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New hydrogenated styrenic block copolymers for medical applications

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Hydrogenated styrenic block copolymers (HSBC) have been used in medical tubing for many years due to their high clarity, flexibility, kink resistance and toughness. They do not contain intentionally added phthalate- and BPA-based chemicals and can be sterilized with all common sterilization techniques, even at elevated temperatures. The latest polymer developments from Kraton demonstrate improved performance in critical application requirements such as solvent bonding, surface appearance and processing. Blends with polypropylene (PP) at different ratios can be extruded into medical tubing for IV systems, peristaltic pump systems, homecare equipment and other drug delivery systems, and they can be processed at lower temperatures, thus achieving several advantages.

1 Introduction

Kraton Corporation invented styrenic block copolymers (SBC) and commercialized them in 1959. The anionic polymerisation method used for making SBC leads to a very clean product with minimal catalyst residuals. As a result, Kraton SBC found extensive uses in the medical devices market in applications like medical films, bags, tubing, stoppers and more. Apart from being very clean, SBC also provides high transparency and clarity with minimal haze. They are very soft and flexible, yet provide good mechanical strength. They can be sterilized with most commonly used sterilization methods. An important distinguishing feature of SBC is that they do not contain or need additional phthalate-based plasticizers. Consequently, Kraton has served the medical market for more than 30 years now.

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Kraton SBC is made by copolymerization of styrene monomer forming the polystyrene block, and either isoprene or butadiene or a mixture of isoprene/butadiene monomers, forming the rubber blocks. At room temperature, the polystyrene blocks are hard with a glass transition temperature above 100 °C, and the rubber blocks are soft, with a glass transition temperature below -55 °C. The styrene and rubber blocks are highly incompatible, which results in a strong phase separation. This leads to styrene blocks forming domain structures that are dispersed throughout the rubber phase. The typical size of these styrene domains is of the order of 20 nm. As a result, the hard styrene blocks act as physical crosslinks in the soft rubber network, providing strength and elasticity to the material without the need for vulcanization.

The Kraton SBC's rubber midblock can either be unsaturated (called USBC) or saturated by selectively hydrogenating the midblock (called HSBC). Hydrogenation of the midblock in HSBC leads to greater stability of the material to heat and oxidation as compared to USBC. HSBC can be blended with polyolefins, like PP, where varying the ratio of HSBC and PP will lead to compounds with wide range of properties. A blend of HSBC/PP exhibits several advantages over flexible PVC used in medical applications. HSBC/PP blends are lighter. With no added plasticizers in HSBC/PP compounds, contamination issues due to the plasticizers can be avoided in drug applications. The barrier properties of HSBC/PP compounds are higher as compared to PVC. They have greater temperature stability up to 250 °C, where PVC starts degrading at 130 °C. HSBC/PP blends also have excellent UV, ozone and chemical resistance. They pose no known risk to health and environment during processing and can be easily recycled. PVC, on the other hand, release hazardous chemicals like dioxins at process temperatures and can be difficult to recycle when blended with other polymers.

The properties of typical Kraton HSBC grades commonly used in medical applications are listed in **table 1.** Kraton FG1924 is a

Tab. 1: Kraton HSBC grades for medical tubing and film applications

Polymer	G1645	G1657	G1643	G1730	G1652	G1650	FG1924
Hardness in Shore A[1]	35	47	52	61	69	72	49
PSC in %	13	13	19	20	30	30	13
Diblock content in %	7	29	7	< 1	< 1	< 1	30
MFR in g/10 min at 230 °C, 2.16 kg	3.5	9	19	4	< 1	< 1	—
MFR in g/10 min at 230 °C, 5 kg	—	—	—	—	—	—	40
Tensile strength in MPa[2]	10	23	14	20	31	35	23
Elongation in %[2]	600	750	600	800	500	500	750
HSBC type	ERS	SEBS	ERS	SEPS	SEBS	SEBS	SEBS-g-MA
Product form	Pellet	Pellet	Pellet	Pellet	Crumb	Crumb	Pellet

[1] Typical values on polymer compression molded at 200 – 230 °C.
[2] Typical properties determined on film cast from toluene solution.

functionalized grade, where the rubber block is functionalized with maleic anhydride. Kraton G1645 is the most common grade used in the industry in medical applications for making tubing and films. In recent years, Kraton strived to improve the color, tack, and processability of Kraton G1645. The result of that effort culminated into making a new polymer, Kraton MD1646. Additionally, Kraton developed another new polymer with improved kink resistance and solvent bonding that could potentially be an alternative to PVC in tubing applications.

