

Kraton polymers boost functional life of thermoplastic road marking paints

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ABSTRACT

Thermoplastic road marking paints with longer life and superior performance can be obtained with the addition of Kraton polymers to the binder.

Styrenic block copolymers improve the mechanical properties of the binder which can increase the performance life time of the road marking. Benefits of unsaturated and hydrogenated block copolymers will be discussed. Both clearly reduce the paint erosion after numerous wheel passages, improve the adhesion to glass beads and hence the retro-reflection properties. Processing conditions will also be considered.

It will be shown that sprayable thermoplastic road markings with improved flexibility and functional life can be produced by adding Kraton D1161PTM polymer to the composition. Extrudable thermoplastic road markings with long functional life requirement in low traffic density areas should be formulated with Kraton G1652MU polymer.

INTRODUCTION

A thermoplastic road marking material is a 100% solid, environmentally and user safe compound. It fulfills current requirements on productivity, environmental protection and product performance. Because the products are 100% solid, they do not require drying time and their use keeps traffic disruption to a minimum. The absence of solvent and the easier handling of waste reduce their impact on the environment. They can also be applied in thick layer (2-3 mm) and ensure good coverage, which increases the service life of the marking product. Finally, these materials show good adhesion on asphalt/bitumen roads and to glass bead.

However new regulations clearly strive to enhance driver safety and hence the level of performance of road marking in terms of retro-reflection and erosion. These properties can be further improved by the addition of a thermoplastic elastomer to the composition that would boost the functional life of thermoplastic road markings by improving abrasion and crack resistance. Better retro-reflection performance can also be achieved. This will be shown in this paper.

THERMOPLASTIC ROAD MARKING PAINTS

Thermoplastic road marking paints (RMP) are a mixture of glass beads, pigment and filler held together by a binder. As its names suggests, the composition becomes liquid when heat is applied.

Binders of thermoplastic road markings consist of low molecular weight petroleum-based resins or rosin derivatives optionally mixed with a plasticizer to reduce the brittle nature of the resin by reducing the glass transition temperature (T_g) of the binder. They provide toughness, flexibility and bond strength while holding all the components together. The low molecular weight of these binder ingredients results in a relatively low abrasion resistance of the road marking. The

addition of a styrenic block copolymer (SBC) such a Kraton polymer improves the mechanical properties of the binder, which increases the performance life time of the road marking. The use of polymers to improve the quality of road marking paints will become more widespread as regional regulations become more stringent in order to improve driver safety.

A typical thermoplastic road marking composition can be found in Table 1.

Table 1: Typical thermoplastic road marking paint composition

	Range, weight %	Material
	8-15	Hydrocarbon resin
Binder	1-5	Plasticizer
(15-25%w)	0-5	Thermoplastic elastomer
	5-10	Pigment (e.g. TiO ₂ , ZnO)
Fillers	20-40	Extender (e.g. CaCO ₃)
(75-85 %w)	15-20	Glass Beads
	20-40	Aggregates

WHAT ARE STYRENIC BLOCK COPOLYMERS?

Styrenic block copolymers are thermoplastic block copolymers consisting of polystyrene domains in an elastomer-continuous phase. This provides elasticity to the system: the polystyrene domains give cohesion to the system and act not only as physical cross-links in the three-dimensional network, but also as reinforcing filler for the elastomeric matrix. The polymer behaves like a cross-linked rubber at ambient temperature, but as these cross-links result from physical interactions, they start to soften at temperatures close to the polystyrene T_g. This allows them to flow under shear when heated, yet they recover their strength an elastomeric properties on cooling. These characteristics make them suited for the formulation of hot melt or extrusion applied coatings. They can also be milled into a fine powder and applied by various melt spray processes. These polymers dissolve readily in resins used in thermoplastic road markings at typical melting temperatures of 180°C to 220°C.

