Improved Adhesion of Polyurethane to Rubber Krasol® Functionalized Resin

BENEFITS

- Improved adhesion
- Improved performance of specialty composites
- Viable alternative to surface treatment

TARGET MARKETS/ APPLICATIONS

- Automotive
- Industrial
- Construction

ADDITIONAL INFO

- SDS: Krasol® SDS
- Technical data sheet: Krasol® LBH 2000

Introduction

Elastomer-based materials enable development of composites with improved properties in various applications, such as automotive, industrial and construction. In specific cases, adhesion between the rubber phase and high-polarity substrates is considered as a key parameter to optimize the performance of specialty composites.

It is well known that rubber compounds can be characterized by low surface energy. To increase the affinity of rubber compounds with more polar components, surface treatments can be performed. However, these treatments have variable efficiency, and additional processing steps can add cost.

Modification of rubber compounds is a viable alternative to surface treatment. To achieve this aim, it is possible to use a functionalized diene resin with an average molecular weight less than 5000 g/mol, such as a hydroxyl-terminated polybutadiene. Indeed, this low-molecular-weight additive modifies the surface of the rubber compound to improve its wettability, as well as adhesion to polar systems.

Cray Valley supplies Krasol® liquid hydroxyl-terminated polybutadiene derivatives with different molecular weights and vinyl and hydroxyl contents. This technical document provides some insights about Krasol® modified EPDM adhesion to a polyurethane matrix.

TotalEnergies

Krasol® for EPDM modification

Krasol® grades are liquid polybutadienes having hydroxyl end groups. Anionic polymerization is used to manufacture all Krasol® products in order to obtain liquid polyenes with a narrow molecular weight distribution and a well-defined microstructure (vinyl content: 65%).

Krasol® LBH 2000 is a commercial grade, selected to determine the effects of bulky modification of EPDM rubber compounds by a functionalized polybutadiene. According to Table 1, this commercial grade possesses hydroxyl functionality to react with several functionality types. It also contains double bonds on its backbone to crosslink with standard curing systems used in rubber such as sulfur and peroxides.

Table 1: Typical characteristics of Krasol® LBH 2000 grade.

Grade	OH Type	OH Content by Chain	Vinyl Content (%)	Mn (g/mol)	Viscosity (mPa.s @ 25°C)
Krasol® LBH 2000	2nd	1,9	65	2,000	10,000

A model composition based on standard EPDM grade is defined to evaluate the concept described previously. The latter can be crosslinked either by a standard sulfur-based system or by an organic peroxide at a temperature of 160°C.

Table 2: Model composition of rubber compound for the study.

Components	Type	Quantity (phr)
Keltan® 6950C (EPDM)	Rubber	100
Omyalite 90-OM	Filler	150
N330	Filler	20
Plaxene® 25110	Paraffinic mineral oil	20 – 5
Krasol® LBH 2000	Hydroxyl polybutadiene	0 – 15
Zinc oxide	Metal oxide	3
Stearic acid	Fatty acid	1
Antioxidant	Protective	1
Curative package	Crosslinking system	Variable

To determine the effect of hydroxyl-terminated polybutadiene on the properties of EPDM rubber and its adhesion with a standard coating system, a portion of oil in the model compound is substituted with Krasol® LBH 2000 (considered as a functional plasticizer). The overall plasticizer content remains constant. In contrast, the content of curatives is variable to compare the properties and the adhesion performances of rubber compounds at ISO hardness at room temperature (Shore A: 60 ± 2).

Krasol® LBH 2000 and properties of EDPM rubber compounds

Mooney and mechanical tests are performed on sulfur- and peroxide-cured EPDM rubber compounds to highlight potential effects of the substitution of paraffinic oil with Krasol® LBH 2000.