2 Experimental

2.1 Mechanical properties and hardness

Mechanical properties were measured according to tensile test method of ASTM D412 using a mini D-die dogbone sample. The tests were conducted on Instron 3366 fitted with a 1 kN load cell. The gauge length of the sample was 25.4 mm, and the test was carried out at an extension rate of 254 mm/min. Shore A hardness of all samples was measured using an automatic hardness tester. Three sheets of the same compound with 2 mm thickness were stacked, and the hardness was measured at four corners and the center. The hardness was noted 10 s after the durometer tip made contact with the material. The average value of the five measured hardness values was reported.

Fig. 1: Photo of test set-up developed to measure kink resistance of tubes

2.2 Dynamic mechanical analysis and ODT rheology

The glass transition temperature (T_g) of all polymer samples were measured by Dynamic Mechanical Analysis using a TA Instruments DMA Q800. Temperature sweep experiments were conducted from -80 °C to 120 °C, where storage moduli (G'), loss moduli (G") and loss factors (tan δ) were obtained as a function of temperature. All experiments were done at a frequency of 1 Hz. Glass transition temperature was reported as the temperature at the peak value of tan δ.

Tests to determine ODT rheology were done on a Bohlin rheometer by Malvern instruments. Temperature sweep experiments were conducted at two frequencies of 0.005 Hz and 0.2 Hz, where complex viscosity was measured. The ODT was reported as the temperature where the complex viscosity of the polymer was the same at both frequencies.

2.3 Kink resistance

A test setup for measuring kink resistance was developed internally. A picture of the setup is shown in **figure 1.** A tube is bent and placed between the grips with a distance of 100 mm. The tube is then bent by downward movement of the crosshead until it kinks, and this distance, x mm, is noted. The apparent kink diameter is then calculated as: apparent kink diameter = (100-x) mm.

Kink resistance was also measured by a "hand-test" method, where the tube was folded into a loop. The loop was then slowly closed, just until a kink appeared in the tube. The ends of the loop at kink were pinched, the loop opened, and the length between the pinch points were measured. This length was called "kink diameter."

In both Instron testing and hand-test method, a smaller kink diameter indicates higher kink resistance.

2.4 Solvent bonding

Solvent bonding of extruded tubes was conducted with ABS connectors. The solvents used were the most commonly used solvents in the industry – cyclohexanone (CH), methyl ethyl ketone (MEK), tetrahydrofuran (THF), and two combinations of 50:50 CH in MEK, and 80:20 THF in CH. The tubes were dipped instantaneously in the solvent. As the connectors were tapered, the tube was inserted only two thirds of the length of the connector shaft. The assembly was allowed to dry for seven days at room temperature. The bond strengths were then measured on an Instron 3366, with 25.4 mm gauge length at an extension rate of 500 mm/min.

The aging of the tube-connector assemblies was done by subjecting them to a temperature and humidity cycle over a time period of 22 days.

3 Results and discussion

3.1 Comparison between Kraton G1645 and Kraton MD1646

Both Kraton G1645 and Kraton MD1646 are HSBC polymers from Kraton's Enhanced Rubber Segment (ERS) family, where the microstructure of the rubber midblock was modified. The ERS structure makes the polymers soft, provides better compatibility with a polyolefin like PP, and leads to higher melt flow. The ERS grades have relatively lower

Polymer	MD1646VO	G1645MO
Solution viscosity (cP), 25 % @ 25 °C	570	955
MFR in g/10 min @ 230 °C, 2.16 kg	13	3.5
MFR in g/10 min @ 230 °C, 5 kg	49	13
PSC in %	13	13
Hardness in Shore A	38	38
Tensile strength in MPa	10.4	11.9
Ultimate elongation in %	1,050	1,180
Product form	Pellet	Pellet

Tab. 2:
Comparison of properties between Kraton G1645 and Kraton MD1646

polystyrene content (PSC), which makes them highly elastic with good recovery, low hysteresis and good kink resistance.

Kraton MD1646 is a low molecular weight version of Kraton G1645, but with a similar PSC of 13 %. As a result, Kraton MD1646 has a higher melt flow rate (MFR), which makes it amenable to processing at lower temperatures, and easier to handle due to lower tack during processing. Kraton MD1646 can potentially be used in applications like medical tubing, medical film, as PVC alternatives in coated fabric or wire/cable applications, hot melt adhesives, impact modifier for PP, and in TPE compounds.

