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EFFECT OF THE QUENCHING TEMPERATURE ON THE IZOD IMPACT STRENGTH OF POLYCARBONATE: EXPERIMENTAL DATA AND EMPIRICAL MODELING

VPLIV TEMPERATURE KALJENJA NA IZOD UDARNO TRDNOST POLIKARBONATA: EKSPERIMENTALNI PODATKI IN EMPIRIČNO MODELIRANJE

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In this study, the development of a mathematical model of the effects of free quenching on the Izod impact strength of polycarbonate (PC) has been investigated. Three different thermal treatments were used: the first quenching from the melt state to different temperatures, the second quenching from T_g + 15 °C and, finally, the annealing. The results have shown that an improvement in the impact strength can be obtained after the second quenching at 40 °C. The impact tests experimentally performed on the molding prototypes yield useful data for a particular structural and impact-loading case. But, it is generally not practical, in terms of time and cost, to experimentally characterize the effects of a wide range of design variables. A successful numerical model for the Izod impact strength of polymers can provide convenient and useful guidelines on product design and, therefore, decrease the disadvantages arising from purely experimental trial and error. It is expensive to prepare the samples for the tests. Therefore, it is necessary to develop a mathematical model that will predict the fracture toughness of polycarbonate as a function of the quenching temperature. Mathematical models for the mechanical properties like the tensile strength, Young's modulus and Izod impact strength as functions of the quenching temperature are not available. There is no sign that they can be built up from a simple theory; a polynomial interpolation was, therefore, used to generate a fracture-toughness model using the data obtained from the experiments. The shifted model represents the Izod impact of the samples as a function of the first- and second-quenching temperatures.

Keywords: Izod impact strength, polycarbonate, quenching temperature, mathematical modeling

Ta študija preučuje razvoj matematičnega modela vpliva prostega kaljenja na Izod udarno trdnost polikarbonata (PC). Uporabljeni so bili trije različni načini toplotne obdelave: najprej prosto kaljenje iz staljenega stanja na različne temperature, nato drugo kaljenje iz T_g + 15 °C in nato končno žarjenje. Rezultati so pokazali, da je mogoče doseči izboljšanje Izod udarne trdnosti po drugem kaljenju pri 40 °C. Eksperimentalno izvedeni preizkusi na modeliranih prototipih so dali uporabne podatke za posebne primere strukturno in udarno obremenjenih primerov. Vendar pa na splošno ni praktično – s stališča časa in stroškov – eksperimentalno določanje vplivov različnih oblik. Uspešen numerični model za Izod udarno trdnost polimerov lahko zagotovi zanesljive in uporabne napotke za načrtovanje proizvodov in s tem zmanjša pomanjkljivosti, ki izvirajo iz eksperimentalnih preizkusov in napak. Priprava vzorcev za preizkuse je draga. Zato je treba razviti matematični model, ki bo napovedoval lomno žilavost polikarbonata v odvisnosti od temperature kaljenja. Na razpolago ni modelov za mehanske lastnosti, kot so natezna trdnost, Youngov modul in Izod udarna trdnost, v odvisnosti od temperature kaljenja. Ni znamenj, da se lahko postavijo z enostavno teorijo: zato je bila z uporabo eksperimentalnih podatkov uporabljena interpolacija polinomov za izdelavo modela lomne žilavosti. Predstavljeni model predstavlja Izod udarno trdnost v odvisnosti od prve in druge temperature kaljenja.

Ključne besede: Izod udarna trdnost, polikarbonat, temperatura kaljenja, matematično modeliranje

1 INTRODUCTION

Engineering polymers have been increasingly used in the applications such as housings for electronic appliances, lenses and windows that have to sustain accidental impact without showing signs of damage. Due to good thermal- and electrical-insulation properties, low density, high resistance to chemicals and ease of manufacturing, engineering polymers have been increasingly used in the applications where the impact performance is the primary concern.[1–4] One of the biggest advantages of polycarbonate (PC) is its impact strength. It is widely used as a transparent protective material because of its low density and excellent mechanical properties. However, when defects such as cracks or notches are introduced, it is subject to a dramatic brittle failure at relatively low loads. PC applications are also limited to thin molded articles because its impact strength is highly sensitive to the presence of notches. The presence of sharp notches, or even small notches, caused by a microscopic surface degradation decreases the impact strength.[5] However, an addition of appropriate polymers or terpolymers and core-shell impact modifiers can be an effective toughening method for the PCs used in thick sections.[6,7] To expand the usefulness of PC in a variety of applications, it is important to explore the ways to prevent or minimize the loss of toughness during sub-T_g annealing and to reduce the sensitivity to the presence of notches and, consequently, the loss of the impact strength. Residual-stress (*RS*) generation with the quenching process under severe conditions (0 °C) is known to be an effective method of toughening glassy polymers.[8–11] Recently, our study showed that, in the case of polycarbonate, the improvement of the impact strength after the second quench at 40 °C is linked to the existence of the relaxation mode located around 35 °C.[12]

