Faster thermoplastic polyurethane crystallization with an organic nucleating agent

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An organic salt, sodium octacosanoate proved to be an efficient nucleating agent for polyester-based thermoplastic polyurethanes of distinct molecular weights.

A combination of rubber-like properties and easy processing makes thermoplastic polyurethanes (TPUs) an important class of materials. Due to their high toughness and good abrasion resistance, polyester-based TPUs are extensively used in the automotive, footwear, and furniture industries. Reasonably low crystallization time is very important for acceptable productivity for some applications, such as footwear. Beside this, the crystallization process can noticeably affect morphology and, as a consequence, the physical, chemical, and mechanical properties of semicrystalline TPUs.

The crystallization kinetics of thermoplastic polymers have been investigated in many scientific studies. A number of organic and inorganic compounds have been used as nucleating agents, i.e., crystallization initiators and accelerators that allow a higher degree of crystallization, smaller crystallites, and lower crystallization time. For that, polymer/agent interaction must reduce the interfacial free-energy barrier for spontaneous nucleation and growth. Despite the wide use of nucleating agents in polymer technology applications, studies on the crystallization of TPUs in the presence of nucleating agents are hard to find.

Organic salts have an advantage over inorganic nucleating agents in that they promote homogeneous distribution in polymers even with ordinary mixing techniques. Montanic acid salts—i.e., n-octacosanoates, CH3(CH2)26COO−—are organic high-molecular-weight compounds that show low volatility and exudation, being generally applied to polyester and polyamide formulations. We examined the effect of an organic nucleating agent based on sodium octacosanoate (NaC28−32, 0.5 wt%) on the crystallization and material properties of two aromatic crystalline TPUs (Pearlbond® D180) of distinct molecular weight (57,000 and 30,000Da, corresponding to melt flow rates of 19.4 and 81.3g/10min, respectively). These TPUs will be called TPU1 and TPU2.

We performed nonisothermal crystallization runs on the neat TPUs and TPU/NaC28−32 systems using a differential scanning calorimeter. We concluded that the filled TPUs exhibited higher crystallization temperatures (Tc) and lower crystallization times (tc) than the respective neat TPUs (see Table 1), whereas the enthalpy of crystallization (∆Hc) did not show a clear trend. Application of the modified Avrami model, which gives information about nucleation and also growth geometry of the crystalline region of the polymer as a function of time and temperature, to the results revealed that the addition of NaC28−32 did not affect the crystalline morphology but induced instantaneous nucleation and the production of axialites (disc-shaped superstructures).

We used the Avrami-Ozawa model, which is a modification of the Avrami model that allows evaluation of nonisothermal processes, to evaluate the correlation between cooling rate (Rc) and crystallization time (t). The cooling rate required to reach a given degree of

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crystallinity showed a systematic increase with $X_c(t)$ (the relative volumetric crystalline fraction) for neat and filled TPUs. The highest molecular weight TPU required lower cooling rates than its respective filled system up to $X(t) = 0.77$, whereas the other TPU showed that in the whole $X(t)$ range. Images for the former TPU obtained using polarized light optical microscopy (see Figure 1) showed very small crystals, which were smaller for the TPU/NaC$_{28-32}$ system compared with neat TPU for the same crystallization time, again indicating the effectiveness of the agent.

We used isothermal crystallization kinetics and the modified Avrami model to calculate the NaC$_{28-32}$ reduced crystallization times for both TPUs. We plotted curves of the variation of the crystallinity degree ($X_c$) as a function of time at three different temperatures for TPU$_1$ (see Figure 2). The S-shaped curve profile indicates that TPU quickly crystallizes in the primary crystallization stage, up to $X_c = 0.7$ (i.e., 70%), slowing down after that. One can also observe that the addition of NaC$_{28-32}$ increases the slope of the curves, confirming its positive effect on TPU nucleation, and makes the crystallization time less temperature-dependent. We also evaluated tensile properties (such as strength and modulus) of all samples, but we did not observe consistent variations between neat and filled TPUs. The degree of crystallization was also unaffected.

In summary, we have shown that TPU crystallization was favored in the presence of sodium octacosanoate, which caused an increase in its temperature and rate of crystallization, consequently reducing the crystallization time. This effect was partly credited to the development of a larger number of crystallization nuclei. The use of well-established kinetics models to the study of the crystallization process indicated that TPU crystallization occurred with the development of 2D lamellar aggregates—axialites—which were not affected by the incorporation of the nucleating agent. Reduction of the crystallization time of this polymer may enable its wider application in the shoe industry, considering the short processing times required in this sector. Our next step is to determine the percentage of rigid segments within the TPU in an attempt to optimize the action of this additive. We also plan to study other nucleating agents that could further reduce crystallization time.

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Continued on next page
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