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Cavity formation and stress-oscillation during the tensile test of injection molded specimens made of PET

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Summary

Behavior of specimens produced from one-way polyethylene terephthalate (PET) bottles by milling, drying and injection molding was studied under tensile load. Uniform and stable necking and neck propagation during tensile testing has been replaced under certain tensile rates by an oscillation of stress and neck propagation. Studying the crystallinity and density of specimens undergoing oscillation it was observed that they exhibit more than 50% cavitation. Results of acoustic emission measurements performed during tensile testing revealed that cavitation occurred simultaneously with neck propagation, periodically. Cavities were studied by scanning electron microscopy. In order to study the heat effects coupled with uniform neck propagation heat radiation of the surface was also detected. Infrared thermograms taken by an camera have shown that, within the oscillation cycle, simultaneously with the increase of the stress the temperature of the deformation zone increased, but when the stress decreased (during neck propagation) the temperature decreased.

Introduction

Handling the large amounts of waste coming from beverage bottles made of polyethylene terephthalate (PET) is a serious environmental problem nowadays. As compared to environmentally un-aesthetic deposition and wasteful incineration physical recycling provides a better solution. An indispensable prerequisite of using this technology is, however, the knowledge of the properties of the recycled material. It is well known that under tensile load PET may undergo several hundred percent deformation accompanied by the so-called "necking" phenomenon [1-4]. Stress-oscillation (or self-oscillation) occurring under certain circumstances during the necking of PET was first reported in 1970, when the neck propagation induced by static tensile loading in amorphous PET was studied [5]. Stress oscillation means that the stress developing during necking is not constant anymore, but exhibits periodic fluctuations as a function of time [6]. The causes of this oscillation are not clear and are strongly debated in the technical literature [7]. Explanations include: local heating caused by orienting elongation [8-12]; oscillation of local deformation rates in the critical stress range during necking [13]; crystallization during orientation induced by adiabatic heating [14]. Barenblatt used the concept of local heating to describe the phenomenon of unstable neck propagation [8]. He concluded that the elasticity of the whole system (consisting of the elasticity of the test specimen and that of the testing system) is the parameter, which determines the stability of the whole system. When the elasticity reaches a critical value, the system becomes unstable and starts to oscillate. From the fact that during the tensile tests performed by Adrianova et al. [9] under water no oscillation appeared, Barenblatt came to the conclusion that, due to the higher heat conductivity of water as compared to air the thermal effect was not large enough to induce the oscillation.

Pakula and Fischer [13] described a transition in the deformation behavior of PET induced by stress. In experiments performed under constant stress two ranges were found where a critical stress changed the neck propagation rate abruptly. They found that this critical stress depends on the temperature and on the elongation-distribution within the transformation zone. Below and above the critical stress the neck propagation is homogeneous. This transition was brought in connection with the oscillation, as the critical stress is approximately equal to the stress maximum of oscillations. Similar transition was found in other polymers prone to crystallization, such a polypropylene (PP), polyamide (PA) or PET, but in non-crystallizable polymers (e.g. polycarbonate (PC)) no such transition was found. Pakula and Fischer modified somewhat the under-water test and applied local cooling. This local cooling, however, could not prevent the oscillation. They came to the conclusion that the effect of water bath is related to the deformation and not to the increased heat transfer at the test specimen. Nevertheless molecular orientation and crystallization invariably lead to heat release, so temperature increase can be observed in each tensile test. According to their opinion, however, these heat effects are the result of the deformation process and not the cause of the transition in the deformation behavior. The cause of the oscillation is – according to their opinion – is the crystallization appearing above the critical stress.

Godovsky [14] also proposed a crystallization model. He mainly took into account the increased temperature in the transformation zone. He refers to the work of Ward [15], where the temperature step of PET is calculated as a function of the neck propagation rate. The theoretical temperature step is much smaller in the case of homogeneous neck propagation than the temperature step calculated for the formation of a non-translucent band, so a further heat source must be present during the oscillation process. Such a heat source can be orienting crystallization. According to him the local temperature increase is not the cause but the consequence of the unstable neck propagation.

Based on recent results [16] stress-oscillation may appear also in polymers (e.g. in PC), which do not undergo stress-induced crystallization.