Notched Izod testing is a common qualitative measure of the toughness of a material, measuring the energy absorbed prior to failure under high triaxiality and high-rate loading conditions. In industrial applications, it is important to know the impact behavior and the safe operating limits of polymeric structures. In our case, the evaluation of the impact-design failure of polymeric structures has to be experimentally performed on molding prototypes. The experimental trial-and-error method significantly delays the design progress and optimization, wasting a lot of time, money and efforts.

There are several types of standard tests to evaluate the impact strength of polymers. The most commonly used are the Charpy and Izod tests.[13] A successful numerical model for an impact deformation and failure of polymers can provide convenient and useful guidelines on the product design, therefore decreasing the disadvantages arising from just experimental trial and error. In this work, we have investigated the development of a mathematical model predicting the effects of the first- and second-quenching temperatures on the Izod impact strength of PC.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

The polymer used in this study is a commercial polycarbonate, Makrolon® 2620, supplied by Bayer (Germany) with the average molecular mass of about 57 400. The melt index at 300 °C is 19.6 g/(10 min), the polydispersity index is 2.16 and the glass transition temperature is about 144 °C (the value obtained from DMA measurements[14]).

2.1.1 First-quench procedure

Pellets were dried in an oven at 120 °C and then put into the mold and pressed at 25 bar for 12 min at 230 °C. Then the samples were immediately quenched from the moulding temperature in the water baths at three different temperatures of (0, 20 and 80) °C or in the air at room temperature for 15 min. All the samples have a thickness of 3 mm and this step was named "the first quench".

2.1.2 Second-quench procedure

Another free quenching was carried out only for the samples molded at 230 °C at different quenching temperatures. These specimens were heated in the oven at 160 °C (T_g + 15 °C) for 3 h and were immediately quenched for the second time in the water baths at different temperatures (0, 20, 30, 35, 40, 45 and 60) °C for 15 min. This procedure was named "the second quench".

2.1.3 Annealed samples

Finally, in order to get reference samples, an annealing was performed. The annealed specimens were prepared using the samples first quenched in air at 25 °C. Then, these samples were heated at 160 °C for a period of 2 h and, finally, slowly cooled in the oven at room temperature at a rate of about 0.5 °C min^{-1}. These samples were named "annealed samples".

2.2 Notched Izod impact strength

Izod impact-strength properties were determined at room temperature with a CEAST 6546/000 machine with a 15 J pendulum according to ASTM D256-73. The specimens with the dimensions of 3 mm × 12.7 mm × 63 mm were compression molded. Parts of them were milled with a notch radius of 0.5 mm. This radius was chosen so that the tip of the notch was located in the residual compressive zone. These stress zones were determined with a photoelastic examination of a sample between the cross Polaroids under white light. In the case of the thermal stress (symmetrical free quenching), due to the non-uniform cooling of the outer and central layers, compressive and tensile stresses are formed in the material. Two neutral lines symmetrically separate the stress zones. The extension of this zone can reach a certain percentage of the sample thickness.[14]

These stresses are frozen in, and the material conserves some internal stresses, revealed in the polarized light by certain colors. Using a standard polariscope, the photoelastic color sequence, with the increasing stress, observed from the neutral line includes: black (zero), yellow, red, blue-green, yellow, red, green, yellow, red, green and so on.[14] At least five specimens were tested and the average value was used for plotting the experimental data.

2.3 Numerical method

The polynomial curve-fitting technique was used to derive analytical terms that match the given data points.[15] Polynomial curve fitting is a mathematical procedure for finding the best fitting curve for a given set of points by minimizing the sum of the squares of the offsets of the points from the curve. This includes finding the coefficients of polynomial $p(x)$ of degree n that fits the computed values $p(x_i)$ with experimental data y_i, where $i \in \{1, 2, ..., N\}$ and N is the number of experimental data points. The following definition has been used for determining the residual standard deviation (*RSD*), which is a statistical term used to describe the standard deviation of the points formed around a function, and it is an estimate of the accuracy of the dependent variable being measured. The lower the *RSD*, the greater is the agreement between the experimental data and the model. The *RSD* is computed as follows:

$$RSD = \sqrt{\frac{\sum_{i=1}^{N} \left[y_i - p(x_i) \right]^2}{N-q}} \tag{1}$$

where q is the number of estimated parameters (note that for a polynomial fit, $q = n + 1$) and the y_i values correspond to the experimental results of the Izod impact strength (a_k).

