Improvement of the Long-Term Performance of Impact-Modified Polycarbonate by Selected Heat Treatments

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Next to the intended increase of the impact toughness, impact modification of polycarbonate generally results in an unwanted decrease in yield stress and time-to-failure under constant stress. It is demonstrated that this loss in strength can be fully compensated for by an annealing treatment, or by increasing the mold temperature. The influence of impact modification on the short- and long-term strengths of glassy polymers is predicted by the extension of existing models with a scaling rule based on the filler volume percentage. Introduction of this scaling rule in the evolution of yield stress during physical aging even allows for the direct prediction of yield stress on the basis of processing conditions.

Introduction

Polymers are frequently used as structural materials partly due to the ease with which complex geometrical parts can be produced. Not all polymers are suited and, for instance, polystyrene (PS) and poly(methyl methacrylate) (PMMA) show brittle behavior, whereas polycarbonate (PC) is tough. However, also PC can, under certain conditions, fail in a brittle manner, e.g. after prolonged exposure to high temperatures still below the glass transition temperature \(T_g\) or when high (positive) triaxial stress states are reached as for instance observed under a notch. The intricate interplay between strain softening and strain hardening determines a material’s ability to delocalize strain, and it was shown that they are indeed the parameters governing the macroscopic behavior of all glassy polymers.

A common route to increase the toughness of brittle polymers is the addition of a rubber phase. High impact polystyrene (HIPS) is toughened by the introduction of a co-continuous polybutadiene phase, where multiple cavitation and crazing intermediately contribute to energy dissipation. A similar effect can be found for carboxyl-terminated butadiene acrylonitrile (CTBN) rubber modified epoxies where multiple cavitation and shear yielding are observed. PS is extremely sensitive to stress triaxiality: a positive hydrostatic stress level of ±40 MPa will lead to brittle failure, whereas in compression yield stresses in excess of two times that value can be easily reached. PC shows large plastic deformation and ductile failure in a normal tensile test. But, in the presence of a notch, hydrostatic stress builds up, resulting in a change to brittle failure via crazing. In contrast to PS, the hydrostatic stress at which brittle failure is expected for...
PC is much higher: ±90 MPa.\textsuperscript{[20,21]} As a result of this stronger resistance to cavitation, even a simple voided structure suffices in toughening PC.\textsuperscript{[22]} which in practice can be accomplished by using easy cavitating methyl methacrylate-butadiene-styrene (MBS) core-shell impact modifiers.\textsuperscript{[23–26]}

Addition of impact modifiers enhances the impact behavior, but frequently causes a loss in transparency and, more importantly, negatively affects the load-bearing capacity of the polymer, by reduction of the yield stress.\textsuperscript{[15,23,27,28]} A decrease in yield stress can be termed a short-term material property, but also a decrease in the static and dynamic fatigue strength is found, which clearly are long-term properties. This negative effect on short- and long-term properties has been shown for HIPS\textsuperscript{[29,30]} and acrylonitrile-butadiene-styrene (ABS)\textsuperscript{[31,32]}, with respect to their unfilled counterparts PS and styrene-acrylonitrile (SAN), respectively.

A possible solution to correct this negative effect on long-term strength may be found in selected heat treatments. Amorphous polymers below \( T_g \) are in a state of non-equilibrium and, as a result, their physical and mechanical properties are subject to change over time, a phenomenon known as physical aging.\textsuperscript{[33,34]} During annealing, a heat treatment at elevated temperature below \( T_g \), the aging process is accelerated, and a marked increase in yield stress can be achieved in relatively short time.\textsuperscript{[35–39]} Simultaneously the lifetime under static and dynamic loading will also improve.\textsuperscript{[40–46]} A drawback of these treatments is that polymers will show a stronger tendency to localize,\textsuperscript{[6]} resulting in more brittle behavior under impact conditions.\textsuperscript{[1–5]} Annealing thus leads to enhanced short- and long-term properties, but diminished impact properties.

Here, we will investigate both experimentally and theoretically whether an impact modified polymer can be given identical long-term strength as the unfilled polymer, by increase in the yield stress by annealing, while maintaining improved impact properties.

### Experimental Part

#### Materials

Materials used are an injection molding grade PC, Lexan 141R (Sabic Innovative Plastics, Bergen op Zoom, the Netherlands): \( \mathcal{M}_w = 9 \times 200 \text{ g mol}^{-1} \) and \( \mathcal{M}_d = 25 \times 800 \text{ g mol}^{-1} \) and a low temperature impact modifier, Paraloid EXL-2600 (Rohm&Haas), a MBS core-shell copolymer with a diameter of 100 nm. Three blends were prepared on a Werner&Pfleiderer ZSK 28 extruder, containing 0, 4.5, and 9% by volume MBS.