A comparison of physical and mechanical properties between Kraton G1645 and Kraton MD1646 is presented in **table 2.** It can be seen that Kraton MD1646 has lower solution viscosity and significantly higher MFR. However, the mechanical properties, specifically tensile strength and elongation at break, and the hardness of both polymers are the same. The mechanical properties were measured on films cast from a solution of polymer in toluene.

3.1.1 Comparison of properties in melt cast film applications

Melt cast films of Kraton MD1646 and Kraton G1645 were prepared by blending with random copolymer PP (rcPP) at different ratios. The films were prepared at a thickness of 200 µm. Tensile tests were conducted on the films in the machine and transverse direction (MD and TD respectively) relative to the direction of film extrusion. The tensile strength of the films made with both Kraton polymers are shown in **figure 2.** It can be seen that the tensile strengths are very similar for films made with Kraton G1645 and Kraton MD1646 at all ratios of the blends with PP. The difference between tensile strength in MD and TD for Kraton G1645 films is also very similar to that of films made from Kraton MD1646 compounds.

The ultimate elongation of the films made with Kraton G1645 and Kraton MD1646 is given in **figure 3,** which shows that films from PP blends of both polymers can be stretched to more than 700 %, and the ultimate elongation is similar.

3.1.2 Properties in medical tubing applications

Tubing samples of Kraton MD1646 and Kraton G1645 were prepared by blending with random copolymer PP (rcPP) at different ratios. The tubing diameters are 3 mm ID and 4 mm OD. Melt flow, hardness and haze value of the blends were measured. Kink force and apparent kink diameter of the tubings were also measured and listed in **table 3.** Both hardness and haze drop with higher HSBC content. Kink resistance, on the other hand, does not change within the ratios tested. Kraton MD1646 performs just as well as Kraton G1645, but with better clarity.

3.1.3 Comparison of optical properties

A comparison of the Yellowness Index (Y.I.) values and other optical properties like

Fig. 2: Tensile strength of melt cast films made from a blend of PP with Kraton MD1646 (left) and Kraton G1645 (right).

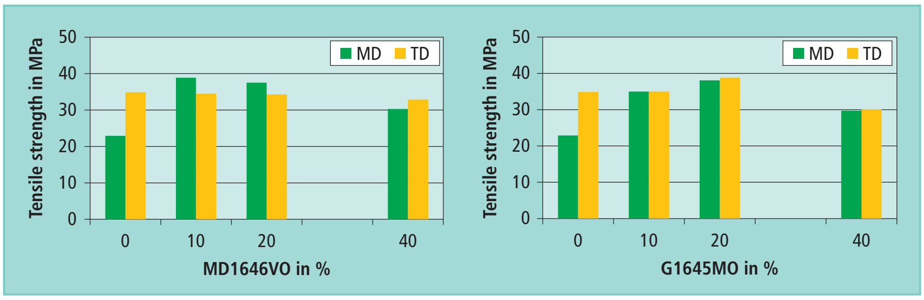


Fig. 3: Ultimate elongation of melt cast films made from a blend of PP with Kraton MD1646 (left) and Kraton G1645 (right).

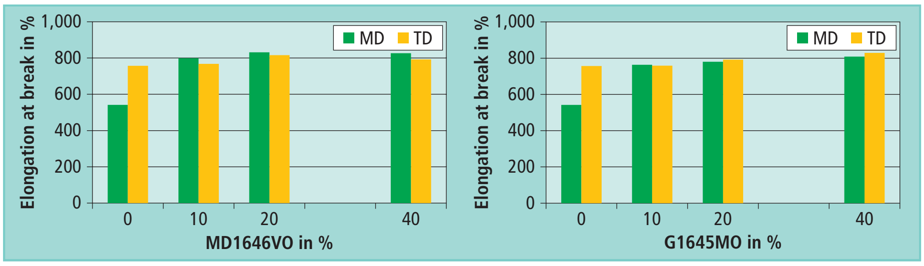
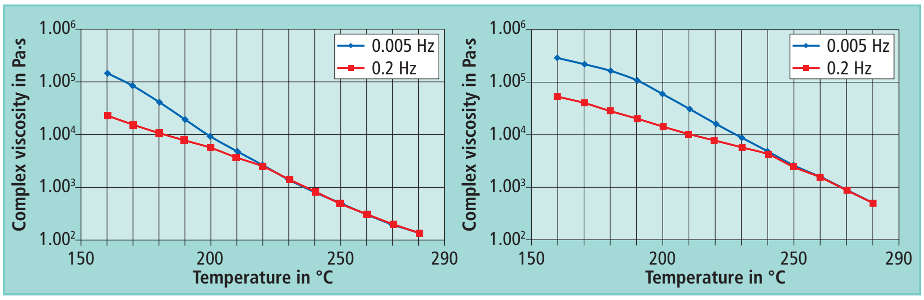


