A New Semi-Crystalline Styrenic Block Copolymer for Elastic Films, Fibers and Compounds

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Introduction

Professor Richard Register and his group at Princeton University have been working with polyethylene crystallinity in block copolymers since the late 1990s (1,2). William Gergen et. al., with the Shell Chemical Company, describe polyethylene crystallinity in styrenic block copolymers in the classic book on elastomers "Thermoplastic Elastomers" (3). A new semi-crystalline block copolymer is being developed at Kraton that takes a different approach (4). The new polymer offers polyethylene-like crystallinity but is also elastic, high modulus and strong. It is compatible with polyethylene and can be used in conjunction with polyethylene and oil to make elastic and soft compounds. In addition, unlike conventional styrenic block copolymers, the new polymers are resistant to oil and organic solvents. Other potential applications are elastic film for packaging, automotive soft touch skins, fabric coatings, yarns and nonwoven fabrics.

Experimental

The new semi-crystalline block copolymers (designated SCBC1(6 melt flow rate(MFR)) and SCBC2 (38 MFR) in this study) were made at the Kraton Semi Works plant in Belpre, Ohio. Conventional anionic polymerization chemistry was used to make both polymers. The viscosity-shear rate data were generated on a Dynisco model LCR 7000 capillary rheometer. A TA Instruments model DSC Q20 was used to determine the polymer glass transition temperatures ($T_{g)}$, melting temperature (T_m), crystallization temperature and heat of fusion. Film samples were made on a 25 cm wide single layer Davis-Standard Killian cast film line. Film mechanical testing was done on an Instron model 4465. ASTM D638 test conditions were used to evaluate the film mechanical properties.

Polymer Descriptions, Rheology and Mechanical Properties

Both SCBC polymers are relatively low molecular weight, low diblock, triblock copolymers. The diblock concentration is less than 10 wt % and the melt flow (230 ^{o} C @ 2.16kg) is between 3 and 7 g/10 min for SCBC1 and 25 to 40 g/10min for SCBC2; refer to Table 1 for a comparison to other conventional poly(b-styrene-b-ethylene-r-butylene-b-styrene) or SEBS styrenic block copolymers. Typical melt processing temperatures are between to 220 ^{o} C and 250 ^{o} C. Figures 1 and 2 are DSC scans for SCBC1 and SCBC2 respectively. Note both scans are similar because, except for molecular weight, the molecule designs are similar. There is a distinct melting peak close to 100 ^{o} C and a crystallization peak close to 70 ^{o} C. A typical heat of fusion for these polymers is between 22 to 30 J/g, with percent crystallinity ranging from 8 to 10 wt%. Percent crystallinity in just the crystalline block is between 25 and 30 wt%. As a comparison, selectively hydrogenated SEBS styrenic block copolymers (38-40 wt % butene in the midblock) have a broad, not well defined, melting endotherm with a crystallization peak between -5 to 0 ^{o} C; see Figure 3 for a DSC scan of MD1653 (5).

Figure 4 is a plot of viscosity versus shear rate for MD1653 (22 MFR), G1652 (2 MFR) and the new SCBC polymers. SCBC1 was designed for compounds and films and has a similar viscosity/shear rate response as G1652 which is used in compounds and coatings. SCBC2 was designed for elastic fiber applications and high flow compounds and has a similar to viscosity/shear rate response as MD1653. All four polymers are melt processable and can be used as standalone polymers.

Table 2 lists the melt cast film tensile properties for the SCBC polymers, G1652 and MD1653. Even though SCBC1 is similar viscosity to G1652, its film properties are more equal biaxial; refer to the 100%, and 300% moduli in Table 2. SCBC1 is probably closer to a single phase melt than G1652 (two phase melts exist above the T_g of polystyrene because of strongly phase separated styrene domains) at the typical process temperatures used to make the films (240 ^{o} C for SCBC1 and 265 ^{o} C for G1652). Both MD1653 and SCBC2 have almost equal biaxial properties because they are single phase melts at typical film processing temperatures (240 ^{o} C for SCBC2 and 260 ^{o} C for MD1653). From a modulus perspective, it probably better to compare the properties of SCBC1 and SCBC2 to MD1653 because all three films have almost equal biaxial mechanical properties. Consequently, except for the 500 % modulus, it interesting to note the SCBC polymers have similar moduli to a 30 % styrene SEBS polymer (MD1653) but lower tensile strength than either MD1653 or G1652. However, even though the tensile strength is lower for the SCBC polymers, the tensile strength is still reasonable for most applications. The 500% modulus is lower for the SCBC polymers because they do not appear to have the same strain hardening mechanism as the SEBS polymers. Lastly, the elongation to break for the SCBC polymers is equivalent to conventional SEBS polymers; refer to Table 2.