Tensile bars were injection molded according to ASTM 638 type I using an Arburg 320S 500-150 Allrounder. Izod impact bars with dimensions 80 \( \times \) 10 \( \times \) 4 mm\(^3\) were molded according to ISO 180 using an Engel 75 ton injection molding machine. Rectangular plates with dimensions 70 \( \times \) 70 \( \times \) 1 mm\(^2\) were molded using an Arburg 320S 500-150 Allrounder. The mold (Axxicon Mould Technology) guaranteed uniform filling of the cavity, demonstrated by short shot experiments. Different thermal histories were realized to investigate the influence of temperature history during processing on the resulting mechanical properties by changing the mold temperature in three steps (30, 90, and 120 °C). A plate of 1 mm thickness was chosen since this allows for the largest variation in cooling rate.\textsuperscript{[45]} From the plates, bars of 70 \( \times \) 10 mm\(^3\) were cut in flow direction and perpendicular to flow direction, applying gauge sections of 33 \( \times \) 5 mm\(^2\), see Figure 1.

#### Annealing Treatments

Annealing treatments were performed in air circulated ovens at the temperatures as indicated in the respective figures. Equilibration time to the annealing temperatures was determined to be approximately 15 min. After the required annealing period, samples were removed from the ovens and allowed to slowly cool to room temperature prior to testing.

#### Testing

Tensile tests were performed on a Zwick Z010 tester applying either a constant linear strain rate or a constant engineering stress. In the case of constant strain rates, experiments were performed in triplicate and the yield stress was taken as the maximum engineering stress in the obtained stress--strain curves. In case of applied stresses, single measurements were performed for each test condition. A default strain rate of \( 10^{-3} \text{s}^{-1} \) was used. Moduli were measured on a servo-hydraulic MTS 831 Elastomer Testing System equipped with an Instron strain gauge extensometer type 2620-620. Izod impact tests were performed on a 2Zwick pendulum impact tester with five samples per test condition, according to ISO 180. Differential scanning calorimetry (DSC) experiments were performed on a Mettler Toledo DSC823e equipped with a FRS5 sensor. Calibration was performed by melting peaks of indium, lead, tin, zinc, benzophenone, and benzoic acid. Scans were performed in duplo from 20 to 280 °C with a heating rate of 10 K min\(^{-1}\). Standard 40 µl aluminum crucibles were used and samples weighed approximately 20 mg. Nitrogen was used as a purge gas.

#### Results and Discussion

Figure 2 shows the results of notched impact tests performed at different temperatures: PC is brittle even at room temperature, whereas the 4.5 and 9% MBS modified PC samples show ductile behavior (order five times higher impact than pure PC) and ductile to brittle...
transitions at $-31$ and $-46$ °C, respectively. Note that the ductile to brittle temperature is taken to be the temperature at which half the initial impact energy remains.

Along with the increase in absorbed impact energy, a decrease in the strength of the materials, expressed in their yield stress (Figure 3 left) and time to failure (Figure 3 right), is observed. The 9% impact modified PC shows a reduction in the yield stress of almost 10 MPa and a reduction in time-to-failure of more than two decades, a factor of 350, with respect to its unfilled counterpart. The 4.5% impact modified PC shows a decrease in the yield stress of 5 MPa and in the time-to-failure of a factor 15. This decrease in the strength of MBS impact modified PC is similar to those observed in HIPS\(^{29,30}\) and ABS\(^{31,32}\).

The tensile, Figure 3 (left) and creep, Figure 3 (right), behavior of glassy polymers was shown to be governed by the same deformation process.\(^{40,46}\) It follows Eyring’s flow rule,\(^{46–48}\) and the yield stress as a function of strain rate under isothermal conditions is given by

$$\sigma_y(\dot\varepsilon) = \sigma_0 \cdot \sinh \left( \frac{\dot\varepsilon}{\dot\varepsilon_0} \right)$$  \hspace{1cm} (1)

where $\sigma_y$ is the yield stress, $\dot\varepsilon$ the strain rate applied, $\sigma_0$ a characteristic stress, and $\dot\varepsilon_0$ is a rate constant, and with the introduction of a critical plastic strain, $\varepsilon_{cr}$\(^{49}\) the time-to-failure, $t_f$, as a function of applied stress, $\sigma_a$, is given by

$$t_f(\sigma_a) = \frac{\varepsilon_{cr}}{\dot\varepsilon_0} \left[ \sinh \left( \frac{\sigma_a}{\sigma_0} \right) \right]^{-1}$$  \hspace{1cm} (2)

where $\sigma_y$, $\dot\varepsilon_0$, $\varepsilon_{cr}$, and $\sigma_a$ are the yield stress of the impact modified PC, the yield stress of the unmodified PC and the volume fraction impact modifier, respectively.