Fig. 4: Visual comparison of Kraton G1645 and Kraton MD1646 pellets (left) and solution cast film (right)

Fig. 5: ODT temperature analysis of Kraton MD1646 (left) and Kraton G1645 (right). The data was obtained by an oscillatory temperature sweep experiment at 0.005 Hz and 0.2 Hz.



haze, clarity and transmittance between pure Kraton G1645 and Kraton MD1646 is shown in **table 4.** It can be seen that the optical properties of Kraton MD1646 is much better than that of Kraton G1645 polymers. A comparison of the color of the pellets and color of a solution cast film is also shown in **figure 4.**

3.1.4 Comparison of processability

The SBC's order-disorder transition (ODT) temperature is the temperature at which there is no phase separation in the polymer and is in a single phase melt state. The ODT temperature indicates the lowest temperature that the polymer can be melt processed.

	MD1646VO/rcPP			G1645MO/rcPP		
	60/40	70/30	80/20	60/40	70/30	80/20
Melt flow in g/10 min	17.9	17.3	16.3	8.3	6.8	5.4
Hardness in Shore A	84	77	64	86	76	65
Haze in %	13	10	7	16	15	9
Tubing OD in mm	4.05	4.00	4.07	4.05	4.05	4.05
Tubing wall thickness in mm	0.53	0.55	0.53	0.53	0.55	0.52
Kink force in N	0.53	0.28	0.18	0.53	0.28	0.17
Apparent diameter in mm	28	26	28	28	27	29

Tab. 3: Comparison of tubing properties between Kraton G1645 and Kraton MD1646

	Yellowness Index	Haze in %	Clarity in %	Transmittance in %
MD1646 VO (lot# 11WXH1012)	2.1	16	92	91
G1645MO (lot# 05RBL7132)	4.6	24	65	91

Tab. 4: Comparison of optical properties between Kraton G1645 and Kraton MD1646

Fig. 6: Melt viscosity of Kraton MD1646 and Kraton G1645 measured by capillary rheometer at 230 °C

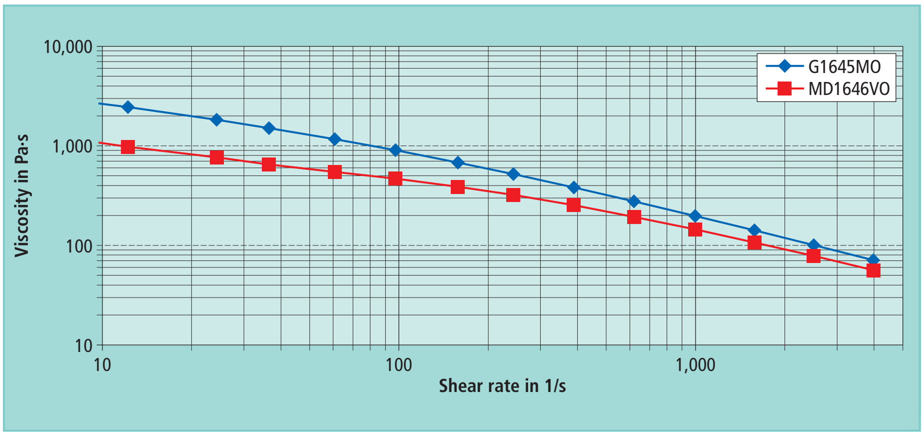
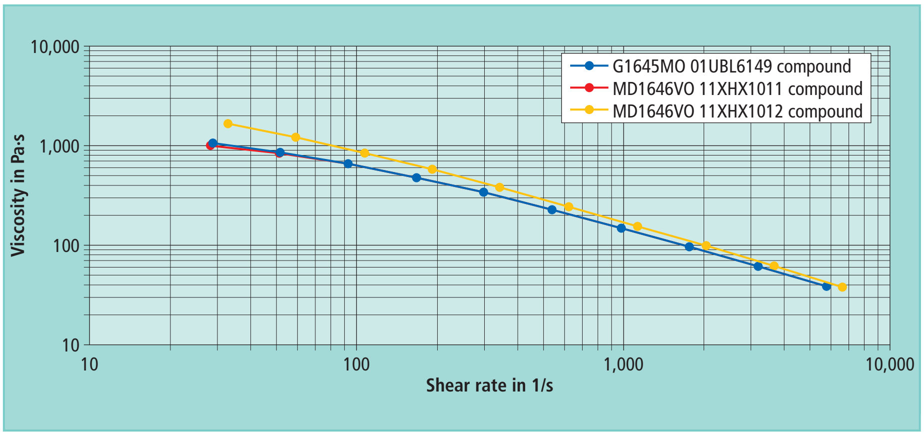