Table 3 lists the elastic properties for the polymers in this study. Note the significantly better elasticity of the SCBC polymers compared to MD1653 and G1652; refer to the tensile set and recovered energy in Table 3. MD1653 and G1652 can and are used in many elastic applications and compounds because they are typically compounded with oil and other non-elastic, but compatible, polymers to manipulate their polystyrene domain structure into a domain structure that is more elastic. Similarly, the SCBC polymers can be compounded with oil and compatible polymers to improve their performance for certain applications; refer to the presentation for more details.

Summary

SCBC polymers are a new class of block copolymers being evaluated by Kraton (6). Because of their crystallinity, they are more resistant to oil and organic solvents than conventional SEBS polymers. At the same time, they are elastic and strong like conventional SEBS polymers and can be easily melt processed into compounds, films and fibers.

References

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4. K. Tan and J. E. Flood, “ New Styrenic Block Copolymers”, The 2016 Fall Fiber Society meeting, Cornell University, **2016**
5. John E. Flood and Bing B. Yang, A New Styrenic Block Copolymer for Polyolefin Modification, Coatings and Adhesives, *Society of Plastics Engineers*, Annual Technical Conference, Anaheim, California **2017**.
6. Contact Lana Culbert at lana.culbert@kraton.com, 713-724-3646 for more information.

Table 1. Polymer Descriptions. A comparison of the semi-crystalline block copolymers to commercially available styrenic block copolymers.

Polymer/ Property	Molecule Design	MFR (230ºC@2.16 kg) (g/10 min)	Polystyrene Concentration (wt. %)	Diblock Concentration (wt. %)	Shore A Hardness	Polymer Form
G 1652	SEBS, Normal Vinyl	2	30	< 10	73	Crumb
MD1653	SEBS Normal Vinyl	20 - 28	30	<10	73	Dense Pellet
SCBC1	Semi-Crystalline Block Copolymer	4-6	25	<10	63	Dense Pellet
SCBC2	Semi-Crystalline Block Copolymer	22-40	25	<10	N/A	Dense Pellet