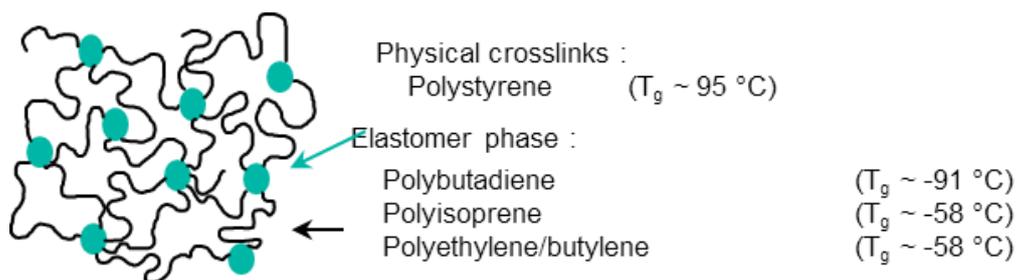


Figure 1: Microstructure of styrenic block copolymers

Kraton polymers are based on different types of block copolymers, differing mainly by their rubber type: styrene-butadiene-styrene (SBS) types, styrene-isoprene-styrene (SIS) types and their saturated versions: styrene-ethylene/butylene-styrene (SEBS) and styrene-ethylene/propylene-styrene (SEPS). They have an elastomer T_g of -60°C (SIS-SEBS) or -90°C (SBS) and a PS T_g of +95°C.

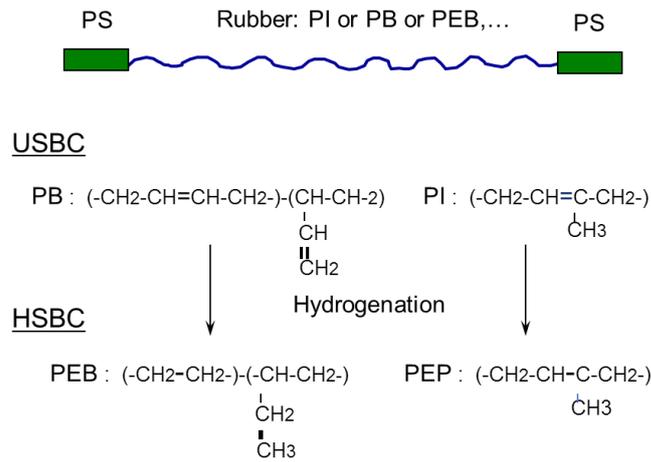


Figure 2: Styrenic block copolymer types

USBC polymers like SIS and SBS polymer show good cohesion and excellent flexibility at low temperature. When superior resistance is required against UV, then HSBC might be required. Because of the saturated nature of the rubber midblock, SEBS and SEPS polymers show excellent weatherability, thermal stability and high tensile strength. Because of their higher cohesion, they can be used in more diluted formulations and show excellent oil absorption properties. These grades can also be functionalized to introduce reactive polar group for improved adhesion to certain surfaces or for crosslinking reactions. Finally, as they exhibit higher viscosities as USBC, they might be more suitable for extrudable than for sprayable RMP.

In this presentation we will concentrate on SIS and SEBS polymers.

STYRENIC BLOCK COPOLYMERS FOR THERMOPLASTIC ROAD MARKINGS

Among suitable polymer additives for use in thermoplastic road markings, styrenic block copolymers are the preferred materials of choice. Their unique structure of polystyrene blocks in an elastomer continuous phase provides them specific visco-elastic properties, as can be seen on Figure 3.

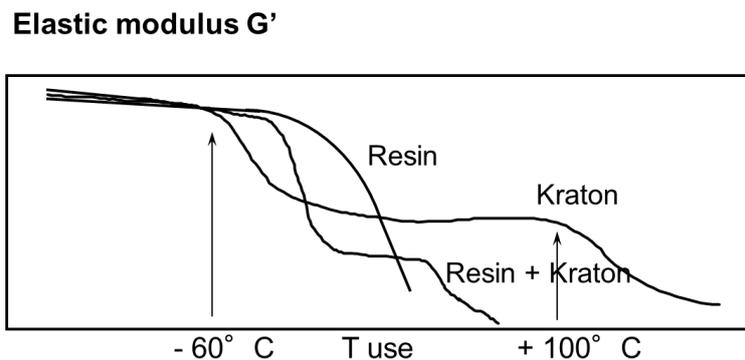


Figure 3: Elastic modulus G'

Their addition to the resin shifts the composition T_g to a lower value and significantly reduces the elastic modulus. It can also be clearly seen that the mixture remains thermoplastic and shows a strong elastic modulus decrease above a temperature, which is higher than the resin melting point. Therefore, the use of styrenic block copolymers in the paint formulation can result in binders with improved flexibility at lower temperatures, reduced brittleness, and higher elasticity at higher temperatures compared to binders based on petroleum or rosin-derived resins and modified with other polymers such as waxes.