Fig. 7: Melt viscosity at 190 °C of Kraton MD1646/PP and Kraton G1645/PP blends



The ODT temperature analysis of Kraton MD1646 and Kraton G1645 is shown in **figure 5.** It can be seen that the ODT temperature of Kraton G1645 is higher at 240 °C as compared to Kraton MD1646, which has an ODT temperature of 220 °C. This shows that Kraton MD1646 can be processed at a lower temperature than Kraton G1645.

The lower ODT also leads to a lower melt viscosity of Kraton MD1646 at a typical processing temperature of 230 °C (above its ODT temperature) as compared to Kraton G1645. The melt viscosity as measured on a capillary rheometer is shown in **figure 6.**

The melt viscosity of a blend of Kraton MD1646 and PP was also compared to a compound of Kraton G1645/PP at 190 °C. The data is shown in **figure 7.** It was found that Kraton MD1646 compound had a lower melt viscosity as compared to the Kraton G1645 one, indicating better processability of Kraton MD1646 at a lower temperature.

3.2 Development of a new polymer for tubing applications

In recent years, Kraton worked on developing a new polymer for medical tubing applications that can be used either as a neat polymer or by compounding with other polyolefin polymers. Use of the polymer in the neat form allows for a very clean product, which is highly desirable in medical tubing application. The aim of this development was to make a polymer that resulted in a tube with better kink resistance and solvent bond strengths. This polymer belongs to the family of Kraton A grade polymers. In this grade line, SBC not only have end blocks that are polystyrene, but also have a controlled distribution of styrene in the rubber midblock. The new developmental polymers show interesting properties owing to a higher amount of total PSC in the end blocks and the midblock.

Following is a summary of the property set that is desired in a polymer for use in a neat or compounded form in medical tubing application:

- melt flow rate range of 3 – 6 dg/min at PP conditions (230 °C, 2.16 kg),
- hardness range of 70 – 75 Shore A,

- transparent appearance so air bubbles in the fluid being transported are visible,
- low surface tack,
- low sensitivity to temperature changes in the range of 0 – 40 °C,
- ability to undergo sterilization by the commonly used sterilization techniques,
- good kink resistance,
- solvent bondable with typically used solvents in the industry like cyclohexanone. (CH), THF or MEK.

The physical properties of the new Kraton A polymers, named Kraton A-1 and Kraton A-2 are provided in **table 5.**

3.2.1 Kink resistance tests

Tubings of dimension 4/3 mm and 7/5 mm (OD/ID) were extruded using neat Kraton A-1 and Kraton A-2. 4/3 mm diameter tubing was also extruded with Kraton G1645/PP and Kraton MD1646/PP compounds with 70/30 ratio of the SEBS to polypropylene. The results of the Instron test method on 4/3 mm tubes is shown in **figure 8,** along with kink resistance of PVC tubing of the same dimensions.

It can be seen from the above figure that while tubing made from new Kraton A-1 polymer shows kink resistance equivalent to that of the PVC reference, the kink resistance of tubing made with Kraton A-2 is even better than PVC. The kink resistance of tubes made with the new polymers is significantly better than those made from SEBS/PP compounds. A comparison of the kink diameter obtained with hand test and Instron test methods is shown in **figure 9.** The tests were conducted on the same tubing with 4/3 mm dimensions. It can be seen that the trend for kink diameter by both tests is the same, where new Kraton A polymers have kink resistance comparable to the PVC reference.

Tab. 5: Summary of physical properties of new Kraton A polymers.

	Kraton A-1	Kraton A-2
Total PSC in %	54	58
ODT in °C	210–220	280
T_g (tan δ peak) in °C	25	36
MFR, 230 °C/2.16 kg in dg/min	6.3	5.6
Hardness in Shore A	71	76
M50 in MPa	2.0	3.8
M100 in MPa	2.9	4.1
M300 in MPa	5.6	6.8
M500 in MPa	12.7	14.5
Tensile strength in MPa	17.6	17.8
Elongation at break in %	580	580

Fig. 8: Apparent kink diameter of tubes made from SEBS/PP compounds and the neat developmental Kraton A polymers as compared to a PVC reference.

