Physical recycling of the material of PET bottles

PhD Dissertation
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Theses

Thesis 1 I revealed that stress oscillation occurs in injection molded specimens made of original and recycled PET in the 35-135 mm/min tensile speed range at room temperature, and this is accompanied with significant void formation in the specimens. I verified through measurements that voids are formed simultaneously, in an intermittent way before the stress peaks are reached. I showed that the heat insulation capability of the material increases significantly owing to the formed voids, the temperature of the deformation zone increases rapidly, and as a result stiffness decreases and elongation occurs. However, the material cools down during neck propagation, molecular orientation takes place, and stiffness increases again, and the process becomes periodical. I verified my results with electron microscopic images, acoustic emission measurements and stress optical investigations.

Thesis 2 I created a mathematical model to describe the stress oscillation phenomenon that occurs during the tensile tests of PET. During modeling the amorphous molecule chains were considered as special fiber bundles containing wavy fibers attached to a two-element Maxwell model, hence I described the periodic local transformations and the viscoelastic, speed-dependent behavior of specimens. I compared the model and the characteristic of the measured tensile curves using the parameters determined from the measurements, and I found that the developed, simple model can be applied well to describe the phenomenon.
The stress-strain relation that describes the model in the $(n+1)^{th}$ interval ($t_n<t\leq t_{(n+1)}$) of oscillation is:

$$\sigma(t) = \sigma_o e^{-(t-t_n)/\tau_n} + E_n \dot{\varepsilon}_n \tau_n \left(1 - e^{-(t-t_n)/\tau_n}\right),$$

where $\sigma(t_n+0)=\sigma_o$; t is time; E_n is the model parameter of the spring that follows the law of Hook, η_n is the model parameter of the viscous element that follows the law of Newton; τ_n is the time constant ($\tau_n = \frac{\eta_n}{E_n}$); while $\dot{\varepsilon}_n$ is the rate of elongation.

Thesis 3 I concluded that the $l_c=2l_s$ critical fiber length can be determined using the following formula if the length distribution of fibers in the composite is known, and the mathematically calculated and measured fiber length distribution, as well as the average fiber length (l_{p1}) are compared for fibers protruding from the fracture surface – formed in tensile tests – of unidirectionally reinforced short fiber composites:

$$\bar{l}_{P1} = \frac{\int_{l_1}^{l_S} x dS_m(x)}{S_m(l_S) - S_m(l_1)},$$

where $\bar{l}_{P1}$ is the average of fibers longer than a given l_1 threshold vale, protruding from the fracture surface; and $S_m(x)$ is the distribution function of the active staple length.

The critical fiber length determined with my new measurement and evaluation method turned out to be higher than the critical fiber length calculated from the microdroplet test in case of glass fiber reinforced PET. I proved with the help of this and a simple simulation calculation that in case of the local type microdroplet test the conditions of fiber-matrix connection are better than the real ones, and the value of critical fiber length is not constant in the examined composite. I verified that in this case the resultant critical fiber length characteristic of the composite changes depending on the selection of the l_1 threshold value. These changes can be revealed and traced with the developed method.

Thesis 4 I proved that the mechanical properties of recycled PET can be maintained and improved not only using the different additives (e.g. elastomers and polycarbonate) suggested by the literature but also by modifying the technological parameters of processing. I revealed that the temperature of the injection mold in the range examined by me, i.e. between 7 and 65°C, which is below the glass transition point of the material, is in an exponential connection with the impact strength of recycled PET described by the following formula:

$$a_{cN} = 41{,}186 \frac{kJ}{m^2} \cdot e^{-0{,}007 \frac{1}{K} \cdot T},$$

where a_{cN} is impact strength; and T denotes temperature of the mold.

The increase in the impact strength achieved due to the low mold temperature can be explained by the change in the core-skin structure of the product: the crystallinity of the core decreases, while the volume ratio of the amorphous skin part increases.

Thesis 5 I determined the optimal technological parameters – considering the mechanical properties – of self-reinforced PET composites produced with the 'film stacking' method. I verified with measurements that 45-50 weight% fiber content and 190-220°C processing temperature provide ideal properties for PET fiber reinforced polyethylene-terephthalate-glycol copolymer matrix self-reinforced composites. I found that consolidation is not sufficient at lower temperatures or higher fiber contents what leads to a decrease in the mechanical properties.