K-RESIN®
Styrene-Butadiene Copolymers

Plastics Technical Center Report #410

Odor in Blends of Polystyrene with K-Resin® SB Copolymers

INTRODUCTION. K-Resin styrene-butadiene copolymer has been used widely in the packaging market for cups, lids and other containers. Most of these parts have been manufactured by sheet extrusion and thermoforming and using K-Resin blended with crystal polystyrene. The reason for blending the polystyrene in K-Resin is to improve the stiffness of the K-Resin, and reduce the material cost. When the two materials are blended together, the combination can have a styrenic smell, more pronounced than the odor of either of the virgin resins. This report will outline the reasons for that odor development and methods to minimize that odor.

PROCEDURE AND EXPERIMENTATION. The key to the odor in the blends lies in the residual volatile components of the virgin resins. This value is measured by dissolving a sample of the polymer in solution and evaluating the total level of the volatile components contained in the resin sample.

Crystal polystyrene contains moderate levels of unreacted styrene monomer as well as impurities in the styrene monomer feedstream such as ethyl benzene and propyl benzenes. Analysis of some recent polystyrene samples gave the results shown in Table 1. Many polystryrene samples have between 100 and 800 ppm of styrene monomer as the principal volatile component. Ethyl benzene will show up at low levels in most polystyrenes, but if ethyl benzene is used as a diluent in the process it will be present at higher levels. K-Resin is very low in residual styrene monomer.

Previous experimentation by an in-house trained sensory panel showed K-Resin and K-Resin/polystyrene blends demonstrated a strong correlation between the level of residual styrene monomer and ethyl benzene and the odor of the sample. That data is being used to monitor residual volatile components in K-Resin production to maintain a consistent low odor polymer from the plant. Our experience

Table 1

Residual Volatiles Analysis of Commercial Grades of Crystal Polystyrene

	Styrene	Ethyl Benzene	Isopropyl Benzene	n-Propyl Benzene	Toluene
Nova 3500	257	8	4	2	2
Nova 2500	482	19	6	4	2
Dow 615	589	62	14	6	1
Huntsman 208	435	33	10	4	2
Chevron 3710	232	3	1	<1	3

indicates that the K-Resin has a greater capability to release these volatile components than does polystyrene. A K-Resin sample with 100 ppm of styrene monomer will have a much stronger styrenic smell than will a polystyrene with much higher levels.

To demonstrate this point, 16 ounce Boston round bottles were made from a KR05 sample and a KR05/polystyrene (50/50) blend. A total of five groups of bottles was evaluated from the following compositions:

1. 100% KR05
2. 50/50 Blend of KR05 and GPPS
3. 50/50 Blend of KR05 and GPPS with GPPS coextruded on the inner and outer surface
4. 50/50 Blend of KR05 and GPPS with GPPS coextruded on the inner surface
5. 50/50 Blend of KR05 and GPPS with PETG coextruded on the inner surface

These bottles were heated to 50°C for 20 minutes, and a 5 ml gas sample was withdrawn from the bottle to evaluate in the GC. The data in Table 2 indicates that the K-Resin bottle, low in styrene monomer, had very few styrenic volatiles in the head space, while the bottle made from the blend with crystal polystyrene had a significantly increased level of styrene monomer, which was contributed by the higher monomer levels in the polystyrene. Some of the bottles were made with a thin coextruded layer of crystal polystyrene. The bottle with a crystal polystyrene inner layer had a much lower level of residual styrene monomer present, more than 20 times less, indicating that the styrene monomer does not migrate nearly as easily through the polystyrene as it does through the blend. The bottle with a crystal polystyrene layer on the inner and outer layer also had a lower level of styrene monomer in the headspace. It appears that by blocking the migration of the volatiles from the exterior wall, slightly higher levels accumulated within the bottle. A layer of PETG on the inner surface was even more effective in reducing the migration of the styrene to the inside of the bottle.

This indicates that by coextruding a thin layer of crystal polystyrene on the surface of a K-Resin blend, the styrenic volatiles and the odor can be significantly reduced. However the added layer of crystal polystyrene can serve to make the blended part more brittle.

There had been some speculation that the cyclohexane in the K-Resin was acting as a carrier to accelerate the release of the styrenic volatiles and hence increasing the odor in the blends. To evaluate its effect, two samples of K-Resin were taken from the same lot. One sample was left in its original package, and the other was put in a hot room at 140°F for several weeks to lower residual cyclohexane levels. After exposure in the hot room, the cyclohexane level dropped from 461 ppm to 56 ppm. These samples were blow molded into 16 oz. bottles, and 50/50 K-Resin/polystyrene blends from each sample were also made into bottles.