3 RESULTS AND DISCUSSIONS

3.1 Effects of the first and second quenching on the Izod impact strength

The evolution of the milled notched Izod impact strength is presented as the function of the second-quenching temperature (**Figure 1**). In both cases, the maximum second-quenching temperature is 40 °C. The second thermal treatment including a heat treatment for 3 h at 160 °C (i.e., at T_g + 15 °C) has not totally erased the first thermal treatment. Indeed, the same evolution is observed for the samples that were first quenched in water at (0, 20 and 80) °C and in air at room temperature (25 °C). The influence of the first quenching is reflected on all the properties. The properties obtained after the first quenches at 0 °C and 20 °C are close; they correspond to the rapid first quench. Again, the properties corresponding to the first-quenching temperature of 80 °C and to the cooling in air are close, indicating a slower first quench.

In a previous work,[12] the minimum density observed for the second-quenching temperature of 35 °C was associated with an increase in the free volume. This increase leads to a higher molecular mobility. This explains the increase in the Izod impact strength. The maximum ductility reached during the second quenching from 160 °C to 40 °C is linked to the existence of the β_1 molecular relaxation at around 35 °C.[12]

As already reported for the PMMA and PS,[14] the Izod impact-strength values are maximum at the same second-quenching temperature, i.e., at 40 °C. However, with polycarbonate, the improvement in the Izod impact strength is more pronounced.

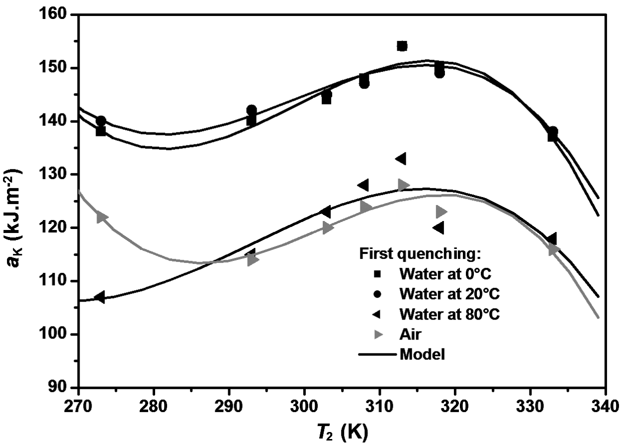

Figure 1: Milled notched Izod impact strength of PC as a function of second-quenching temperature T_2 of the PC first quenched in water at (■) 0 °C, (●) 20 °C, (◄) 80 °C and (►) in air at 25 °C; for the milled annealed sample, a_k = 45 kJ m^{-2}

Slika 1: Izod udarna trdnost brušenega in z zarezo PC-vzorca v odvisnosti od druge temperature kaljenja T_2 PC-vzorca, ki je bil najprej kaljen v vodi pri (■) 0 °C, (●) 20 °C, (◄) 80 °C in (►) na zraku pri 25 °C; pri brušenem žarjenem vzorcu je bila a_k = 45 kJ m^{-2}

3.2 Comparison of the experimental data with the empirical model

In order to obtain an analytical expression of the variation of the Izod impact strength of PC with the thermal-treatment parameters, i.e., the first- and second-quenching temperatures, we decided to use an empirical model. First of all, the model chosen in this study to fit the experimental behavior as the function of the second-quenching temperature has a third-degree polynomial form as follows:

$$a_k = a_0 + a_1 \times T_2 + a_2 \times T_2^2 + a_3 \times T_2^3 \qquad (2)$$

where a_k is the notched Izod impact strength (expressed in kJ m^{-2}), T_2 is the absolute second-quenching temperature (in K) and a_0, a_1, a_2 and a_3 are the constants obtained by fitting.

The parameters estimated from the polynomial model (equation 2) are displayed in **Table 1**. The expression chosen to describe the experimental result, with the usual meanings for constants a_0, a_1, a_2, and a_3, gives a fairly good agreement between the calculated and the experimental values, as seen in **Figure 1**. Indeed, it can be seen that the model matched the experimental data for the entire process. This is supported by the low *RSD* values obtained. However, we must note a slightly higher value of the *RSD* for the first quench in water at 80 °C, indicating a lower agreement between the experimental data and the model in this particular case.