Equation 3 is taken from reference\(^{50}\) and is based on the results obtained with rubber-toughened PMMA.\(^{28,51}\)

In Figure 4, we verify its applicability on experimental data of rubber-toughened materials taken from literature; PMMA\(^{28,51}\) \(23,24,52\) and a PC/PET blend\(^{27}\). The scaling rule proposed is empirical by nature, and not based on any theory of deformation processes involved like it is done for elastic moduli of two-phase systems,\(^{53–55}\) or for the influence of voids or rigid fillers on compressive yield.\(^{56}\)

The time-to-failure, $t_f(\sigma_a, \phi)$, which also gives an excellent description of our experimental data, using the same parameters as for the unmodified PC.

From the data presented so far it can be concluded that although the addition of a MBS impact modifier significantly increases the impact toughness of PC,
the strength of the material is severely diminished, i.e. a decrease in the yield stress of 5 and 10 MPa and a decrease in the time-to-failure of one and two orders of magnitude for the 4.5 and 9% impact modified material, respectively. The yield stress of all polymers, including PC, can be significantly increased by annealing,\cite{35–39,57–59} and indeed the same increase can be realized for impact modified PC. This is demonstrated in Figure 5, where the yield stress is plotted as a function of annealing time for different annealing temperatures and increases linearly with the logarithm of the annealing time. From Figure 5 it is estimated that annealing treatments of 1.5 h at 110 °C for 4.5% MBS and 8.5 h at 120 °C for 9% MBS are required to increase the yield stresses to the level of the unmodified PC. It is well known that the application of long annealing periods at elevated temperatures may result in the yield stress reaching its equilibrium value,\cite{60,61} however, the treatments applied in this study did not lead to increases of such extent.

The results of these treatments are presented in Figure 6, where it is shown that the strain-rate dependence of the yield stress (left), as well as the lifetime under applied stress (right), can be restored to the level of the unmodified PC. Similar to the untreated samples, all annealed samples failed ductile by necking.

The following question now arises. To what extent does the annealing treatment influence the impact properties? Figure 7 shows the Izod impact energy versus test temperature for the two annealed impact modified PCs and the pure PC. It is clear that the impact modified materials, although having received annealing treatments, still have a considerably enhanced impact toughness. Compared to their un-annealed counterparts (Figure 2), a small increase in the ductile-to-brittle temperature of 3 °C for the 4.5% and 7 °C for the 9% impact modified materials is found. An upper limit in the effectiveness of annealing treatments, however, does exist, since annealing at too high temperature (135 °C) leads to degradation of MBS and formation of active radical species that cause molecular weight reduction in the PC.\cite{24}

Where annealing treatments unambiguously lead to an increase in yield stress and a decrease in impact toughness, the modulus of annealed polymers can either increase,\cite{29} or decrease,\cite{2,62} depending on the relaxation of possible frozen-in orientation.\cite{63} The moduli for the pure PC and impact modified PCs are given in Figure 8 (right) and are seen to decrease on annealing, both for the pure PC and for the modified PCs. The decrease in modulus for the modified PCs is ~4%, and for the unmodified PC maximum ~6%, and therefore not significant. The initial moduli can be described by a modified Halpin–Tsai relation,\cite{64,65} the solid drawn line in Figure 8:

\[
E_c = E_m \frac{1 + \zeta \eta \phi}{1 - \eta \phi} \quad (5)
\]

\[
\eta = \frac{(E_f/E_m) - 1}{(E_f/E_m) + \zeta} \quad (6)
\]

\[
\phi = 1 + \frac{1 - \phi_m}{\phi_m^2} \phi \quad (7)
\]

where \(E_c\) is the modulus of the composite, \(E_m\) the modulus of the matrix, \(\zeta = 1.5\), \(\phi\) the volume percentage filler, \(E_f\) the modulus of the filler, and \(\phi_m\) is the maximum packing fraction of filler (0.637 for randomly packed spherical particles, all of the same diameter).