Karger-Kocsis et al. [17,18] studied the oscillation phenomenon is sPP. In their opinion necking, which is a necessary preprequisite for stress oscillation in each polymer, produces a deformed, entangled network. Nodes of this network are mainly the crystallites of all-trans conformation. This network resembles in many respects partly crystalline thermoplastic elastomers. The deformation of this composite system is strongly inhomogeneous. This, by itself, induces the onset of shear deformation. According to their reasoning when some smaller crystallites dissolve during elongation, shear deformation becomes even stronger and cavities are formed at the crossings of shear bands. When the density of the shearing micro-waves of these crossings reaches a critical level, the material is weakened, its load-bearing capacity drops – due to the sudden cavitation. This explains the stress-drop in the amplitude of the stress oscillation. According to this explanation shear bands can rarely cross at the surface of the specimen. This is corroborated by the experimental observation that cavities can always be found in the interior of the test specimen. Based on this model it can be predicted that an increase of the molecular mass and crystallinity of sPP should result in even more frequent stress oscillation. It has to be taken into account, however, that this model assumes that that each model exhibiting stress-oscillation behavior, should fail by shear bands.

According to Ebener [19] the oscillation appears if the test specimen can store enough elastic energy. For this the initial length of the test specimen should be large enough. The elastic energy storing ability can also be achieved by using an external spring. According to his measurements if the deformation rate is increased during the oscillation, then the mean stress and amplitude decrease, while the local heat conduction leads to an increase of the mean stress. According to his opinion – as both strong orientation and heat release occur – the polymer may crystallize both the non-transparent and in the partially crystalline bands. As the local deformation rate is higher when the non-transparent bands are formed the crystallization is easier here. But not all of the non-transparent bands were found to be partially crystalline.

From the literature review it can be concluded that the main causes of the stress oscillation are identified as heating, stored elastic energy and crystallization. In contrast to the previously mainly used film specimens our scope was to study thick, injection molded specimens where, due to the larger cross-section cavitation and thermal processes can be better studied. Combining the test methods used so far we could investigate the heat and sound emission during the oscillation phenomenon in a complex manner, as well as the density variations and cavitation phenomena.

Materials and test methods

In our study regranulates produced from cleaned and milled PET bottles collected by Lamba Ltd. (Hungary) were used to produce test specimens. First step was the extrusion and granulation of the milled material to prepare it for injection molding. Before extrusion the material was dried for 12 hours at 110 °C. Extrusion was performed on a twin-screw extruder of Brabender Plasti-Corder PL2100 type. Zone temperatures from the orifice to the nozzle were as follows: 244, 248, 244 and 242 °C. Dog-bone tensile test specimens were made from the granulate by an Arburg Allrounder 270C injection molding machine. Zone temperatures of the injection molding machine were as follows: 235/240/245/250/255 ºC, injection pressure was 500 bar. The mold was cooled with a water of 15 °C temperature.

Mechanical properties (tensile stress, Young's modulus, elongation at break) were measured according to the ISO 527- 1993 (E) standard, using a Zwick Z020 universal tensile tester, at room temperature, using different deformation rates.

Cavitation of the test specimen was inferred from the crystallinity and density data. The crystallinity was determined by a Perkin-Elmer DSC-2 type scanning calorimeter, at a heating rate of 20 K/min. The density was measured by weighing 1 cm^3 pieces by an Explorer Ohaus type balance.

The damage process was monitored by acoustic emission (AE) technique, using a SENSOPHONE AED-40/12 (Hungary) type instrument. Tensile specimens were equipped with piezoelectric microphones of A-11 type. Photographs were taken of the cavities and cracks formed in the material by a Philips XL-30 type electron microscope. Temperature variations of the specimen were monitored by a Paytek TI 30 type infrared thermocamera.

Results and discussion

Tensile test specimens were investigated at deformation rates of 1-160 mm/min. Oscillations were observed in the range of 30-130 mm/min. Amplitude and repetition time of the stress oscillation were studied as a function of the deformation rate (Figure 1). Based on our experiments it was observed that the amplitude of the oscillation decreased from 358 N to 172 N, while the repetition time decreased from 1.76 s to 0.97 s with increasing deformation rate (Figure 2).

