

TPC-ET with enhanced crystallization rate

Development of modified copolymers and study of their crystallization kinetics via DSC

I. Cucchi, M. A. Ortenzi

Thermoplastic copolyester elastomers (TPC-ET) offer excellent mechanical properties and due to their partial polyester backbone chemical resistance superior to most other thermoplastic elastomers. A weakness of these high performance elastomers is their relatively slow hardening speed. Sipol developed modified copolyesters with improved crystallisation kinetics. The following article summarizes the route to these new grades by using DSC (Differential Scanning Calorimetry).

1 Introduction

Thermoplastic copolyester elastomers are segmented block copolymers obtained through the combination of rigid segments (polyesters) and soft segments (polyethers). These products are called TPC-ET according to ISO 14910-1 but are also well known as COPE or TEEE.

TPC-ET offer outstanding properties for what concerns the mechanical properties (tensile strength, tear strength, impact strength, and creep resistance) which, compared to most other thermoplastics, are much less affected by temperature variations. In addition, their partial "polyester" backbone provides these products with a chemical resistance which is superior to other common thermoplastic elastomers.

Typically the crystalline part of a TPC-ET is a PBT short chain (or a modified PBT) and the amorphous component is a polyether based on polytetramethylene ether glycol (PTMEG). The ratio of the two components as well as

the length of their polymer chains provides the product different combinations of hardness, melting point and other distinctive properties. The Sipolprene range, developed and manufactured by Sipol SpA, covers hardnesses from 25 Shore D to 72 Shore D with melting points between 150 °C and 220 °C.

One of the main weaknesses of TPC-ET is connected to their processing: their relatively slow hardening speed from the molten state to the solid leads to longer cycle times in injection molding because of the long cooling time in the mold. Similar limitations can be observed when TPC-ET is extruded.

2 Effect of different polyethers on the crystallization rate

Studies proved that hardening speed of a TPC-ET can be improved by using PTMEG with higher molecular weight. Disadvantage is a deterioration of the behavior at low temperatures.

An alternative way to increase the hardening speed without compromising on the low temperature behavior is to use a different polyether than PTMEG.

Sipol started working on the evolution of Sipolprene 55200 (PTMEG-based TPC-ET, 52 Shore D) by testing various polyethers chemically different from PTMEG to develop a poly-ether-ester with increased crystallization rate. After several tests, a class of polypropylene glycols end-capped with polyethylene oxide, offering a good balance of reactivity, availability, and performance, was identified. The selection of the most efficient polyether grades, in terms of chain length and % end capped polyethylene oxide, has been done by conducting polymerization tests in a 2 l glass reactor at Sipol R&D Lab. The improvement of the crystallization rate was measured via DSC (Differential Scanning Calorimetry).

The crystallization kinetics of semicrystalline polymers can be effectively studied by means of DSC. This technique is fundamental both for the study of dynamic and for the

Tab. 1: Injection molding conditions

Injection molding machine	Oima Stratos 400-90
Clamping force	90 t
Nozzle	Open with 3 mm Ø
Mold	Tensile bars (ISO 527)
Melt temperature	235 °C
Mold temperature	30 °C
Injection speed	50 %
Holding pressure	30 bar

Tab. 2: Cooling and cycle times

	Sipolprene 55211	Sipolprene 55200
Cooling time	11 s	14 s
Total cycle time	19 s	22 s

Tab. 3: Physical and mechanical properties

	Test method	Sipolprene 55211	Sipolprene 55200
Density in g/cm ³	ISO 1183	1.21	1.19
Hardness in Shore D	ISO 868	54	52
Melting point in °C	ISO 3146	215	198
Tensile strength at break in Mpa	ISO 527	39	43
Elongation at break in %	ISO 527	570	650
Izod impact strength (notched at -40 °C) in J/m	ASTM D256	120	135
Water absorption in %	24 h immersion at 23 °C	2.10	0.30

Dr. Ilaria Cucchi
Ilaria.cucchi@sipol.com
R&D Manager
Sipol SpA, Mortara, Italy

Dr. Marco A. Ortenzi
LaMPo – Laboratory of Materials and Polymers
Università degli Studi di Milano, Italy

isothermal crystallization behavior. A quick indication on the speed of a molten polymer to rearrange its structure in crystalline and amorphous clusters is given by the difference between the melting point and crystallization temperature measured via DSC.