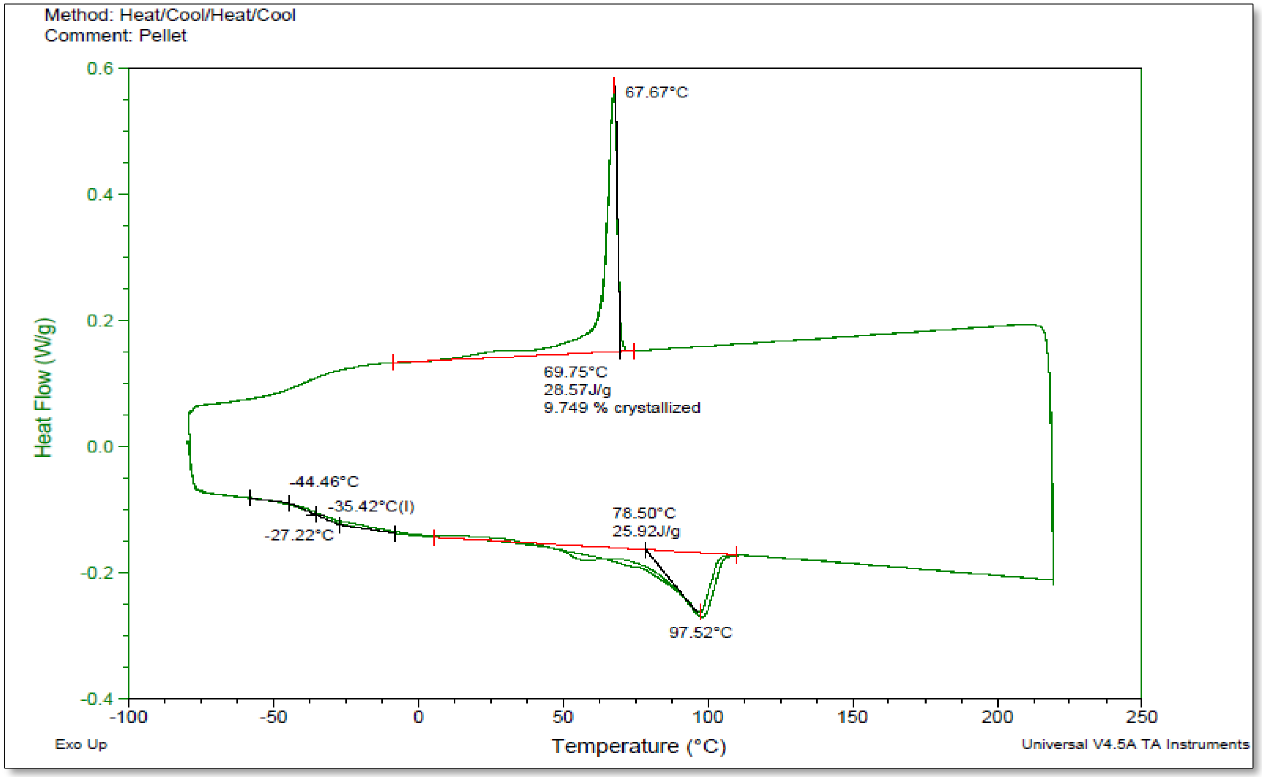

Figure 1. DSC Analysis for SCBC1.

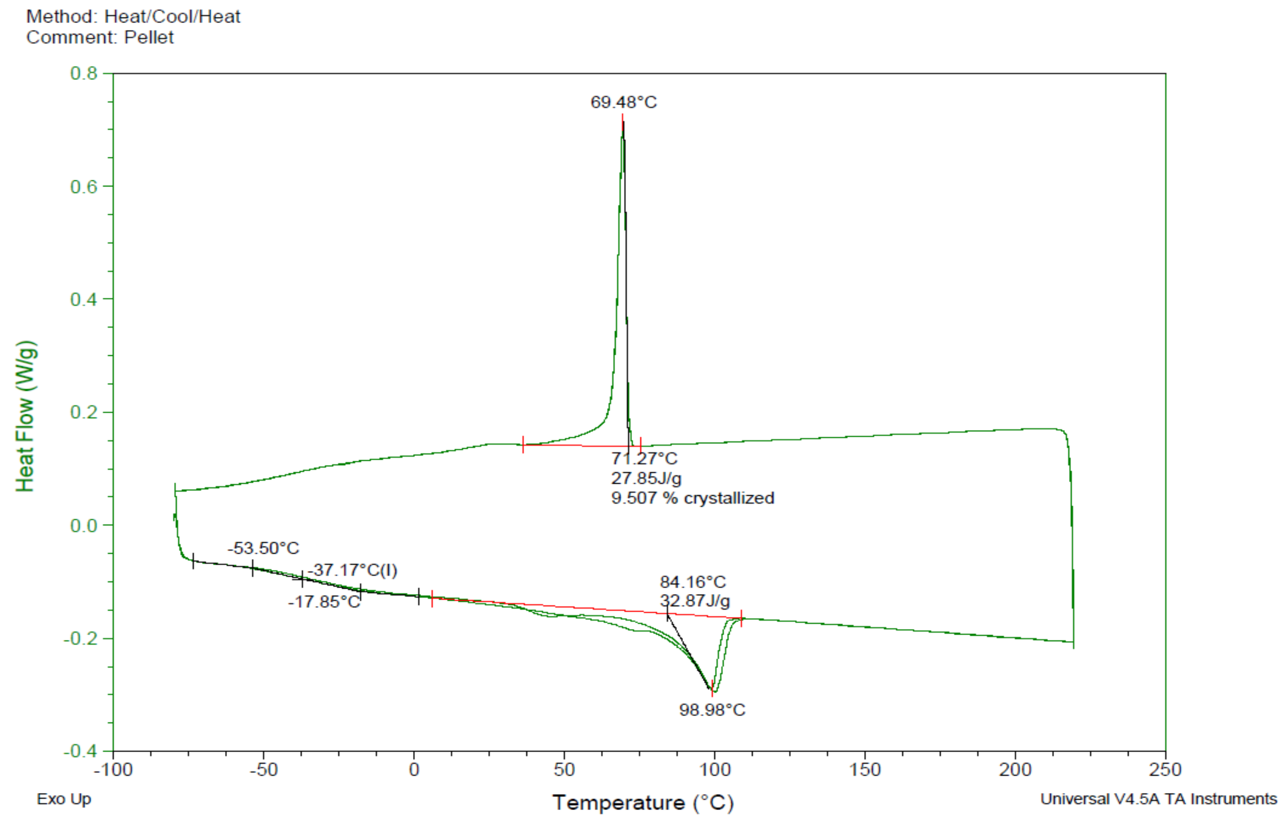

Figure 2. DSC Analysis for SCBC2.