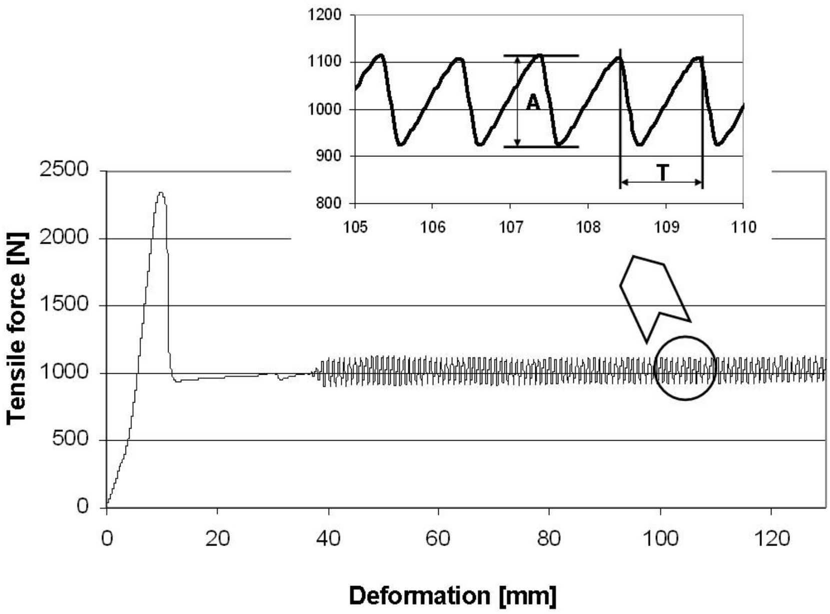

Figure 1. Force-time diagram of a partially crystalline PET sample at a deformation rate of 110 mm/min

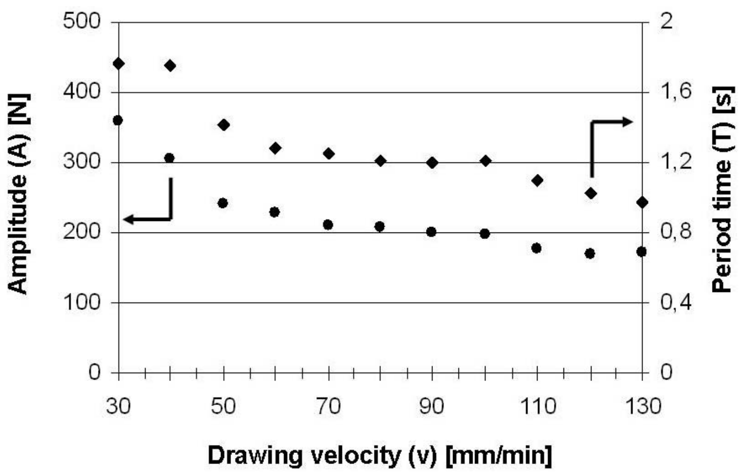

Figure 2. Oscillation amplitude and repetition time plotted against the deformation rate

The macroscopic manifestation of the stress oscillation is the appearance of a ribbed structure under the upper clamping (neck region), oriented perpendicularly to the load direction (Figure 3).

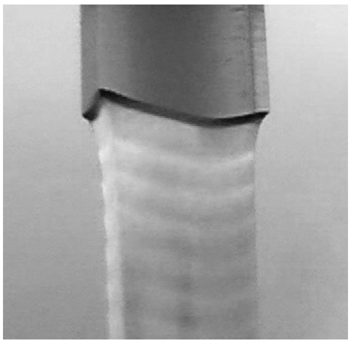

Figure 3. Manifestation of the stress oscillation on the tensile test specimen

Regions developed, which can be distinguished by the naked eye, have been denoted as shown in Figure 4. Average density and average crystallinity were measured in each zone. From the measured crystallinity the theoretical density of the specimen was determined as follows [20]:

$$\rho = [\chi \cdot \rho_{cr} + (1 - \chi) \cdot \rho_a] / 100\ \% \qquad (\mathbf{1})$$

where ρ is the density of the material; χ is the volume fraction of the crystalline phase; ρ_{cr}=1.455 g cm^{-3} is the density of the crystalline phase; ρ_a=1.335 g cm^{-3} is the density of the amorphous phase.