3 Injection molding tests and mechanical characterization

The tests resulted in a development product (Sipolprene 55211). To carry out tests to confirm the quicker crystallization rate of

the development product indicated by DSC, the experimental formulation developed in the glass reactor was scaled up. Sipolprene 55211 and Sipolprene 55200 were processed under similar conditions on the same injection molding machine and trying to achieve the fastest cycle time during the injection molding process (**tab. 1**).

The shortest cooling time achieved for Sipolprene 55200 was 14 s, while with the experimental product (Sipolprene 55211) it was possible to reduce the cooling time to 11 s, an improvement of 21 %. The full cycle

time went accordingly from 22 s for Sipolprene 55200 to 19 s achieved for Sipolprene 55211 (**tab. 2**).

Table 3 shows the comparison of the mechanical properties of the two products. The chosen polyether causes a moderate reduction of tensile/flexural properties but also leads to a substantial improvement of low temperature impact strength. It has also been observed that the change of polyether leads to a higher melting point of the polymers even if the hardness is the same.

4 Crystallization kinetics

The investigation of the crystallization kinetics was carried out at the Laboratory of Materials and Polymers (LaMPo), Università degli Studi di Milano. Being dependent on cooling rates, dynamic crystallization is generally used to assess the ability of a polymer to start the crystallization process in non-equilibrium conditions (i.e. the process is not under thermodynamic equilibrium): since crystallization is an exothermal process, related to the growth of crystals from the polymer melt, higher crystallization temperature indicates that the polymer has the tendency to start nucleation of crystals sooner than polymers with lower T_c .

Another important issue in the dynamic crystallization studied via DSC is related to the shape of the crystallization peak: narrow peaks indicate polymers that have a fast crystallization process (highly desired in injection molding). On the contrary, a broad crystallization peak indicates that crystallization is slow and occurs over a wide range of temperatures, thus making it necessary to increase cycle times. On this regard, Sipolprene 55200 and Sipolprene 55211 were compared using the same thermal cycle:

1. Dynamic segment: from 25 °C to 250 °C @ 10 °C/min
2. Isothermal segment: 250 °C for 5 min
3. Dynamic segment: from 250 °C to 25 °C @ 10 °C/min
4. Isothermal segment: 25 °C for 5 min
5. Dynamic segment: from 25 °C to 250 °C @ 10 °C/min

Fig. 1: Sipolprene 55211 DSC curve (dynamic conditions)

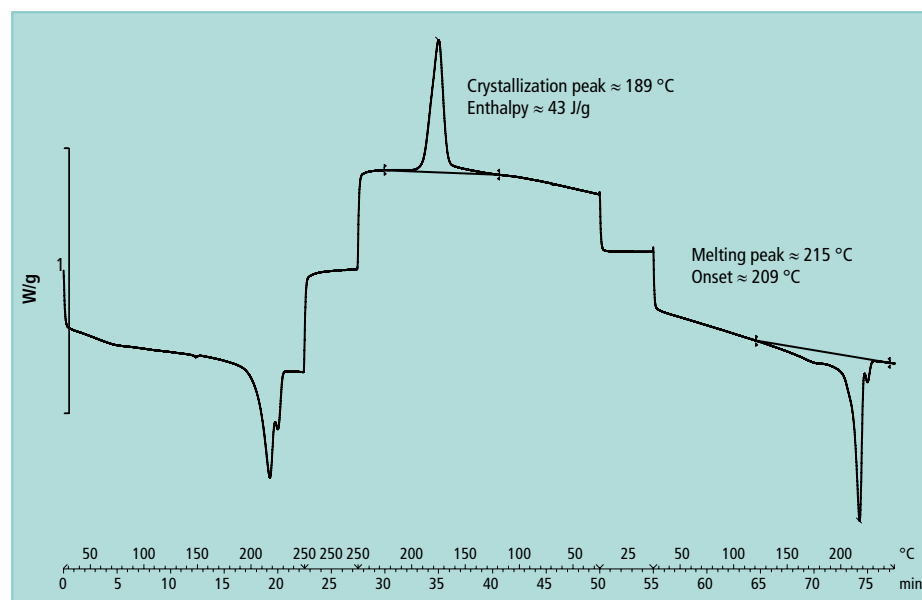
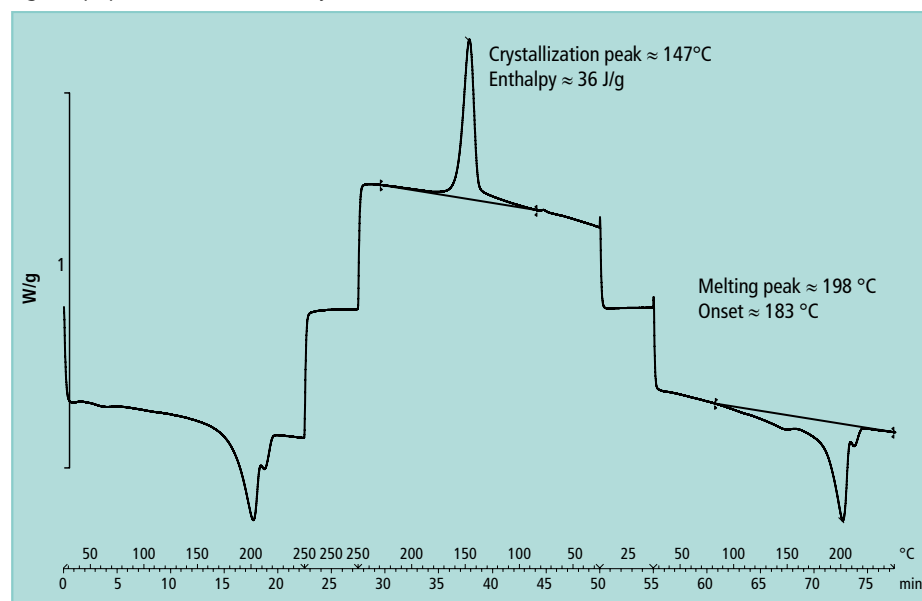