Styrenic block copolymers are also fit for road marking paint processing techniques. Milled or powdered Kraton polymers dissolve readily in resins used in thermoplastic road markings at typical melting temperatures of 180°C to 220°C (patented technology EP 0 499 326 B1).

The use of polymers in road markings can however lead to a longer dissolution time and higher hot melt viscosity compared to binders comprising only low molecular weight resins and plasticizers. Therefore, the choice of type, morphology and amount of styrenic block copolymer depends on the application technique (extrusion or spray), and on the ultimate road marking performance desired.

Wear simulator



Figure 4: AETEC turntable detail: wheel on paint test panels

To highlight the benefits of styrenic block copolymers in thermoplastic road markings, we carried out wear simulation tests according to norm EN13197. The wear simulator selected is described in annex F of this norm. Detail of the turntable can be seen on the picture above.

In this study, one SIS polymer (Kraton D-1161PTM) and one SEBS polymer (Kraton G-1652MU polymer) are compared to a binder without polymer additive.

Kraton D-1161PTM polymer has low polystyrene (15%) and di-block (17%) contents, which allows formulating with a good balance between elasticity-flexibility and cohesion-erosion resistance.

Kraton G-1652MU polymer has a saturated elastomeric block: it is harder and shows higher cohesion and better stability.

Viscosity data

The type of polymer has an influence on the viscosity of the paint as can be shown in Table 2 .

Table 2: Viscosity data

Polymer	Type	Resin type	Dissolution time at 200°C (h)	HMV 200°C (cp)	HMV after 4h at 200°C (cp)
Kraton D1161PTM	SIS	C5 HC resin	2	815	660
Kraton G1652MU	SEBS	Hydrogenated C9 resin	2.5	1370	1340

In this table, viscosity data and dissolution times for the two polymers are given; all binders consisted of 3 parts by weight of SBC and 14 parts by weight of resin. The SIS polymer resulted in the lowest Brookfield hot melt viscosity (HMV) and showed only marginal degradation after storage of the binder for 4 hours at 200°C. Polyisoprene degrades by chain scission which results in a reduction of viscosity over time. HSBC polymers with a saturated elastomer mid-block can demonstrate very good thermal stability resulting in almost no change in viscosity over time. Their higher viscosity might however require an adaptation of the application equipment. Their higher thermal stability could afford higher application temperatures, but those could be detrimental to the other ingredients of the formulation.

Paint application and composition

A typical Central European paint formulation was chosen. The paints were produced in Germany. Kraton Polymers in cooperation with Sovitec - Group R&D applied the paints via spray on flat test substrates, according to EN13197 (Figure 5).



Figure 5: test plate

The paint composition is given in Table 3.

Table 3: paint composition

formulation composition (%)	ref	KD1161	KG1652
		SIS	SEBS
C5 resin	15	15	15
oil	2	2	2
rosin resin	1	-	-
PE wax	2	2	2
styrenic block copolymer		2	2
TiO2	10	10	10
fillers	30	29	29
premix glass bead, 1000-125 μm	40	40	40
g/m ² applied paint	3300	3000	3000
drop on beads, g/m ² , 3F coated, 600-125 μm	300	300	300

Superior erosion resistance

Figure 6 demonstrates the effect of the addition of styrenic block copolymers to the binder of road marking paints.