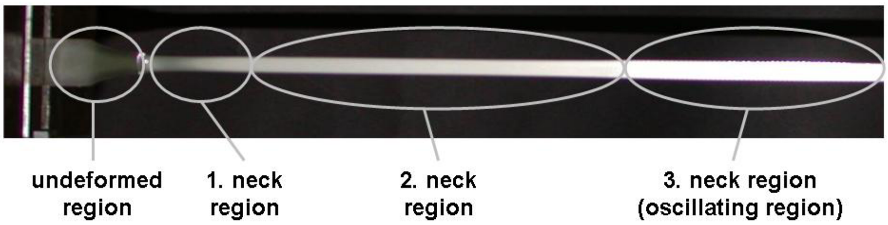

Figure 4. Zones found in oscillating test specimens

The density calculated from the crystallinity did not vary considerably in the various zones of the test specimen. A slight increase was attributed to the crystallization caused by the deformation, resulting in a denser crystalline phase. The actual density obtained form weighing a unit volume is identical to the theoretical one in the undeformed region. In the neck region, however, the measured actual densities are much lower than the calculated values, which can only be explained by discontinuities, by the presence of porosity in the material. The highest degree of porosity (exceeding 50%) was observed in the oscillating region, while the degree of porosity in the non-oscillating neck region varied between 10-30% (Table 1).

Table 1. Average density and crystallinity measured in the various zones and the calculated density (from crystallinity) and porosity (from the actual and calculated densities)

Regions	measured density (weighing unit volume) (g/cm^3)	crystallinity (%)	density calculated from crystallinity (g/cm^3)	porosity (%)
un-deformed	1.34	8.2	1.34	~0
neck 1	1.26	42.1	1.38	~ 10
neck 2	0.97	40.9	1.38	~ 30
oscillating	0.64	38.2	1.38	~ 54

Cavitation was investigated by SEM in the un-deformed, in the 2nd necking and in the oscillating regions. Figure 5 shows the cross-section of the un-deformed region, where no cavitation is observed. In Figure 6 significant cavitation can be observed in the 3rd neck zone (oscillating region). The cross-section of the tensile specimen is much less than that of the un-deformed region, due to the necking phenomenon. Cross section of the cavities can be approximated by circles or by ellipses. Their average diameter is about 30 μm, no orientation is discernible on the micrograph. Cavities can be found only in the central part of the cross section, none in the outer 0.4 mm rim. Longitudinal sections of the cavities are parallel with the tensile force, their average length is about 1 mm.

Events observed by acoustic emission can be attributed to material failures occurring during cavitation. Events appeared simultaneously with neck-propagation, stepwise (Figure 7), in contrast to uniform neck propagation, where the events were observed continuously. The amplitude of the acoustic events varied between 13-33 dB in both cases (uniform neck propagation and oscillation), typical of matrix material deformation and failure (tear) [21].

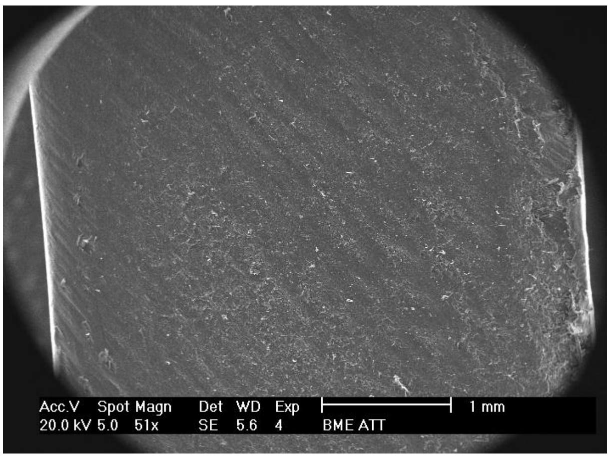

Figure 5. SEM micrograph of a cross-section in the un-deformed region (cross section, 51x magnification)