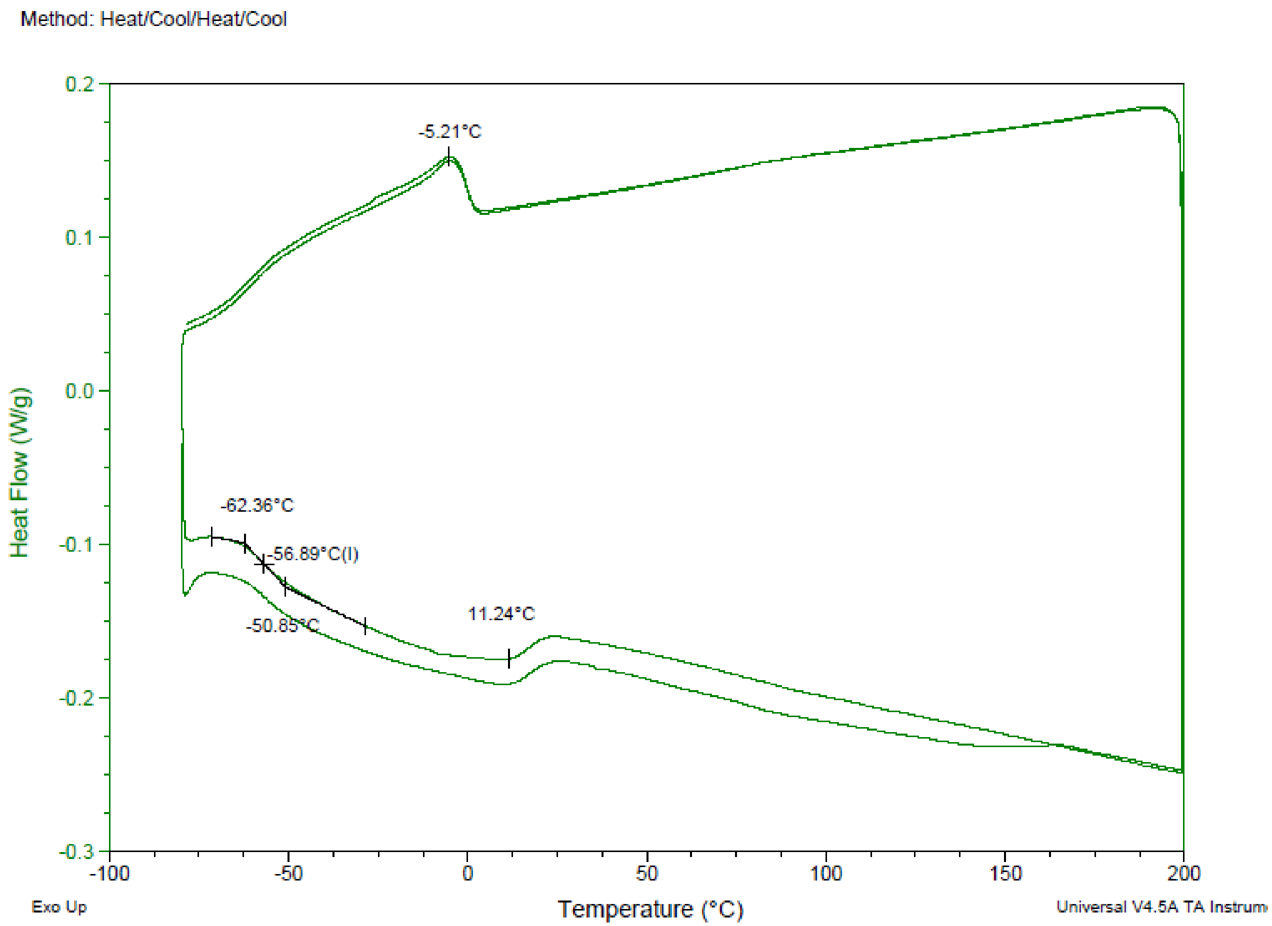

Figure 3. DSC Analysis for a Typical Normal Vinyl SEBS (MD1653).