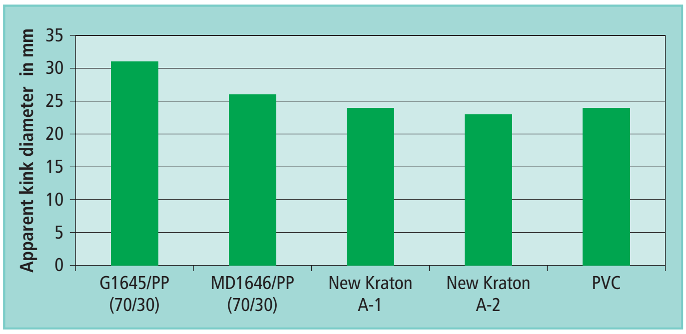


Fig. 9: Comparison of apparent kink diameter of 4/3 mm tubing made with Kraton G1645/PP, new Kraton polymers and PVC by hand test method and Instron test methods

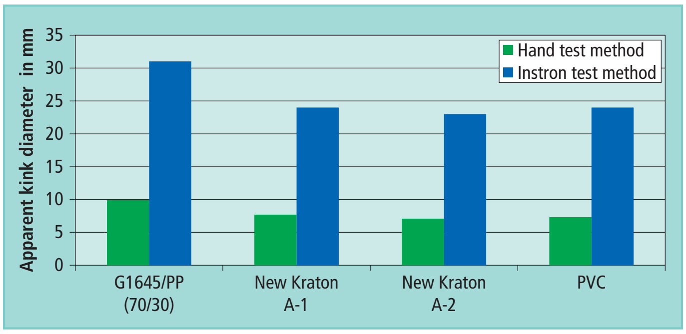


Fig. 10: Kink diameter of 7/5 mm tubing with hand test and Instron test method. The data for PVC tubing is not included due to unavailability of this size.

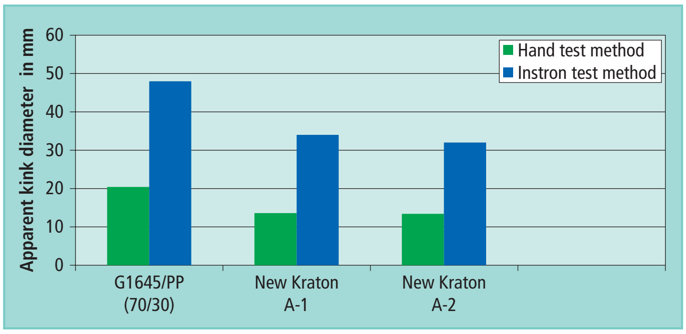


Fig. 11: Bond strength of tube-connector assemblies with ABS female luer connectors and polymers bonded to it by different solvent systems as shown in the legend

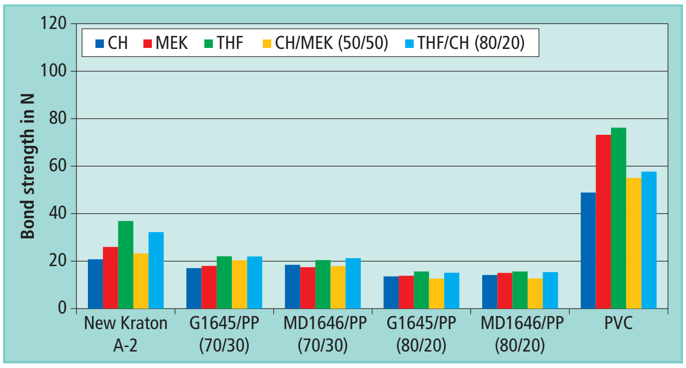
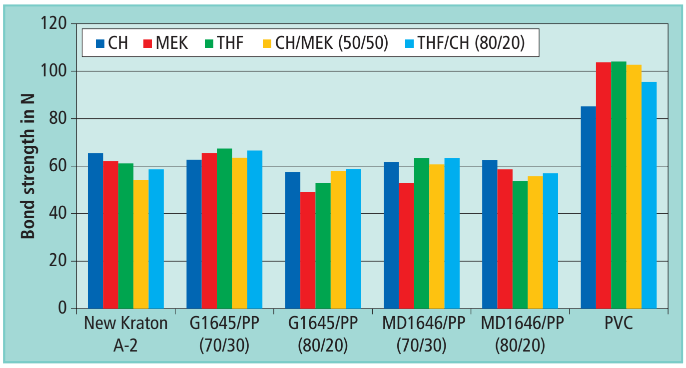


Fig. 12: Bond strength of tube-connector assemblies prepared by ABS male luer connectors



Additionally, Kraton conducted kink resistance tests on tubing of larger size (7/5 mm), both by hand test and Instron test methods and the data is shown in **figure 10.** PVC tubing data is not included here due to unavailability of the tubing in this size. However, again observe the same trend, validating that even with tubing of different sizes, the new Kraton A polymers' kink resistance are higher than typical SEBS/PP compounds.