Close values of the estimated parameters were obtained for both the samples first quenched in water at 0 °C and the ones first quenched in air. Moreover, the values of the Izod impact strength are higher for the samples first quenched at 0 °C than for the ones first

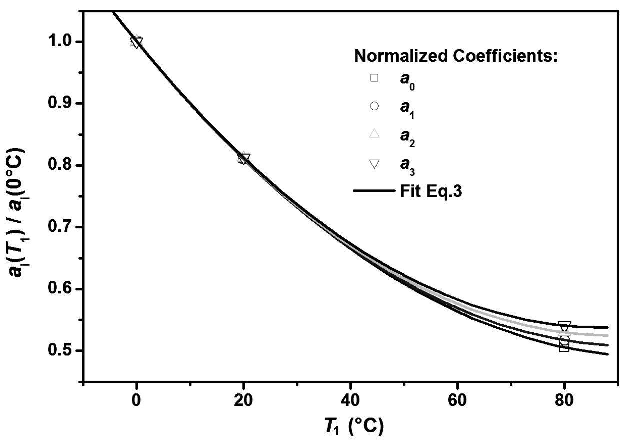

Figure 2: Plot of the normalized a_i coefficients from equation 2 as a function of first-quenching temperature T_1 (for the samples quenched in water)

Slika 2: Prikaz normaliziranih koeficientov a_i iz enačbe 2 v odvisnosti od kalilne temperature T_1 prvega kaljenja (za vzorce, kaljene v vodi)

Table 1: Parameters estimated from the model and residual standard deviation between the experimental Izod impact strength (a_k) and the calculated one, for the PC first quenched at different temperatures (T_1) in air and water

Tabela 1: Parametri, določeni iz modela in preostale standardne deviacije med eksperimentalno določeno Izod udarno trdnostjo (a_k) in izračunano za polikarbonat, ki je bil najprej kaljen pri različnih temperaturah (T_1) na zraku in v vodi

Sample	First quenched in water			First quenched in air
T_1/°C	0 °C	20 °C	80 °C	25 °C
a_0 (kJ m^{-2})	20422	16556	10326	21591
a_1 (kJ m^{-2} K^{-1})	–204.89	–166.00	–105.97	–214.28
a_2 (kJ m^{-2} K^{-2})	0.68764	0.55780	0.36427	0.71084
a_3 (kJ m^{-2} K^{-3})	-7.6663×10^{-4}	-6.2266×10^{-4}	-4.1476×10^{-4}	-7.8382×10^{-4}
RSD	1.25	1.61	4.02	2.22

Table 2: Parameters b_i of equation 3 estimated from the plots of normalized coefficients a_i presented in **Figure 2**

Tabela 2: Parametri b_i iz enačbe 3, določeni iz odvisnosti od normaliziranih koeficientov a_i, predstavljenih na **sliki 2**

Estimated parameter of Eq. 3	Values for each Eq. 2 polynomial coefficient a_i			
	a_0	a_1	a_2	a_3
b_1/°C^{-1}	-1.056×10^{-2}	-1.064×10^{-2}	-1.063×10^{-2}	-1.061×10^{-2}
b_2/°C^{-2}	5.476×10^{-5}	5.759×10^{-5}	5.938×10^{-5}	6.088×10^{-5}

quenched in air. The selected first quench in ambient atmosphere is generally preferred because it is moderate and less costly than the first quench in water at 0 °C, which requires more resources and is more expensive. These results are supported by the model used. It has to be noted that we could not find a model in the literature to compare it with our results.

Even if the model proposed is in agreement with the experimental behavior, we must note that the fitting parameters a_i obtained do not have, at this time, any physical significance. However, it seems interesting to study their dependence upon first-quenching temperature T_1, when the samples are first quenched in water. In order to describe the general variation of these parameters with T_1, we present, in **Figure 2,** a plot of the a_i values normalized to the values obtained for the first quenching at 0 °C as the function of T_1. We can see that the normalized values of polynomial coefficients a_i of equation 2 seem to obey the general rule that can be approximated using the following relationship:

$$a_i(T_1) = a_i(0°C) \times \left[1 + b_1 \times T_1 + b_2 \times T_1^2\right] \quad \forall i \in \{1,2,3,4\} \tag{3}$$

where T_1 is the first-quenching temperature expressed in °C, while b_1 and b_2 are the coefficients, whose values are given in **Table 2**. The values of the b_1 parameter seem to be quite independent of the polynomial coefficient order *i,* whereas a slight dependence on this coefficient order can be noted for the b_2 parameter. By using equations 2 and 3, along with the empirical values of parameters a_i and b_i reported in **Tables 1** and **2**, it is now possible to compute the Izod impact strength of PC as the function of the first- and second-quenching temperatures, namely, T_1 and T_2. The results of this computation are presented in **Figure 3**. This kind of simple modeling can be useful for manufacturing polymers since it can predict the value of the impact strength as the function of the parameters characterizing the thermal treatments imposed on the material. This kind of modeling can be carried out on the basis of the experiments performed for a limited number of the selected quenching temperatures.

