K·RESIN®
Styrene-Butadiene Copolymers

Technical Service Memorandum 317

Coextruded K-Resin® Styrene-Butadiene Copolymer/PETG Sheet

INTRODUCTION. K-Resin styrene-butadiene copolymers have long been the economical choice for applications requiring clarity, gloss and toughness. Specifically, blends of K-Resin and general purpose polystyrene can be extruded into sheet and thermoformed on conventional equipment at high output rates. Favorable economics, along with high productivity, have made possible tough clear drinking cups, lids and other packaging applications. A feature that makes K-Resin more economically attractive than other clear plastics is its low density. There can be a 30 percent yield advantage over non-styrenic clear resins. Also, K-Resin blends can be reprocessed in multiple passes with minimal change in properties and processing.

K-Resin meets the requirements of FDA regulation 21 CFR 177.1640. However, there are some stress cracking limitations on K-Resin for the storage and packaging of certain foods, especially fatty foods. K-Resin also participates heavily in the medical market and qualifies as a USP VI-50 material. K-Resin can be sterilized by either ethylene oxide gas or gamma irradiation. Inadequate chemical resistance has eliminated K-Resin from medical packaging of certain flexible polyvinyl chloride tubing.

The Chevron Phillips Chemical Company LP Plastics Technical Center (PTC) has developed technology for the coextrusion of K-Resin/ general purpose polystyrene (GPPS) /high-impact polystyrene (HIPS) blends with a cap layer of glycol-modified polyethylene terephthalate (PETG) , resulting in a clear sheet with excellent physical properties and greatly improved stress cracking resistance. Structure, properties, processing, applications and recycling of the coextruded K-Resin/PETG sheet are discussed in detail in this Technical Service Memorandum.

STRUCTURE. Either two- or three-layer K-Resin/PETG structures may be desirable for packaging. It is more common in Europe to produce a three-layer structure with a K-Resin/GPPS blend on the inside, and two PETG layers on the outside. This ensures that PETG is always in contact with the reactive product. This is especially important when the sheet rolls are stored or shipped prior to thermoforming, rather than thermoforming online.

An adhesive is not required for the coextruded K-Resin structure provided that the PETG cap layer is 1 mil or less. Adhesion drops as the PETG gauge increases. A study of properties and peel strength was conducted for samples of 15-mil 50/50 K-Resin/GPPS blended sheet, with the PETG cap layer ranging from 0.75 to 4.5 mil (Table 1). PETG layers could not be peeled from samples with PETG representing five to ten percent of the structure. However, samples with PETG making up 15 to 30 percent of the structure were easily peeled, with a peel strength of only 0.1 to 0.2 lbs.

PROPERTIES. Similarly, tensile and impact

Table 1

Variable PETG cap layer study of 15-mil 50/50 KR03/GPPS coextruded sheet

Properties	.075 mil PETG Cap	1.5 mil PETG Cap	2.25 mil PETG Cap	3.0 mil PETG Cap	3.75 mil PETG Cap	4.5 mil PETG Cap
Flexural modulus, Msi						
MD	0.353	0.317	0.355	0.306	0.292	0.292
TD	0.287	0.258	0.384	0.314	0.456	0.379
Tensile yield strength, psi						
MD	5150	4850	4700	5050	4850	5300
TD	3000	2700	3150	3800	4250	4250
Break elongation, %						
MD	15	26	7	16	7	31
TD	44	46	7	12	8	23
Falling dart impact, g						
PETG side	186	202	174	266	302	478
KR03/GPPS side	250	258	258	434	570	654
Total energy dart drop, ft-lb						
PETG side	1.296	1.056	0.663	1.565	2.461	3.003
KR03/GPPS side	2.325	1.765	0.436	3.133	3.899	4.087
Hunter Color						
+b	6.8	6.4	8.4	7.3	7.0	7.4
-b	-6.4	-6.6	-7.7	-7.0	-6.5	-6.6
Light transmission, %	91	91	90	90	90	90
Haze, %	2.0	1.8	1.9	2.5	2.1	2.1
Peel strength, lb	No peel	No peel	0.21	0.16	0.12	0.13

PETG = eastman Kodar PETG copolyester 6763

properties of 65/34/1 K-Resin/GPPS/HIPS blends with and without a l-mil PETG cap layer are fairly close (Table 2). There is a slight increase in Gardner impact strength and falling dart impact strength for the PETG capped material, however, the total energy dart drop appears higher for the monolayer K-Resin blend. Optical properties of both sheets are excellent.