3.2.2 Solvent bonding

The bond strength of tube-connector assemblies prepared with different solvent systems is shown in **figure 11.** The tests were done after drying the tube-connector assemblies for seven days at room temperature. It can be seen that the new Kraton A polymer's bond strength is much higher than SEBS/PP compounds for all the solvents used. However, bond strengths are lower as compared to PVC tubing. It should be noted that the bond strength depends significantly on the connector design. This is exemplified by the data shown in **figure 12,** where ABS male luer connectors were used for preparing the tube-connector assemblies.

It can be seen from **figure 12** that the Kraton A polymer's bond strengths is almost double the strength that was obtained with the female luer connectors. Moreover, even tubes with SEBS/PP compounds show similar bond strengths as the Kraton A polymer with the male luer connectors. The difference in bond strengths of PVC tube-connector assemblies between male and female luer connectors is not very large.

Bond strengths were also measured after subjecting the tube-connector assemblies to aging cycle. The aging was conducted after drying the tube-connector assembly for seven days at room temperature. Aging was done over a period of 15 days, where the samples were subjected to varying conditions of temperature and humidity. The comparison of bond strengths before and after aging is shown in **figure 13** for tubes made with SEBS/PP compounds and Kraton A polymers for the solvents THF, CH, and MEK.

It can be seen from the figure above that the solvent-bonded tube connector assemblies withstand the aging cycle, and there is no significant change in bond strengths observed before and after aging for the solvents studied.

3.2.3 Effect of temperature on storage modulus

An important property for materials that are used in medical tubing applications is that the material's hardness should not undergo drastic changes in the typical application range of 0 – 40 °C. This was characterized by the slope of the storage modulus curve as a function of temperature in the 0 – 40 °C. The data of storage modulus versus

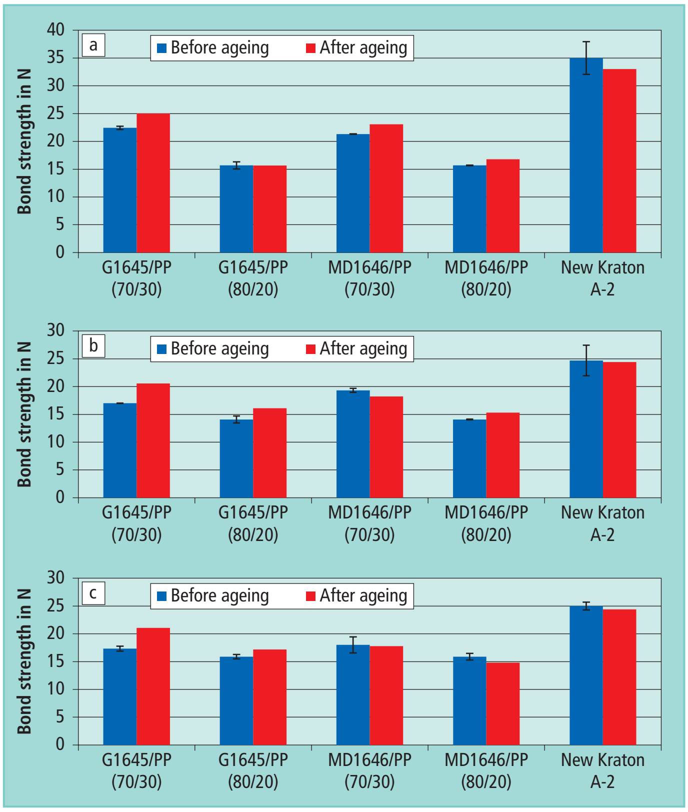
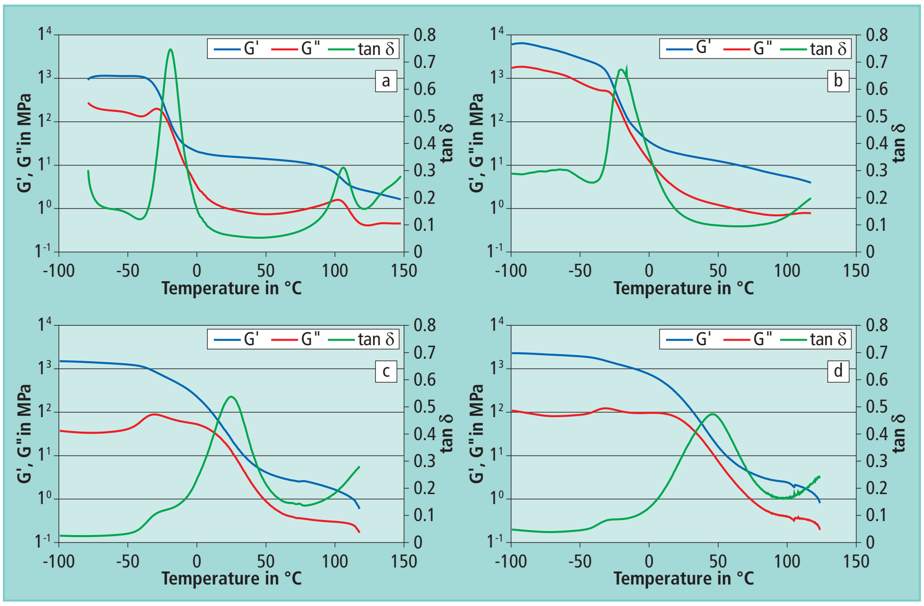


