

## Compatibility of Hydrocarbon Resins in Elastomers



### Benefits

- Non-migratory processing aids
- Improved tack properties
- Modification of viscoelastic properties

### Target Markets

- Tires
- Fluid routing
- Power transmission belts
- Conveyor belts

### Additional Information

**MSDS/TDS:** Wingtack® Resins, Norsolene® Resins

### Description

Hydrocarbon resins (HCRs) are typically defined as low molecular weight polymers with high softening points produced from various petroleum fractions. They are commonly employed in rubber formulations to improve processing, influence surface tack, or otherwise modify the viscoelastic properties of the compound. In each of these cases, a degree of compatibility between the HCR and the other polymeric ingredients in the formulation is required.

### Background

Compatibility of resins in elastomers is determined primarily by two factors: composition and molecular weight. Compositional parameters such as monomer polarity, microstructure, and other features can be compared. In general, the lower the molecular weight of the resin component, the larger the window of compatibility. For petroleum-based HCRs, composition is primarily measured on a scale of aliphatic to aromatic content. Wingtack® (C5) resins are largely aliphatic, while Norsolene® (C9) resins have high aromatic content. Norsolene W series resins are “pure monomer” grades, essentially copolymers based on  $\alpha$ -methyl styrene. Table 1 describes the relevant properties of Cray Valley HCRs selected for a compatibility study. Note that the materials were chosen to have similar Tgs. Table 1 also provides a relative view of aliphatic to aromatic character of a subset of Cray Valley HCRs, measured on a scale of aliphatic H content (NMR).

# TECHNICAL UPDATE

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Table 1 – Hydrocarbon resins

RESIN	COMMERCIAL GRADE <sup>a</sup>	DESCRIPTION	Tg (°C)	% ALIPHATIC
C5-I	Wingtack 98	aliphatic C5	58	97
C5-II	Wingtack STS	aliphatic C5, aromatic modified	56	91
C9-I	Norsolene A90	aromatic C9, aliphatic modified	59	67
C9-II	Norsolene S95	aromatic C9	54	55
αMS	Norsolene W100	pure monomer	58	48

<sup>a</sup>Cray Valley Hydrocarbon Specialty Chemicals

Table 2 – Elastomers

ELASTOMER	COMMERCIAL GRADE	DESCRIPTION	Tg (°C)
EPDM	Nordel™ IP4640 <sup>a</sup>	ethylene propylene diene rubber	-42
BR	Buna CB 22 <sup>b</sup>	cis-polybutadiene rubber	-103
NR	SMR CV-60	natural rubber	-59
ESBR	Plioflex 1502 <sup>c</sup>	emulsion styrene-butadiene rubber	-50
SSBR	Buna VSL VP PBR 4041 <sup>d</sup>	solution styrene-butadiene rubber	-9
NBR	Nipol® DN3335 <sup>e</sup>	nitrile rubber	-24

<sup>a</sup>The Dow Chemical Company

<sup>b,d</sup>Lanxess Corp.

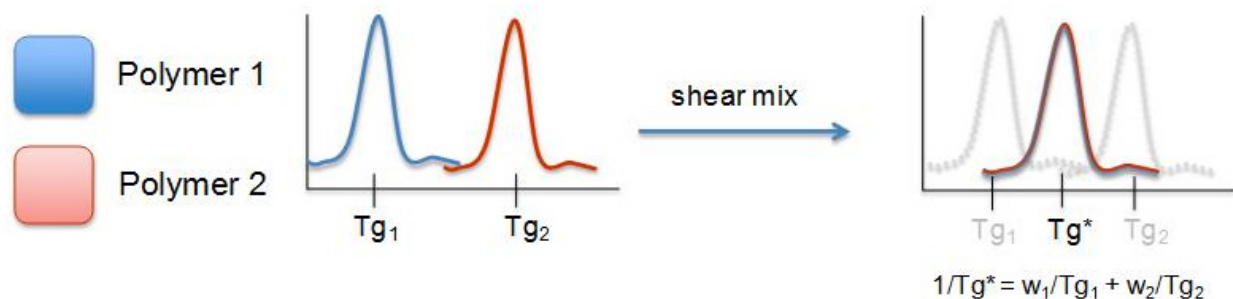
<sup>c</sup>The Goodyear Tire & Rubber Co.

<sup>e</sup>Zeon Chemicals L.P.

## EXPERIMENTATION

An experiment was conducted to broadly measure the relative compatibility of these resins in a variety of commercially relevant elastomers. The elastomers used in our evaluation are listed in Table 2 and run the spectrum of non-polar (EPDM) to highly polar (NBR). The above resins were shear mixed with the elastomers in a binary blend, 20% by weight resin, 80% elastomer. Thermal (DSC) and mechanical testing (DMA) was conducted in order to quantify the compatibility between the materials. In our experimental scenario, the Tg of the elastomer was measured before and after the addition of HCR. There is a large difference between Tgs of the individual blended components (Tables 1, 2), which will result in a movement of the blend Tg to higher values if there is compatibility between the resin and elastomer. The amount of Tg shift correlates to the degree of compatibility. Tg shift values are also compared to the ideal blend case of miscibility (as calculated by the Fox equation) in the analysis (Figure 1). A complete description of the experiment and results can be found in Cray Valley HSC's Fall 2012 ACS Rubber Division Paper #22.

Figure 1 – Characterizing a compatible polymer system



## RESULTS

The results of our study can be summarized in the matrix in Figure 2. The conditions of compatibility, partial compatibility, and incompatibility were determined for the single-blend composition (20% by weight resin in elastomer). The classifications below were determined directly from the magnitude of Tg shift for the elastomer/HCR blend and confirmed with literature references when possible. In some cases, blend composition ladders were evaluated to determine the extent of compatibility as a function of resin content.

Figure 2 – Resin/elastomer compatibility mix

Resin Grade	Type	EPDM	NR	BR	eSBR	sSBR	NBR
Wingtack 98	C5	C	C	PC	PC	PC	I
Wingtack STS	C5/C9	C	C	C	C	PC	I
Norsolene A90	C9/C5	I	C	PC	C	C	PC
Norsolene S95	C9	I	C	PC	C	C	PC
Norsolene W100	αMS	I	C	C	C	C	C

C	Compatible
PC	Partially Compatible
I	Incompatible

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The results indicate that the relative difference in polarity of the polymer components is a good predictive tool for compatibility. Aliphatic resins are more likely to be compatible with non-polar elastomers, while aromatic resins mix better with polar elastomers. Interestingly, the pure monomer  $\alpha$ MS resin demonstrated compatibility with all elastomers except the most non-polar EPDM. In addition, our study compared calculated composition-based solubility parameters for all blend components. By tabulating the difference in solubility parameters, the data set generally supports the experiment results, suggesting that such an approach can be a predictive tool for certain blends of HCRs and elastomers.

## SUMMARY

Many applications require a degree of compatibility when employing blends of hydrocarbon resins and elastomers. It has been shown that the degree of compatibilization can be quantified by comparing the magnitude of shift in both thermal and mechanical measurements of the Tg of binary blends. In general, hydrocarbon resins with higher aliphatic composition (C5 fraction) produced a higher Tg shift in elastomers with low polarity. Hydrocarbon resins with higher aromatic compositions (C9 fraction or styrenic) produced higher shifts in the Tg of higher polarity elastomers.

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