The most notable difference in properties is the superior stress cracking resistance of the coextruded K-Resin/PETG sheet. Environmental stress cracking resistance (ESCR) is defined as the susceptibility of an article to crack or craze formation under the influence of certain chemicals and stress. The PTC test involves thermoforming a lid out of the material to be tested. Approximately one tablespoon of the ESCR medium (usually oil) is placed on the inside of the lid. A corresponding HIPS cup is placed upside down on the lid to obtain a tight fit, thus creating stress on the lid. The cup is then placed on a piece of paper with the lid down, and is carefully monitored over two weeks for any leakage of the ESCR medium onto the paper. Leakage through the lid designates failure of the test material.

Using the PTC test method, an 18 mil K-Resin/GPPS sheet failed within four minutes of exposure to soy oil or red wine vinegar & oil at room temperature (Table 2). In contrast, the 17-mil K-Resin/GPPS sheet capped with a l-mil PETG layer did not fail after two weeks exposure to soy oil or red wine vinegar & oil, at room temperature and 140°F.

Table 2
Physical and ESCR properties of K-Resin®/PETG coextruded sheet[a]

Properties	K-Resin Blended Sheet	K-Resin Blended Sheet with 1-mil PETG Cap
Tensile modulus, Msi		
MD	0.333	0.331
TD	0.207	0.214
Tensile yield strength, psi		
MD	4400	4550
TD	2900	3300
Break elongation, %		
MD	26	28
TD	70	97
Average Gardner impact, cm-kg	2.8	3.8
Average falling dart impact, g	262	286
Average total energy dart drop, ft-lb	4.151	2.516
Hunter Color, -b	-6.9	-5.9
Light transmission, %	90	90
Haze, %	6.6	3.5
Shrinkage, %		
MD	35	32
TD	3	1
Peel strength, lb	-	2.2
ESCR to RWVO, time to failure		
RT	3 min	>14 days
140°F	-	>14 days
ESCR to soy oil, time to failure		
RT	4 min	> 14 days
140°F	-	>14 days

[a]Physical properties were measured for 18-mil 65/34/1 KR03/GPPS/HIPS blended sheet, and for 17-mil blended sheet coextruded with 1-mil Eastman Kodar PETG copolyester 6763. ESCR properties were determined for thermoformed sheet.

ESCR = Environmental stress cracking resistance

RWVO = Red wine vinegar and oil

RT = Room temperature

PROCESSING. The processing of coextruded K-Resin/PETG sheet encompasses PETG drying, coextrusion, thermoforming and regrind utilization. General processing information for K-Resin is given in Phillips Technical Information Bulletin (TIB) 200, whereas TIB 202 relates sheet extrusion and thermoforming of K-Resin/GPPS blends. Processing details unique to the coextrusion of K-Resin and PETG are described below.

PETG Drying - K-Resin blends are not hygroscopic, and, as such, do not usually require drying before extrusion. However, Eastman Chemical Company recommends that PETG be dried for four hours at 150°F to lower the moisture content below 0.08 percent. A dessicant dryer, with both return and supply air indicators, is the best choice for drying PETG. However, the material should not be exposed to high heat for extended periods of time, since blocking of the pellets could cause clogging of the transfer tubes and dryer. After drying, the PETG should be shielded by a blanket of dry air in the hopper to prevent moisture absorption during processing. Unprotected PETG will collect moisture very rapidly, rising above 0.08 percent within fifteen minutes. Although small amounts of moisture may not be detected in the finished sheet or parts, buildup along the die land will cause sticking at the die lips over extended production runs. Larger amounts of moisture will also affect the clarity of the sheet, resulting in die lines or possibly streaking.