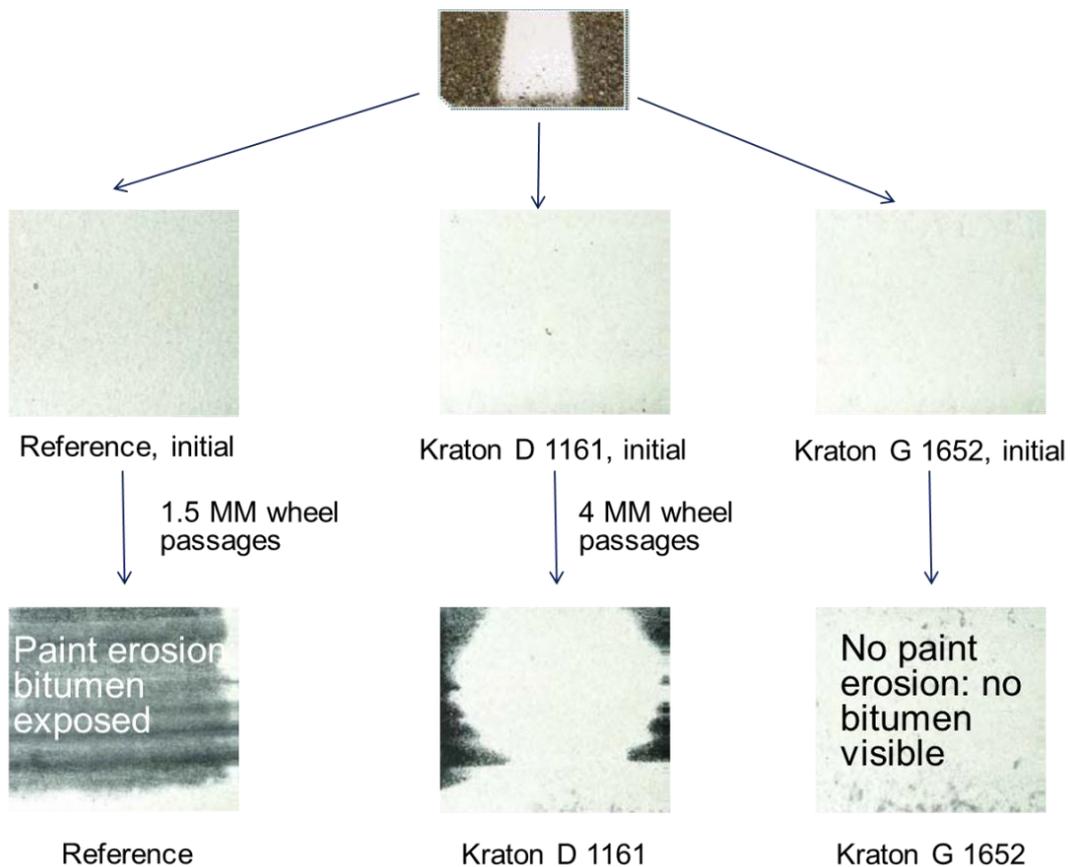


Figure 6: erosion resistance

The thermoplastic reference paint without Kraton polymer failed the test after 1.5×10^6 wheel passages. Adding Kraton Polymer to the binder enables excellent erosion resistance up to 4×10^6 wheel passages.

Kraton G1652MU polymer exhibits superior erosion resistance due to its 30% polystyrene content in combination with the hydrogenated elastomer phase. The paint surface is hardly eroded after 4×10^6 wheel passages.

Kraton D1161PTM polymer erodes to a higher extent due to the presence of diblocks and its low polystyrene content.

Figure 7, showing the paint percentage retained after wear test, confirms the improved erosion resistance for the Kraton polymer containing paints.