Table 2

Barrier Characteristics of Coextruded Cap Layers of K-Resin/GPPS Blended Bottles

	KR05	50% K/R 50% GPPS	GPPS Inner/ Outer Layer	GPPS Cap Inner Layer	PETG Cap Inner Layer
Styrene, µg	< 0.3	66.0	3.2	1.7	0.6
Ethyl Benzene, µg	< 0.3	0.55	< 0.3	< 0.3	< 0.3
Isopropyl Benzene, µg	< 0.3	0.54	< 0.3	< 0.3	< 0.3
n-Propyl Benzene, µg	< 0.3	0.43	< 0.3	< 0.3	< 0.3

The bottles were submitted to an odor panel and the results are shown in Table 3. The odor ratings on the two K-Resin bottles showed that the panel could detect a considerable difference in the odor levels based on the different levels of cyclohexane. The panelists were unanimous in selecting the higher cyclohexane level bottle as having a higher odor. The blended samples, however, were judged as very similar in odor rating. Some panelists evaluated the odor level as equivalent. The sample with lower levels of cyclohexane in the blend was rated as having higher odor by some panelists, and some panelists rated the higher cyclohexane level sample as having more odor.

Table 3

K-Resin Odor Testing Variable Cyclohexane Levels

	Odor Rating Neat Bottles	Odor Rating Blended Bottles
Typical Residuals	5.7	4.7
Reduced Residuals	3.5	4.3

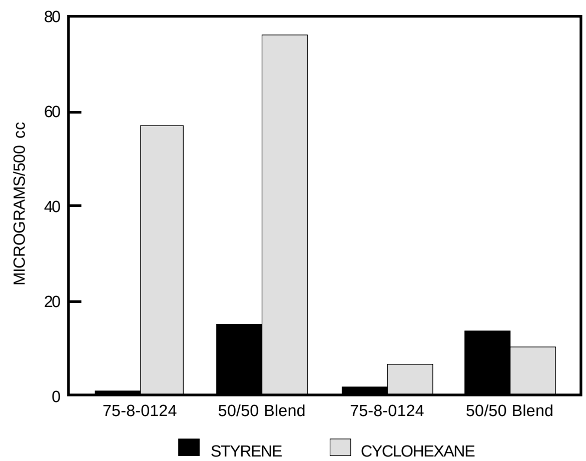
Blend 50% K-Resin/50% Chevron 3710

Results were reviewed with the panelists after their sensory evaluation. Although they rated the K-Resin bottles alone as having a higher odor ranking, they indicated that the styrenic odor of the blends was stronger or more offensive than the cyclohexane smell of the 100% K-Resin bottle. They also indicated that when they smelled the blended bottles, they could not smell the cyclohexane character in the odor, only the styrene, which apparently overpowered the cyclohexane smell.

The head space results shown in Table 4 tend to demonstrate that in spite of the cyclohexane volatiles being significantly reduced in the devolatilized sample, there was only a slight decrease in styrenic volatiles. This is shown more clearly in Figure 1. The samples containing significantly lower levels of cyclohexane did have nearly the same level of styrene monomer in the head space, which agreed with the odor panels sensory evaluation.

Figure 1

Residual Volatiles in K-Resin and Blends with Variable Cyclohexane



CONCLUSION. When K-Resin/Polystyrene are blended together, the combination can have a styrenic smell, more pronounced than the odor of either of the virgin resins. The predominant odor in the blends is from the styrenic volatiles. The cyclohexane level is not a key factor in contributing to the odor. The odor of the cyclohexane is marked by the styrene volatiles, and the amount of styrene in the headspace is not strongly dependent in the cyclohexane level. As we have always recommended, the polystyrene chosen for blending should contain a minimum level of residual styrene and ethyl benzene to minimize the odor. One way to reduce the volatiles in the head space is by coextruding a thin layer of crystal polystyrene on the surface of the blend.

Table 4

Residual Volatiles Analysis of K-Resin

Headspace Bottles Micrograms/500cc

	Normal		Low Cyclohexane	
	KR03NW 75-8-0124	50/50 Blend Chevron 3710	KR03NW 75-8-0124	50/50 Blend Chevron 3710
Cyclohexane	56.81	76.30	6.30	10.54
Toluene	1.30	1.25	1.09	0.65
Ethylbenzene	0.19	0.30	ND	0.17
Styrene	0.14	16.41	ND	14.63

Residual Volatiles Pellets, ppm

	Normal		Low Cyclohexane
	KR03NW	Chevron 3710	KR03NW
Cyclohexane	461	ND	56
Toluene	7	ND	<1
Ethylbenzene	5	3	3
Styrene	3	870	<1
n-Propyl Benzene	2	1	1
Isopropyl Benzene	2	ND	3