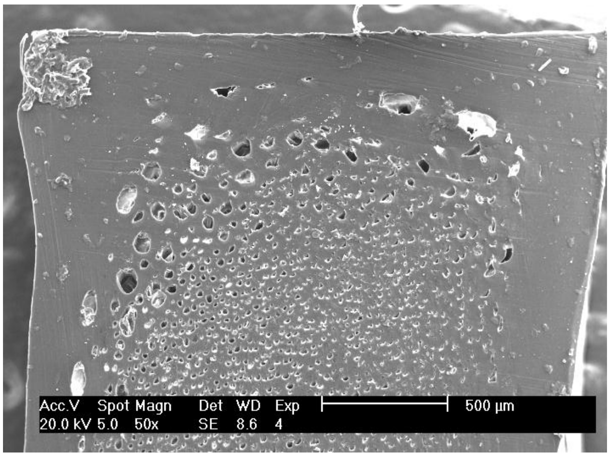

Figure 6. SEM micrograph of the oscillating region (cross-section, 50x magnification)

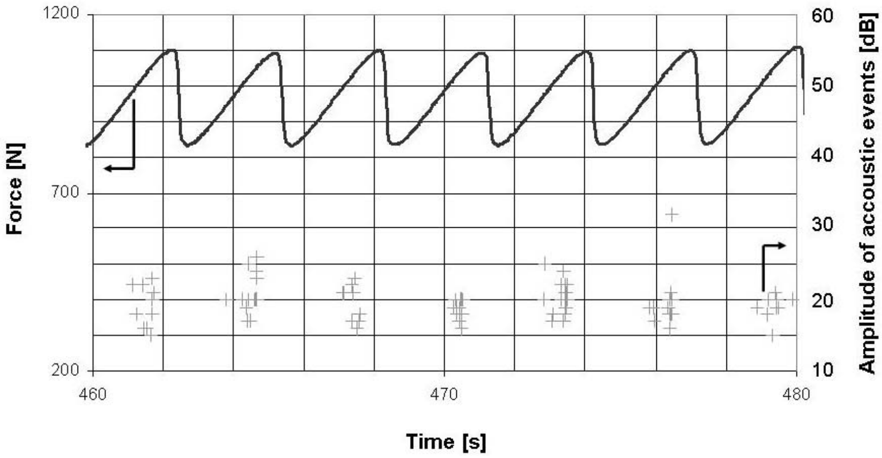

Figure 7. Acoustic events occurring during stress oscillation. (Amplitude of acoustic events [dB], force [N], time [s])

After starting the tensile test the specimen warmed up homogeneously. Up to the yield point this temperature increase reached only 0.5 °C with respect to the original temperature (22 °C). Localization of the extension, i.e. necking is accompanied by a significant, 36-40 °C temperature rise. During uniform neck propagation the temperature distribution in the neighborhood of the neck did not change considerably. The temperature of the hottest point at the deformation zone was about 63 °C, the neck part formed underwent a continuous cooling.

Temperature values cited were observed on the surface, presumably the values inside the specimen could be even higher. In the range of the stress oscillation strong temperature rise to about 73-74 °C were observed around the stress peaks, followed by 10-15 °C cooling in the periods of stress drop (Figure 8).

The fact that the stress oscillation observed during the tensile test of injection molded PET specimens appears at a well-defined deformation rate implies that the heat release

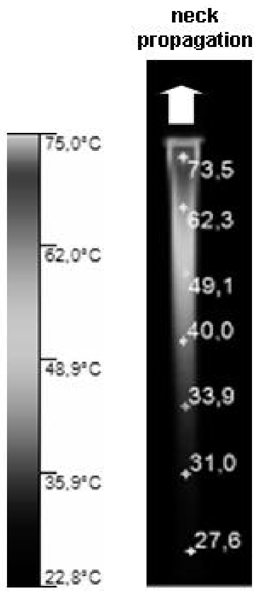

Figure 8. Temperature distribution in the stress oscillation range

and the consequent temperature rise caused by the dissipation of the work input has some effect on the phenomenon. Below 35 mm/min deformation rate necking occurred on the specimens, but no oscillation appeared. Above this deformation rate oscillation was observed up to 135 mm/min deformation rate. Above this deformation rate brittle fracture was observed – without necking.

When measuring the crystallinity it was observed that the crystallinity of the extended material increased abruptly (about 5 times) as compared to the un-deformed material. This can be explained by the so-called cold crystallization [22-23]. The density calculated by taking into account the size of the crystalline and amorphous areas deviates, however, sharply from the observed value, calculated form the weight and volume, indicating the presence of porosity, cavities. The porosity is the highest in the oscillating region, where it reaches 54%.