Summarizing, annealing improves the long-term properties of impact modified PC, while maintaining its
improved impact properties. It should be noted, however, that property modification by thermal treatments is not only limited to annealing, but can also be accomplished during processing. For pure PC the yield stress as it results from the thermal history experienced during processing can even be predicted based on an approach using Time-Temperature-Superposition to calculate the evolution of effective time during the cooling stage\(^{[45,61]}\). This approach is also applied to the impact modified PCs, and the evolution of yield stress with time and temperature, as measured after annealing below \(T_g\) (see Figure 5), from which the evolution of the effective time is derived, is shown in Figure 9. These master curves were constructed using an Arrhenius type of temperature shift, with an activation energy of 205 kJ mol\(^{-1}\), and can be described by\(^{[49]}\)

\[
\sigma_y(t, T, \phi) = \sigma_{y,0} + c \cdot \log \left( \frac{t_{\text{eff}}(t, T) + t_0}{t_0} \right) \cdot (1 - 1.375\phi)
\]

(8)

where \(\sigma_y\) is the yield stress, \(t_{\text{eff}}\) the effective time, \(t\) the time, \(T\) the temperature, \(\sigma_{y,0}, c,\) and \(t_0 = 1\) s are fit parameters, and

\[
t_{\text{eff}}(t, T) = \int_0^t \frac{1}{\tau(T')} \cdot \frac{1}{T(T')} \, dt'
\]

(9)

\[T' = T_0 \cdot \exp \left( \frac{Q}{RT} \right),
\]

where \(Q\) is the activation energy of the isostatic ageing process.

Figure 6. Left: Yield stress versus strain rate. Right: Applied stress versus time-to-failure. For the 0% (○), annealed 4.5% (■), and annealed 9% (▲) impact modified PC.

Figure 7. Izod impact energy of 0% (○), annealed 4.5% (■), and annealed 9% (▲) impact modified PC versus temperature.

Figure 8. Decrease in elastic modulus with annealing. Open symbols are for the as-received materials; closed symbols for the annealed materials. Solid drawn line according to Equation (5).

Figure 9. Mastercurves of the increase in yield stress with effective time, for the 0% (○), 4.5% (□), and 9% (▲) impact modified PCs. (measured at \(\dot{\varepsilon} = 10^{-3}\) s\(^{-1}\))
where \( \Delta U_a \) is the activation energy, \( R \) the universal gas constant, and \( T_{\text{ref}} \) a reference temperature.

The solid drawn line describing the master curves in Figure 9 are obtained by evaluating Equation 8 with parameters taken from a previous study, see Table 2. The master curves describe the experiments rather accurately, although at long annealing times the 9% impact modified yield stress is slightly over-predicted.

The parameter \( t_a \) in Equation 8 can be regarded as the initial age of the material, i.e. the effective (aging) time obtained during processing, \( t_{\text{eff},c} \). Aging during use only leads to an increase in yield stress when the effective time becomes of the same order of, or greater than, the initial age. By evaluating Equation (9) and (10) already during the cooling stage of the injection molding process, \( t_{\text{eff},c} \) can be calculated, and thus \( t_a \) predicted. This will be demonstrated. Thermal histories are obtained by numerical simulation of the injection molding process. Analysis of the thermal behavior of the modified PCs indicates that the presence of the MBS filler has no significant influence on either \( T_g \) or on specific energy, see Figure 10, and we therefore apply the temperature information obtained from the analysis of the unmodified material also to the impact modified materials.

Figure 11 shows the results of the directly predicted yield stresses versus the experimentally determined ones. Note these predictions were obtained without the need of any additional mechanical testing. Clearly an excellent agreement is found between the experimental and numerical results for mold temperatures below 100 °C. At higher mold temperatures the predicted yield stresses overshoot the experimental values. No clear explanation was found for this deviation, but from a practical point of view, the range of (high) mold temperatures, where we see a deviation, is not used in commercial polymer processing. The influence of anisotropy is found to be negligible for the experiments performed here; differences between experiments performed parallel and perpendicular to flow are small (<1.5 MPa; <3%).

If we now compare the yield stress of the 4.5% impact modified PC injection molded at 120 °C with the unmodified PC injection molded at 30 °C, there is only a difference of 1 MPa. This indicates that the performance of these two materials is almost identical when evaluating tensile or creep behavior, whereas the impact modified material still shows far superior impact behavior.

### Conclusion

Rubber modification of PC leads to significant improvement in impact performance, while the strength of the material under constant strain rates and stresses is...
dramatically decreased. The addition of 4.5 and 9% impact modifier leads to a decrease in creep rupture lifetime of more than one and two orders of magnitude in time, respectively. Application of short annealing treatments well below the glass transition temperature (<10 h at temperatures <120 °C), gives rise to an increase in yield stress, and the tensile and creep performance of modified PCs can be made to match that of unfilled PC, while a superior impact strength is maintained.

Using a modeling approach based on the classical Eyring flow theory in combination with an empirical scaling rule enables the description of the deformation behavior of impact modified PC as a function of volume percentage impact modifier. The properties of modified PC after processing are predicted based on the combination of a previously developed modeling approach capturing the evolution of yield stress during processing and the aforementioned scaling rule. The combination of these modeling approaches forms a powerful tool to predict and adapt the overall performance of impact modified PC based on the desired low temperature notched impact strength that determines the volume percentage impact modifier needed.

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