Fig. 2: Sipolprene 55200 DSC curve (dynamic conditions)



Segments 1 and 2 were performed in order to relax internal stresses of the polymer and to let all crystalline fraction melting. The significant part of the analysis is therefore related to segments 3 and 5. The results are shown in **figures 1** and **2**. T_c of Sipolprene 55211 (**fig. 1**) is more than 40 °C higher than T_c of Sipolprene 55200 (**fig. 2**), even if T_m is only 16 °C higher. This is not the only positive feature of the new experimental Sipolprene, since also crystallization enthalpy, directly correlated to the crystalline fraction of the polymer, is higher. This indicates that Sipolprene 55211, under dynamic conditions, can crystallize more than Sipolprene 55200 and it explains why in the new polymer there is only a moderate reduction of tensile/flexural properties and why toughness at low temperatures is maintained.

Isothermal crystallization, on the other hand, is used to assess the thermal properties of polymers under thermodynamic conditions. No thermal stress is provided: the same temperature is maintained for a set period of time and the polymer is free to release all the energy related to the crystallization process over time. This implies that isothermal crystallization is used to determine crystallization kinetics and "behavior" of polymers. One of the most used and reliable equations for this purpose is the Avrami equation:

$$1-X_c = e^{[-K_c \cdot t^n]}$$

or

$$\text{Log}[-\ln(1-X_c)] = n \text{Log } t + \text{Log } K_c$$

where X_c is the crystalline fraction, K_c the crystallization kinetics and n is the Avrami number, depending on the kind of crystallization phenomenon observed.

A first study over isothermal crystallization of Sipolprene 55211 compared to Sipolprene 55200 was conducted to determine the temperature ranges allowing crystallization of the two polymers and ongoing studies will lead to the determination of crystallization parameters according to Avrami equation.

Thermal cycles for isothermal crystallization studies were as follows:

1. Dynamic segment: from 25 °C to 250 °C @ 20 °C/min
2. Isothermal segment: 250 °C for 5 min
3. Isothermal segment: 30 min @ set temperature T_3 for analysis

The difference between the two polymers is evident: Sipolprene 55211 starts a slow isothermal crystallization even at $T_3 = 185$ °C (**fig. 3**), a temperature that is far too high to observe any thermal phenomenon with Sipolprene 55200.

Lowering the isothermal temperature by only 5 degrees, to $T_3 = 180$ °C (**fig. 4**), makes the crystallization phenomenon extremely fast and partially invisible because of the transition between the two heating programs of the DSC instrument. On the contrary, in order to observe a very slow crystallization with Sipolprene 55200, similar to the one observed at $T_3 = 185$ °C with Sipolprene 55211, temperature must be lowered almost 20 degrees to $T_3 = 167.5$ °C (**fig. 5**).

This difference is a direct proof of the high tendency of Sipolprene 55211 to crystallize in comparison to Sipolprene 55200.