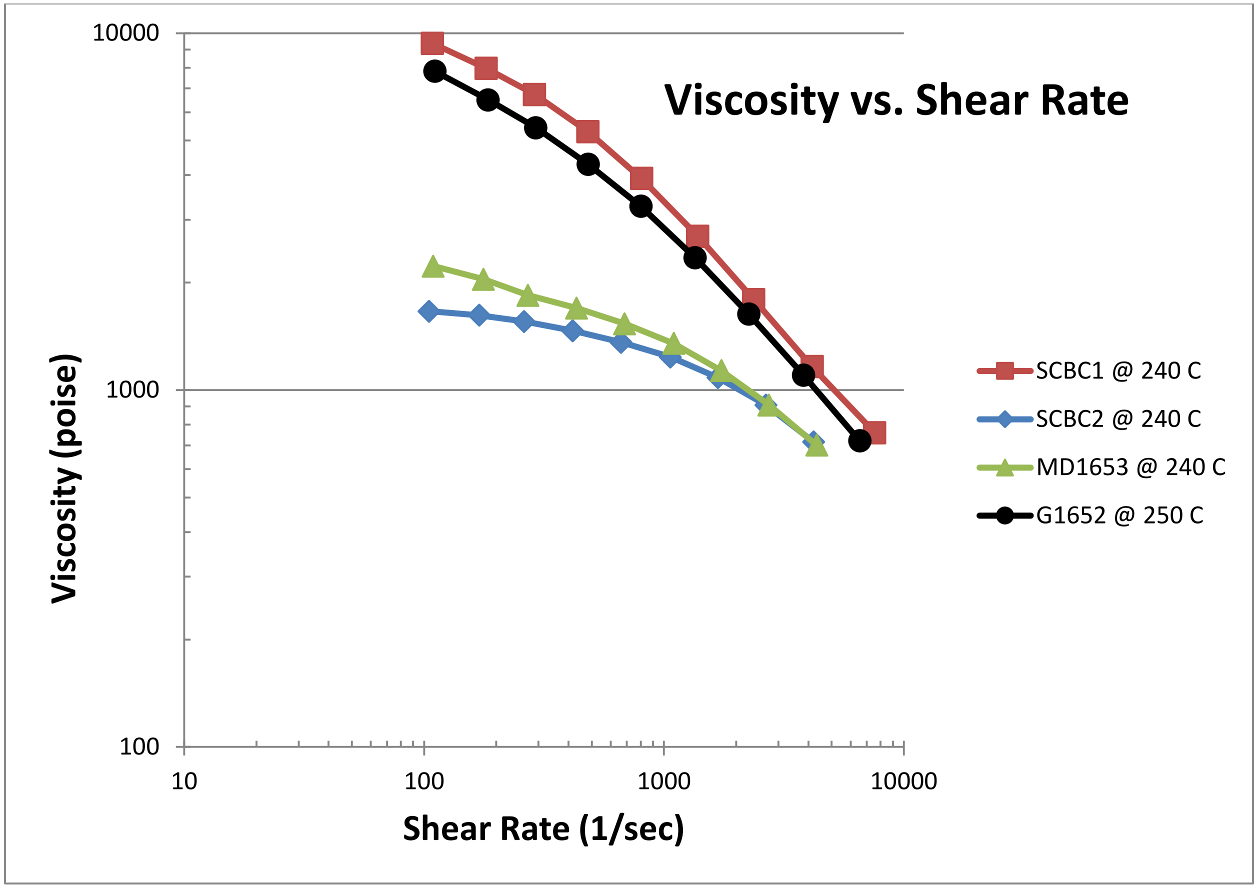

Figure 3. Viscosity vs. Shear Rate for SCBC1 and SCBC2 Compared to G1652 and MD1653.

Table 2. SCBC Mechanical Properties Compared to Commercial MD1653 and G1652 Grades. MD is the machine direction and TD is transverse direction. MD1653 was melt cast at 260° C and G1652 was melt cast at 266° C. The SCBC1 and SCBC2 films were melt cast at 240° C.

Polymers	MD1653		G1652		SCBC1		SCBC2	
Film Direction/Property	MD	TD	MD	TD	MD	TD	MD	TD
100% Modulus, MPa	2.7	2.6	4.9	1.6	3	2.7	3.1	3
300% Modulus, MPa	6.6	5.8	8.4	3.6	6	5.4	6	5.7
500% Modulus, MPa	31	23	17	11	11	9.7	7.3	7.1
Ultimate Stress, MPa	40	38	42	37	19	20	8.3	7.9
Elongation at Break, %	560	620	760	770	610	640	760	770

Table 3. 100 % Hysteresis Properties for Melt Cast Film.

Polymers	MD1653		G1652		SCBC1		SCBC2	
Film Direction/Property	**MD**	**TD**	**MD**	**TD**	**MD**	**TD**	**MD**	**TD**
50% Modulus load, MPa	2.2	2.1	3.7	1.4	2.1	2	2.2	2.1
50 % Modulus unload, MPa	1.2	1.1	1.7	1.1	1.6	1.5	1.7	1.6
Tensile Set, %	16	14	11	4	5.7	7.7	6.6	7.2
Recovered Energy, %	52	52	44	82	82	82	78	78