielding (distinguished by the change of slope above the yield point F_{gy}). This is in contrast with the load-displacement diagrams recorded for the samples with sharp notches (see Fig. 9), which show only linear elastic deformation behavior.

CONCLUSIONS

In general the studied polycarbonate PC0 retains its toughness upon reprocessing well. SEM analysis shows that the contaminated polycarbonate PC1C contains non-homogeneously dispersed particles, which act as stress concentrators facilitating multiple crazing and causing embrittlement of the material. However, the resistance against unstable crack propagation (determined under test parameters promoting plane strain conditions, *e.g.* sharp notching) shows only a moderate change of toughness — the dynamic strain energy release rate (G_{Id}) and the fracture toughness (K_{Id}). Moreover, the dynamic yield stress (σ_d) and dynamic flexural modulus (E_d) are raised. On the other hand, the Izod notched impact strength and PC1C drops significantly which is attributed to the effect of blunt notching. It was shown that polycarbonate PC0 undergoes small scale yielding in contrast to PC1C when blunt notches (ISO 179 standard) are used.

Additionally, the heat deflection temperature (*HDT)* investigations and thermogravimetric analysis shows only a minor changes in thermal resistance. The flow properties of polycarbonate are improved upon reprocessing. In case of the contaminated material the density is increased and subsequently the melt volume flow rate (*MVR*) diminishes. Nevertheless, the flow properties are similar to the original material. On the other hand, the contaminated recyclate is not suitable for applications that are optically demanding since lower transparency and yellowing of polycarbonate is observable due to coating contaminants. The contaminated material can be used as a substitute for polycarbonate grades with lower impact strength (*e.g.* Lexan 121). In case of further use of recycled polycarbonate it is recommended that the recyclate should be injection molded at low thermo-mechanical loading of polymer melt (*e.g.* minimum required process temperature and back pressure) and the minimum water content should be thoroughly controlled.

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