From the appearance of the acoustic signals it can be concluded that the cavities appear before reaching the stress oscillation peak, i.e. the reduced load-bearing capacity caused by the cavitation is not the direct cause of the stress drop observed in the oscillation cycle and of the extension. The material observed between the cavities exhibits fibrillar structure, the fibrils are formed from bundles of parallel molecular chains. A small number of perpendicular fibers within the cavities could be formed from molecules not oriented along the tensile force. The process of molecular bundle orientation is sketched in Figure 9. Large arrows indicate the direction of the tensile force. The conformation of molecular chains in the un-deformed region is not fully extended, this state is reached only in the deformation zone (see Figure 9/a). Extended chains can, however get closer to each other, therefore they occupy a smaller volume and, due to their mutual interactions shear forces play an important role in the deformation zone. At a given limiting stress value molecular chains split into bundles, accompanied by the formation of inter-bundle cavities (Figure 9/b). Molecular chains,

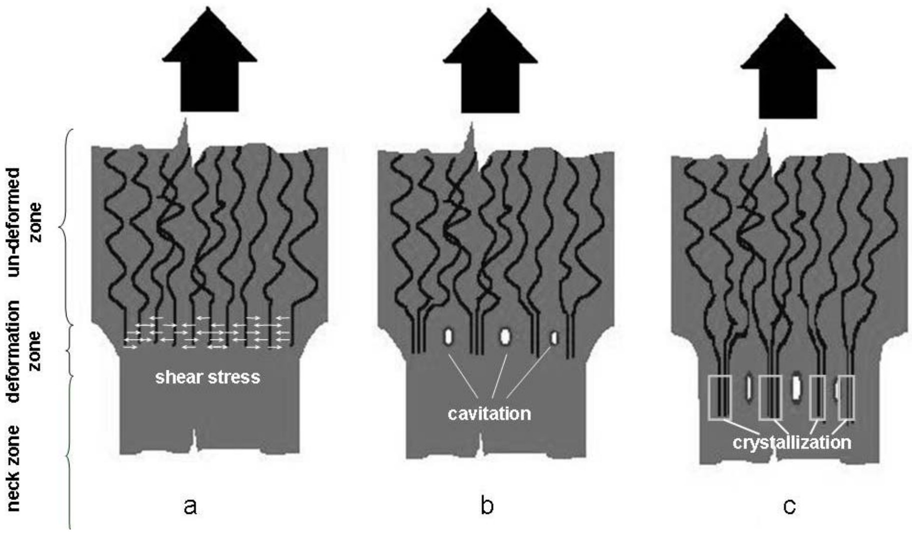

Figure 9. Model of the cavitation process

which are close to each other, can for crystalline structure, accompanied by heat formation (Figure 9/c).

One important consequence of cavitation is that the heat conductivity of the material decreases considerably. When cavities are formed the heat formed (further increased by crystallization) can only be conducted to the surface and transmitted to the air or emitted by radiation. Therefore the temperature of the deformation zone increases abruptly. This phenomenon is clearly manifested on the thermographs. The temperature rise brings the material from glassy into high-elastic state (as the glass temperature is exceeded), therefore in the deformation zone the amorphous molecular chains slip, an extension follows, i.e. the neck propagates. During extension, however, the material transports heat from the critical area, as complete failure does not occur. During cooling strength properties increase again, neck propagation stops, the phenomenon becomes periodical.

Summary

In our study injection molded specimens made of PET recyclate were investigated by tensile testing. It has been observed that in the deformation rate range of 30-130 mm/min stress oscillation occurs at room temperature, accompanied by a significant cavitation of the test specimens. Cavity formation occurs simultaneously with the stress oscillation, periodically, before reaching the stress maxima. Due to the cavity formation the heat conductivity of the material decreases considerably, therefore the temperature of the deformation zone increases abruptly, resulting in reduced strength and elongation. During neck propagation, however the material cools down, the strength increases again, so the process becomes periodic. This picture was backed by scanning electron microscopy and by acoustic emission measurements. In order to describe the phenomenon a physical model was created which traces back the phenomenon to changes in the molecular structure. According to this model strong shear stresses arise between the molecular chains orienting under the effect of the

tensile force and, as a result, the material splits into molecular bundles. This rearrangement into bundles is accompanied by significant crystallization. Microcracks appearing between the bundles decrease the heat conductivity of the material considerably, resulting in local overheating.

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