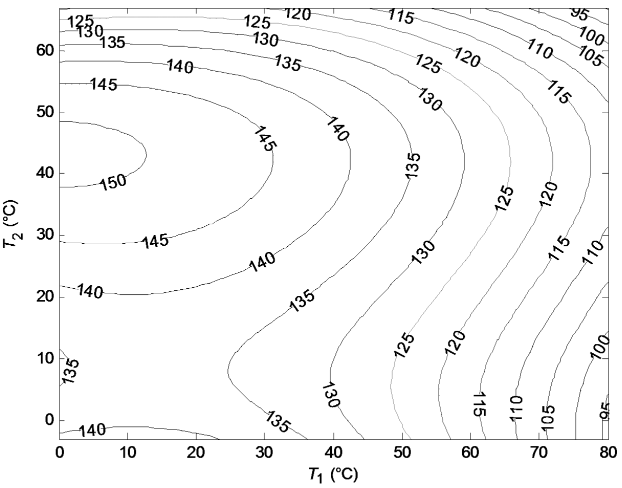

Figure 3: Chart of Izod impact strength a_k (expressed in kJ m^{-2}) of PC as a function of the first- and second-quenching temperatures, namely T_1 and T_2 (quenching in water); computation done using equations 2 and 3, the model and data from **Tables 1** and **2**

Slika 3: Diagram Izod udarne trdnosti a_k (izražene v kJ m^{-2}) polikarbonata v odvisnosti od prve in druge temperature kaljenja T_1 in T_2 (kaljeno v vodi); izračun je izdelan z uporabo enačb 2 in 3, modela in podatkov iz **tabele 1** in **2**

4 CONCLUSION

The effect of the quenching process on the mechanical properties of PC was investigated via Izod impact measurements. The predicted Izod impact strength as the function of the second-quenching temperature was compared with the experimental data and a good agreement was obtained. The results indicated that a generalized constitutive model accurately predicts the Izod impact strength of PC over a wide range of first- and second-quenching temperatures. This kind of modeling could be useful for manufacturers as it can reduce the number of experimental tests necessary to design a manufacturing process. It should be interesting, in future research, on the one hand, to check if this kind of behavior can be extrapolated to the other polymers (e.g., PMMA, polystyrene) and, on the other hand, to find a physical significance of some of these empirical parameters.

5 REFERENCES

[1] O. Delatycki, Mechanical performance and design in polymers, Interscience Publishers, New York 1971

[2] S. M. Walley, J. E. Field, P. H. Pope, N. A. Safford, J. Phys. III France, 1 (**1991**) 12, 1889

[3] S. Kalpakjian, Manufacturing engineering and technology, 3rd ed., Addison-Wesley, Reading, Massachusetts 1995

[4] E. M. Arruda, M. C. Boyce, R. Jayachandran, Mech. Mater., 19 (**1995**), 193

[5] J. C. Falk, K. W. Narducy, M. S. Cohen, R. Brunner, Polym. Eng. Sci., 20 (**1980**) 11, 763

[6] A. F. Yee, R. P. Kambour, In Proceedings of International Conference, Toughening of Plastics, Plastics and Rubber Institute Conference, London, 1978, 20

[7] A. F. Yee, J. Mater. Sci., 12 (**1977**), 757

[8] L. J. Broutman, S. M. Krishnakumar, Polym. Eng. Sci., 16 (**1976**) 2, 74

[9] B. D. Aggarwala, E. Saibel, Phys. Chem. Glass., 2 (**1961**), 137

[10] E. H. Lee, T. G. Rogers, T. C. Woo, J. Am. Ceram. Soc., 48 (**1965**), 480

[11] A. I. Isayev, Polym. Eng. Sci., 23 (**1983**), 271

[12] F. Rouabah, M. Fois, L. Ibos, A. Boudenne, C. Picard, D. Dadache, N. Haddaoui, J. Appl. Polym. Sci., 109 (**2008**), 1507

[13] W. G. Perkins, Polymer. Eng. & Sci., 39 (**1999**), 2445

[14] F. Rouabah, PhD Thesis, University of Sétif, 2007

[15] W. H. Press, S. A. Teukolsky, W. T. Vetterling, B. P. Flannery, Numerical Recipes – The Art of Scientific Computing, 3rd edition, Cambridge University Press, 2007