Fig. 13: Bond strength of tube-connector assemblies before and after aging. Data is shown for three types of assemblies made with solvents (a) THF, (b) Cyclohexanone, (c) MEK

Fig. 14: G', G", and tan δ as a function of temperature for (a) A1536 (commercial Kraton A), (b) MD1646/PP (70/30) blend, (c) new Kraton A-1, and (d) new Kraton A-2.



temperature is shown in **figure 14** for the SEBS/PP compounds, new Kraton A polymers, and for commercial Kraton A polymers.

It can be seen from **figures 14a** and **14b** that the T_g of commercial Kraton A polymer A1536 and that of the compound of Kraton MD1646/PP is much below room temperature, and there is a sharp decrease in G′ at T_g. Moreover, the slope of G′ curve in the region of 0 – 40 °C is very high. On the other hand, T_g of the new Kraton A polymers, both A-1 and A-2, is around room temperature. The storage modulus G′ drops very gradually near T_g, and the slope of G′ curve in the range of 0 – 40 °C is much lower. This shows that the hardness of the tubing made with new Kraton A polymers will not change much when it is used to transport fluids at varying temperatures.

3.2.4 Sterilization

The new Kraton A polymers, along with Kraton G1645/PP and Kraton MD1646/PP compounds were subjected to ethylene oxide (EtO) and gamma sterilization, and mechanical and optical properties were measured before and after sterilization. The SEBS/PP compounds can also be sterilized by steam sterilization technique, and data was collected for that also.

The data has been summarized in **table 6,** where medical grade PVC has been included for comparison. Steam sterilization was conducted at 121 °C for 30 min, with 20 min of drying time. EtO sterilization was conducted at 55 °C in a 4 h cycle. Gamma sterilization on all samples was done at a dosage of 50 kGy.

It can be seen from **table 6** that the change in color after gamma sterilization, as indicated by Yellowness Index, is much worse in PVC. The other properties are mostly unchanged for all polymers in different types of sterilization techniques.

4 Conclusions

The new Kraton MD1646 polymer was made as an easier processing version of Kraton G1645, Kraton's workhorse polymer grade, and retains all of its key properties. Tubing made from the new Kraton A polymers – made of mixed rubber and styrene midblock – show excellent kink resistance where comparable to PVC, better solvent bonding ability than SEBS/PP compounds, and more stable modulus behavior with temperature.

Tab. 6: Summary of the effect of steam, EtO, and gamma sterilization on mechanical and optical properties of SEBS/PP compounds, new Kraton A polymers, and medical grade PVC.

Property	Before sterilization			After EtO sterlization			After gamma sterilization			After steam sterilization		
	Medical PVC	G1645/rcPP & MD1646/rcPP	New Kraton A	Medical PVC	G1645/rcPP & MD1646/rcPP	New Kraton A	Medical PVC	G1645/rcPP & MD1646/rcPP	New Kraton A	Medical PVC	G1645/rcPP & MD1646/rcPP	New Kraton A
Kink resistance	1	2	2	3	3	3	3	3	3	3	3	N/A
Yellowness index	1	1	1	3	3	3	5	4	4	3	3	N/A
Bond strength	1	2	2	3	3	3	3	3	3	3	3	N/A
Shore A hardness	1	1	1	3	3	3	3	3	4	3	3	N/A
Tensile strength	1	1	1	3	3	3	3	3	3	3	3	N/A
1 Similar to PVC; 2 Slightly worse than PVC; 3 No effect; 4 Slight effect; 5 Significant effect												

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