Fig. 3: Sipolprene 55211 DSC curve (isothermal conditions at $T_3 = 185$ °C)

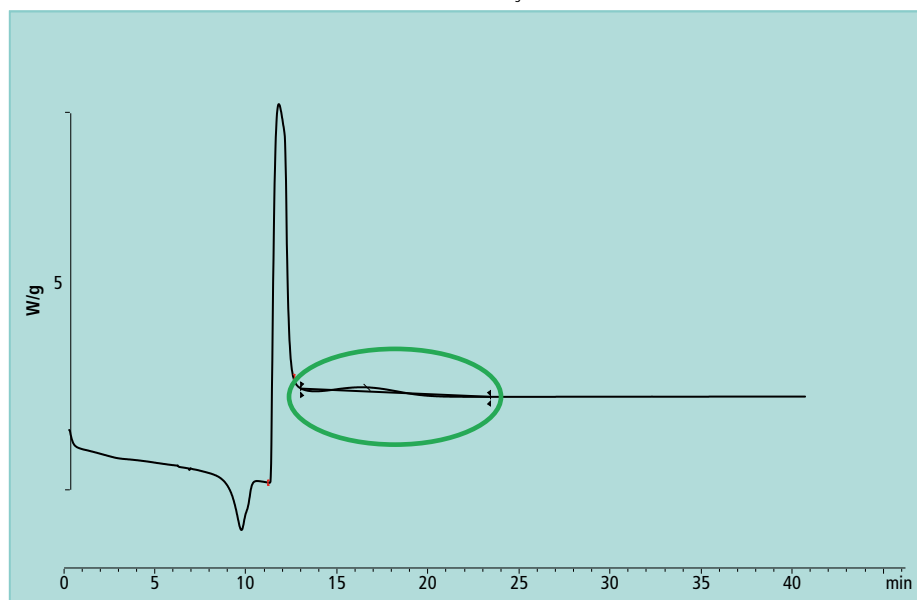
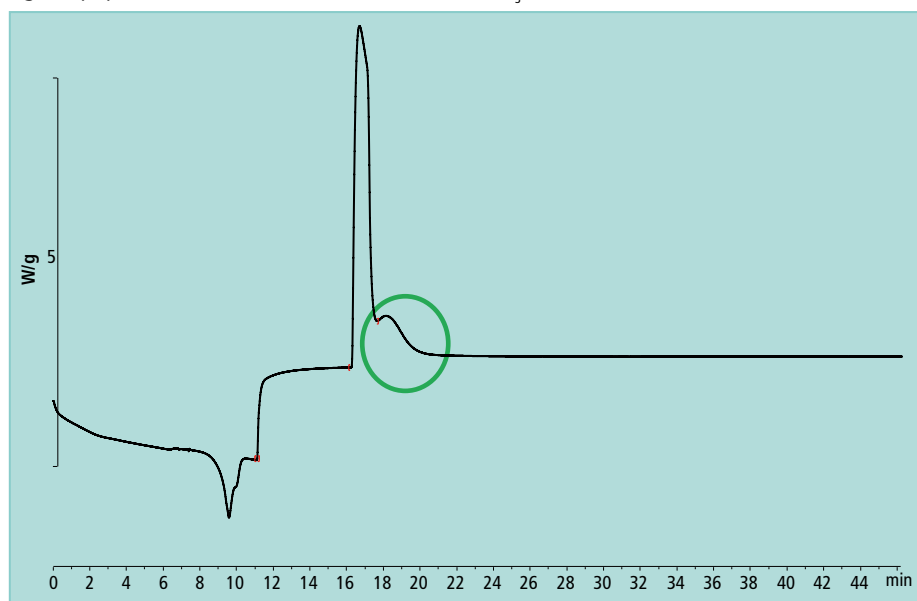


Fig. 4: Sipolprene 55211 DSC curve (isothermal conditions at $T_3 = 180$ °C)