Coextrusion - K-Resin blends and PETG may be coextruded on standard coextrusion equipment. A HIPS or general purpose screw is satisfactory for PETG. Screws with shallow feed and metering sections perform well with PETG. Extruders should measure at least 24:1 length/diameter (L/D), with 32:l L/D providing the best results for both K-Resin blends and PETG. Proper matching of extruder output rates allows good control over melt temperatures, and is critical to the stability of the coextruded layers. Since the base extruder will generally be operated at full capacity, the cap extruder should be sized such that it is not required to run at a slow rate during normal production. For example, a 2.5”-diameter cap extruder is well sized for a 4.5”-diameter base extruder for K-Resin/PETG coextrusion. However, a 3.5”-diameter cap extruder is too large for this base extruder, and would require slow rates of production, perhaps even idling, which would compromise melt uniformity.

For proper temperature control, the die temperature should be set at 420°F, with targeted melt temperatures of 380 - 410° F for the K-Resin/GPPS blend and 440 - 450° F for PETG. Instability between the K-Resin and PETG layers is generally not a concern when processing temperatures are maintained. However, if melt temperatures do deviate, flow lines and a wave front may become visible at the die lips. This may be corrected by adjusting the melt temperature of either material.

The die gap should be set at 15 to 25 percent greater than the targeted sheet gauge to promote some drawdown from the die without a significant increase in machine direction orientation. Sheet dies should be cleaned thoroughly prior to extrusion. In particular, flex die lips must be cleaned and lubricated with silicon grease to prevent PETG from sticking to the die lips during start-up.

The PETG cap layer should not vary more than 0.5 mil across the width of the sheet, and usually can be measured by first scoring the sheet with a knife and then separating the two layers. Although feedblock modifications are not usually needed, such changes do offer the greatest control of layer uniformity. A flex die lip with restrictor bar also permits control of sheet gauge and layer uniformity. Excessive PETG on the outside edges of the sheet is costly, and may be minimized by using the restrictor bar to force the material to the center of the die.

Chrome rolls should be highly polished for optimum sheet clarity. Roll temperatures should be slightly warmer (170 - 190° F) than required in standard K-Resin blend processing. If possible, the PETG layer should be extruded next to the middle roll, to polish out any imperfections or instability between the layers and to provide excellent clarity. Standard slitting techniques work well with coextruded K-Resin/PETG sheet, and delamination is not a concern, even at high output rates.

Thermoforming - Standard K-Resin thermoforming equipment may be used with coextruded K-Resin/PETG sheet. A forming temperature of 280-310° F is satisfactory, with the higher temperature used for thicker PETG-capped sheets. It should be noted, however, that PETG is more tacky than K-Resin blends, and will tend to stick to the pin chains and mold surfaces if heated excessively. Molds which are used for K-Resin blends or HIPS may be used with coextruded K-Resin/PETG sheet without modification. Similarly, coextruded parts may be trimmed and lip rolled in the same manner as for K-Resin blends or HIPS.

Table 3

Seven-pass regrind study of 15-mil 45/45/10 KR03/GPPS/PETG extruded sheet[a]

Properties	Control	After 1st Regrind	After 2nd Regrind	After 3rd Regrind	After 4th Regrind	After 5th Regrind	After 6th Regrind	After 7th Regrind	After 7th Regrind, 1 mil PETG Cap
Tensile modulus, Msi									
MD	0.379	0.380	0.380	0.379	0.392	0.283	0.392	0.387	0.380
TD	0.292	0.282	0.275	0.268	0.281	0.270	0.278	0.270	0.268
Tensile yield strength, psi									
MD	5750	6050	5450	5450	5900	5900	5750	6000	6200
TD	3800	3650	3550	3400	3550	3400	3550	3450	3400
Break elongation, %									
MD	14	11	2	6	3	10	2	8	8
TD	2	2	4	5	3	4	2	3	2
Gardner impact, cm-kg	0.41	0.42	<0.38	<0.38	<0.38	<0.38	<0.38	<0.38	-
Falling dart impact, g	48	41	31	<30	32	<30	<30	<30	-
Total energy dart drop, ft-lb	0.760[b]	1.473[b]	0.302	0.285	0.318	0.252	0.250	0.255	0.411
Hunter Color									
+b	1.4	1.7	1.5	1.6	1.7	1.9	2.0	2.0	2.2
-b	-5.7	-5.6	-5.2	-5.4	-5.4	-4.7	-5.5	-4.2	-5.9
Light transmission, %	89	89	89	89	88	88	88	89	89
Haze, %	9.6	8.6	8.1	9.0	7.2	7.0	6.8	7.6	9.8
Shrinkage, %									
MD	47	49	47	52	56	55	57	56	55
TD	13	19	19	18	24	26	20	24	21