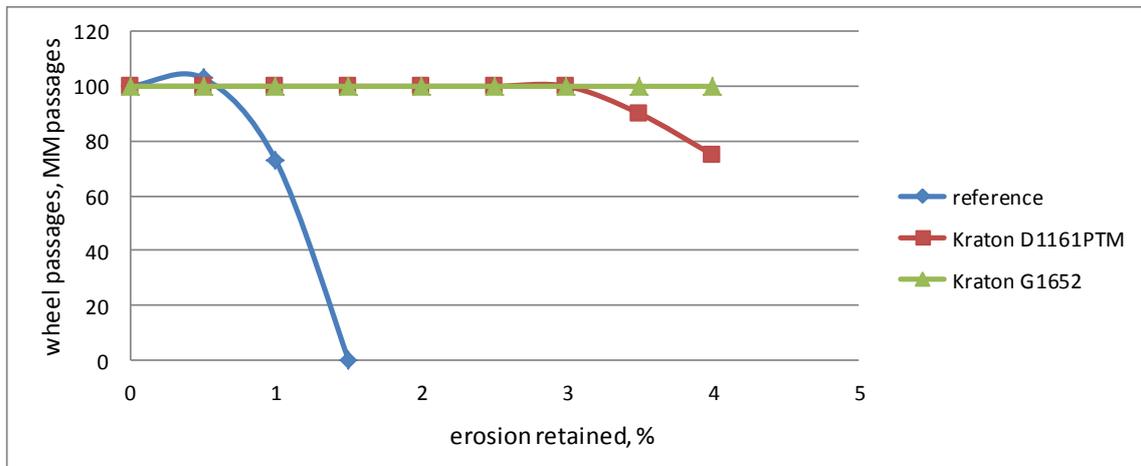


Figure 7: erosion retained in function of wheel passages

Superior retro-reflection

Regulations clearly strive to enhance the level of performance of road markings in terms of retro-reflection and luminance. The coefficient of retro-reflected luminance (R_L), which is an indication of night time visibility, was measured after the wear simulator test. Its evolution as a function of the number of wheel passages can be seen on Figure 8.

This graph confirms improved R_L for the styrenic block copolymers containing paints. The thermoplastic reference paint without Kraton polymers failed the test after 1×10^6 wheel passages. Adding Kraton polymer to the binder enables excellent RL over 4×10^6 wheel passages. After elimination of the drop on beads, the premix beads are exposed to the paint surface. The premix beads are retained thanks to Kraton polymer's elastic properties, leading to improved R_L .

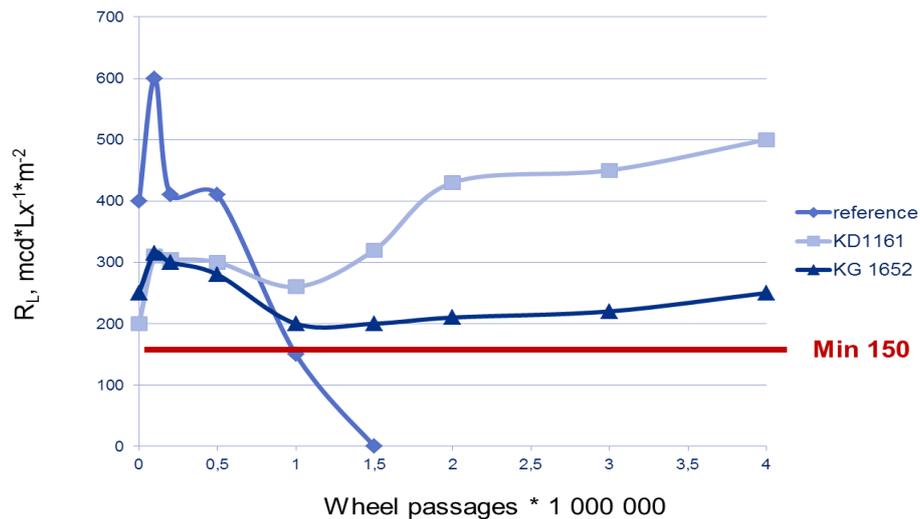


Figure 8: Evolution of the retro-reflection coefficient with number of wheel passages

Kraton D-1161PTM exhibits excellent R_L , due to its SIS nature, polymer structure and balance of flexibility and cohesion. The erosion of the surface and exposure of the premix glass beads leads to a clean paint surface. So, its lower erosion resistance compared to Kraton G1652 polymers appears here to lead to improved retro-reflection performance.

Kraton G1652MU polymer results in lower R_L values, due to its SEBS nature and high cohesive polymer structure. The erosion process is slowed down, leading to less exposure of the premix glass beads and to dirt pick up. This grade is therefore better suitable for road markings with long functional life requirements in low traffic density areas.

CONCLUSION

Thermoplastic road marking paints with longer life and superior performance can be obtained with the addition of Kraton polymers to the binder.

Styrenic block copolymers improve the mechanical properties of the binder which can increase the performance life time of the road marking. Both unsaturated and hydrogenated block copolymers clearly reduce the paint erosion after numerous wheel passages, improve the adhesion to glass beads significantly and, as a result, establish better retro-reflection performance in the medium and long term. Furthermore, styrenic block copolymers can exhibit high extendibility and can increase the durability of the thermoplastic road marking even at a SBC addition level as low as 2%.

Sprayable thermoplastic road markings with increased flexibility and functional life will benefit from the addition of Kraton D-1161PTM polymer in the binder.

Kraton G-1652MU polymer is recommended in the binder of extrudable thermoplastic road markings with long functional life requirements in low traffic density areas.

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