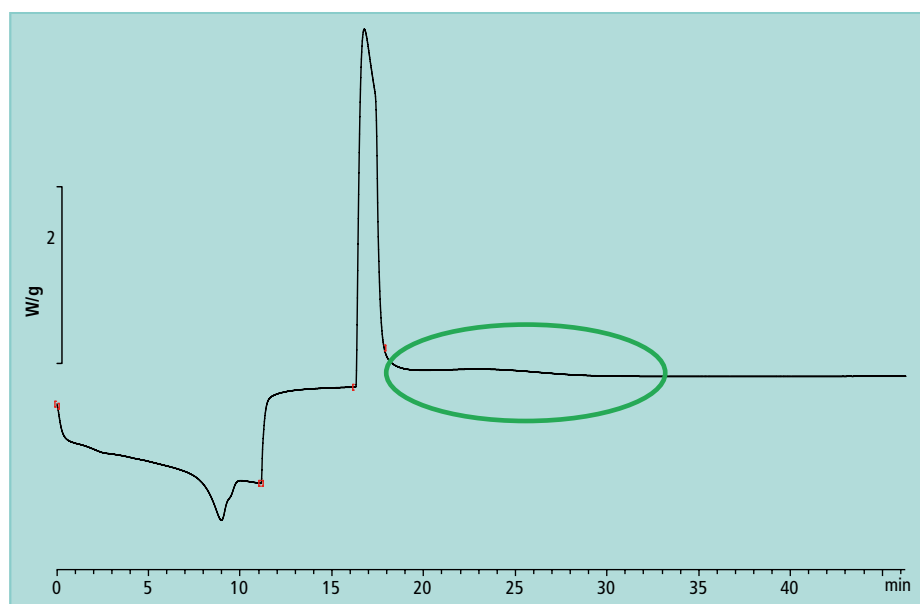


Fig. 5: Sipolprene 55200 DSC curve (isothermal conditions at $T_3 = 167.5^\circ\text{C}$)

5 Conclusions

The partnership between Sipol SpA with LaMPo – Università degli Studi di Milano, who verified the effectiveness of the crystallization rate increase, lead to the commercial product Sipolprene 55211 which is now part of the Sipolprene TPC-ET family. In addition, the route of changing polyether to enhance the identified crystallization rate has a general validity which is currently used by Sipol to extend the range of hardnesses. In addition Sipolprene 55211 and the other products under development using this system (all grades will be identified by "1" as last digit in the product code) provide some cost reductions in the raw materials used that enhance the cost/performance ratio of these TPC-ETs.

30 years PTS – Ready for further growth with new owner and new management

PTS Plastic-Technologie Service, based in Adelshofen, Tauberzell, Germany, recently celebrated its 30th anniversary. Company founder Uwe Stenglin had invited customers and suppliers to share a multitude of memories of minor and major milestones in the company's history of the last thirty years and to take a look into the future with the new owner Teknor Apex Company, Inc.

After several attempts the US compounder finally took over PTS only a few months ago on 31 March 2016 for a non-disclosed amount. Jonathan Fain, owner of Teknor Apex, together with his son and Suresh Swaminathan, Senior Vice President in charge of the global TPE Business at Teknor Apex, came specially from the USA to join the festivities. As PTS, Teknor Apex is a family-owned company.

Uwe Stenglin welcomed the guests and gave an overview of the history of his company il-

lustrated with a series of historic photographs. What started in a garage using second-hand equipment is today a custom compounder operating eight lines at its facility in Steinsfeld and serving about 1,000 customers. Currently a new greenfield plant is taking shape in the Steinsfeld industrial area which is set to start operation in 2018. About 60 % of the PTS business is done in the automotive sector and automotive interiors are, as Stenglin proudly said, a core competence of PTS. As a flagship project Stenglin mentioned the development of Uniflex-S, a scratch-resistant TPE, which allows the production of high-quality interior parts with 100 % recyclability in a cost-efficient single-step process. Another core competence and starting-idea of the company are radiation-crosslinked thermoplastics.

The second day of the celebration was dedicated to the presentation of successful PTS products. Members of the PTS team took the guests on a virtual journey through a day with PTS materials: starting the morning

with a tooth brush, moving to applications in cars and buses that take you to work, and finishing the day by lying down on a pillow with cooling air ventilation. The perfectly organised festivities were rounded up with fireworks and a fascinating performance of motivation coach Johannes Warth.

Only recently PTS announced surprising changes in its management structure. As of 1 September 2016 Uwe Stenglin gave up his responsibilities as managing director and took on a new role as principal consultant. His successor is Walter Baumann. Stenglin said that he wants to concentrate on training of staff and customers, on networking with strategic partners, customers and suppliers, and on the global marketing of the PTS materials. Baumann joined PTS in 2009 as senior automotive business development manager and served after the acquisition of PTS by Teknor Apex as director of integration. Stenglin and Baumann know each other for 40 years. "Walter brings to his new position a deep understanding of the custom compounding business, including not only the vital importance of technical innovation but also the need to work closely with customers as a reliable partner committed to their success," said Stenglin. "It is very satisfying to me to place the leadership of our company in such good hands."



Uwe Stenglin (l.) together with Jonathan Fain (r.)