[a]Eastman Kodar PETG copolyester 6763 was dried in a dehumidfying oven at 150°F for four hours before initial processing of control, and for PETG-capped sample.

[b]Total energy dart drop varied considerably between samples.

Regrind - Standard HIPS regrind equipment is suitable for grinding coextruded K-Resin/PETG sheet. Special care should be taken to keep the blades very sharp, since the PETG-capped sheet is tougher than the monolayer K-Resin blended sheet. The regrind typically does not require drying if it is used soon after processing. A regrind study of a 45/45/10 K-Resin/GPPS/PETG blend was performed at the PTC to determine the permissable amount of PETG in the regrind (Table 3). After seven extruder passes, there was minimal change in physical and optical properties, indicating that 10 percent PETG regrind is acceptable.

FOOD PACKAGING CONSIDERATIONS.

K-Resin copolymers are ideally suited for food packaging due to their excellent clarity, high gloss, and impact resistance. However, testing at the PTC has identified some mechanical limitations in the use of K-Resin and K-Resin/GPPS blends with fatty foods. Specific information regarding the food packageability of K-Resin is given in Technical Service Memorandum 288.

The PETG cap layer of coextruded K-Resin blended sheet proved to greatly enhance ESCR to oils in food packaging applications. The PTC evaluated the stress cracking resistance of a 17-mil 65/34/1 K-Resin/GPPS/HIPS blended sheet coextruded with a l-mil PETG layer to several oil-based foods, including soy oil, corn oil, red wine vinegar & oil, and gravy. No failures were evident after two weeks of contact at room temperature and 140°F. Several factors may contribute to the rate and severity of stress cracking, including molded-in stresses, part design, part loading, the stress cracking medium, and storage conditions. Therefore, the actual product should be tested for compatibility with the part.

MEDICAL PACKAGING CONSIDERATIONS. Clear, tough K-Resin copolymers are typically well-suited to the manufacture of medical devices and packaging. One exception is the incompatibility of K-Resin blends to certain flexible polyvinyl chloride (PVC) tubing. General information regarding medical applications of K-Resin is related in Technical Service Memorandum 292. Medical packaging information specific to coextruded K-Resin/PETG sheet is described below.

PVC Compatibility - K-Resin and flexible PVC tubing may be acceptably compatible for medical packaging applications provided that the level of dioctyl phthalate (DOP) plasticizer in the tubing is not excessive. PVC tubing having a Shore A durometer rating under 75 should not be used in contact with monolayer K-Resin, and the preferred minimum rating is 78 - 80. At lower durometer ratings, the plasticizer migrates out of the tubing, and into the K-Resin, causing stress whitening and softening of the K-Resin sheet.

Coextrusion of a PETG cap layer onto K-Resin blended sheet, however, may provide an effective barrier to the migration of DOP from flexible PVC tubing. The compatibility of coextruded K-Resin/PETG parts and PVC tubing rated at 50, 55, and 72 Shore A durometer was evaluated. Contact at room temperature and 140° F resulted in no adverse whitening or softening of the K-Resin/PETG parts after six weeks of testing. These parts were produced from 15-mil 50/50 K-Resin/GPPS blended sheet, with the PETG cap layer ranging from 0.75 to 4.5 mil. It is essential, however, that the actual product be tested for compatibility with the package.

Gamma Irradiation - Gamma irradiation up to 5 Mrad exposure has little effect on the physical properties of K-Resin copolymers, with the exception of a slight increase in yellowing (TSM 292). Similarly, gamma irradiation at 2.5 and 5.0 Mrad exposure to coextruded K-Resin/PETG sheet showed minimal change in physical and optical properties (Table 4). Coextruded sheet in contact with PVC tubing rated at 72 Shore A durometer was also sucessfully sterilized by gamma irradiation with minimal change in properties.

Table 4

Effect of gamma irradition on K-Resin®/PETG coextruded sheet[a, b]

Properties	Unsterilized	Sterilized 2.5 Mrad	Sterilized 5.0 Mrad
Flexural modulus, Msi			
MD	0.331	-	-
TD	0.241	0.203	0.205
Tensile yield strength, psi			
MD	4550	-	-
TD	3300	3200	3200
Break elongation, %			
MD	28	-	-
TD	97	68	79
Average total energy dart drop, ft-lb	2.516	3.039	3.059
Hunter Color -b	-5.9	-4.7	-4.5
Light transmission, %	90	90	89
Haze, %	3.5	3.3	3.0
Shrinkage, %			
MD	32	28	29
TD	1.3	1.3	1.3

[a]Properties were measured for 17-mil 65/34/1 KR03/GPPS/HIPS blended sheet coextruded with 1-mil Eastman Kodar PETG copolyester 6763.

[b]Gamma irradiation of samples was conducted by SteriGenics International, 3001 Wichita Court, Fort Worth, TX 76140

Table 5
Effect of ethylene oxide sterilization on K-Resin®/PETG coextruded sheet[a, b]

Properties	Unsterilized	EtO Sterilized
Tensile modulus, Msi		
MD	0.331	-
TD	0.241	0.210
Tensile yield strength, psi		
MD	4550	-
TD	3300	3300
Break elongation, %		
MD	28	-
TD	97	17
Average total energy dart drop, ft-lb	2.516	2.992
Hunter Color -b	-5.9	-4.9
Light transmission, %	90	90
Haze, %	3.5	3.0
Shrinkage, %		
MD	32	37
TD	1.3	4.0

[a]Properties were measured for 17-mil 65/34/1 KR03/GPPS/HIPS blended sheet coextruded with 1-mil Eastman Kodar PETG copolyester 6763.

[b]Samples were sterilized at 125°F and 50% relative humidity for four hours, using 650 mg/L ethylene oxide. Sterilization was conducted by Griffith Micro Science, 7775 Quincy Street, Willowbrook, IL 60521.

EtO Sterilization - K-Resin copolymers exhibit minimal change in properties after ethylene oxide (EtO) sterilization. Similarly, coextruded K-Resin/PETG sheet sterilized at 125° F and 50% relative humidity for four hours, using 650 mg/L EtO, demonstrated minimal change in physical and optical properties (Table 5). There was no effect on sheet properties after Et0 sterilization of this coextruded sheet in contact with PVC tubing rated at 72 Shore A durometer.

RECYCLING. K-Resin copolymer, as shipped can be coded with the number “6” under the Society of the Plastics Industry (SPI) voluntary container coding system. The number “6” indicates that K-Resin can be reprocessed with polystyrene. However, the number “6” may not necessarily be appropriate for coextruded K-Resin/PETG material. Since state and local regulations vary widely, these should be consulted to determine the appropriate coding for any specific use and location. K-Resin SBC Health, Safety, & Environmental Review provides more general information concerning the recycling of K-Resin.

SUMMARY. Subject to the foregoing information, coextruded K-Resin/PETG sheet may be used for food and medical packaging applications requiring clarity, gloss, toughness, and improved stress cracking resistance. There can be a significant economic advantage of coextruded K-Resin over traditional packaging materials, such as PETG and acrylic-based multipolymers. The ease of processing coextruded K-Resin has been demonstrated at the Plastics Technical Center, including the use of 10% PETG in the regrind without drying.

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