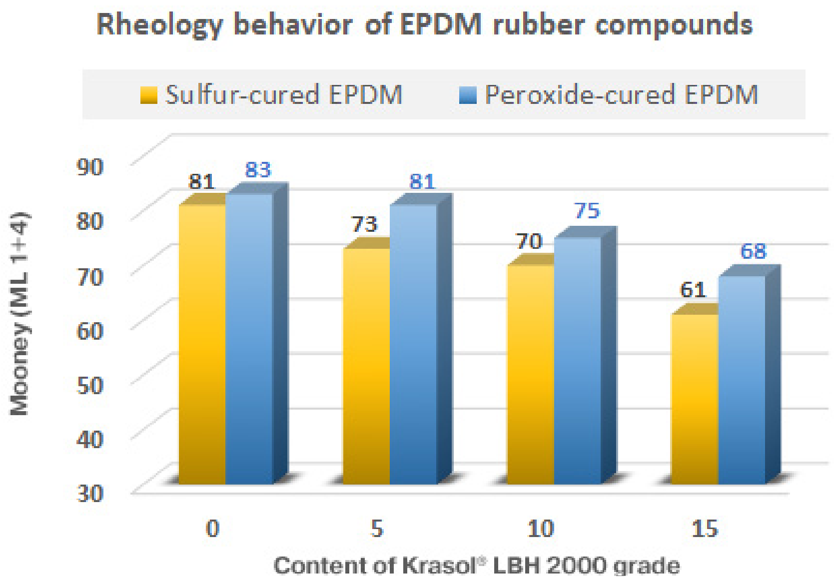

Figure 1: Effect of Krasol® LBH 2000 grade on Mooney (ML 1+4) values of EPDM rubber compounds

By increasing the content of hydroxyl-terminated polybutadiene from 5 phr to 15 phr in sulfur- and peroxide-cured EPDM compounds, their rheology behavior is significantly improved (at ISO hardness). It can be assumed that Krasol® LBH 2000 grade enables a better dispersion of fillers, in particular calcium carbonate (Omyalite 90-OM), during the mixing step without degrading the final properties of EPDM rubber compounds.

Adhesion between EPDM rubber compound and PU binder

T-peel test method is used to evaluate the adhesion between EPDM rubbers and a commercial polyurethane coating formulation supplied by Dow, Voramer™ MR 1165. The quantity of PU formulation deposited between two EPDM rubber compound substrates is of 0.5 g (deposition area: 55 mm x 25 mm — see Figure 2). The maturation time to obtain the complete crosslinking of PU composition is 7 days at room temperature.

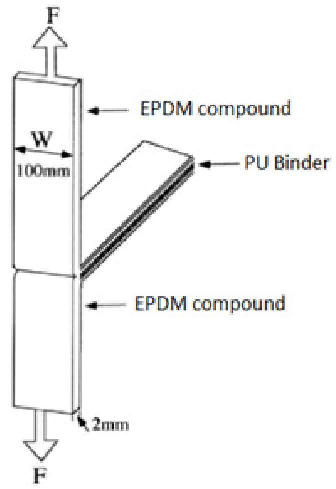

Figure 2: Diagram related to T-peel samples prepared during the study

According to the adhesion results shown in Figure 3, the substitution of paraffinic oil with Krasol® LBH 2000 improves significantly the adhesion strength between the rubber compound and polyurethane coating. Moreover, the failure mode of samples changes from adhesive to cohesive as the amount of Krasol® LBH 2000 is increased.

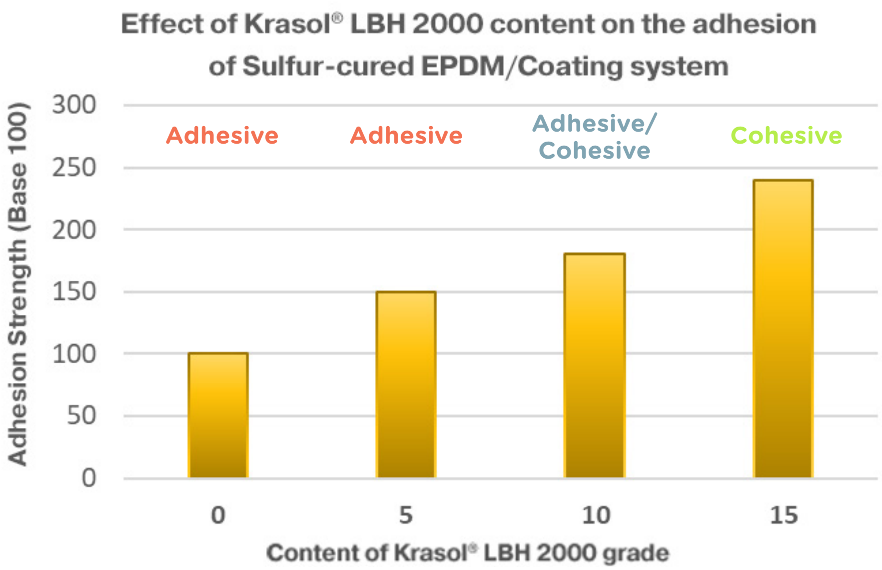

Figure 3: Results of T-peel tests with sulfur-cured EPDM compound and PU binder

In the case of peroxide-cured EPDM compound, it is highlighted that the adhesion strength between rubber substrates and polyurethane coating rises significantly due to the modification of rubber compound by Krasol® LBH 2000 resin. The failure mode evolves also from adhesive to cohesive failure (see Figure 4).

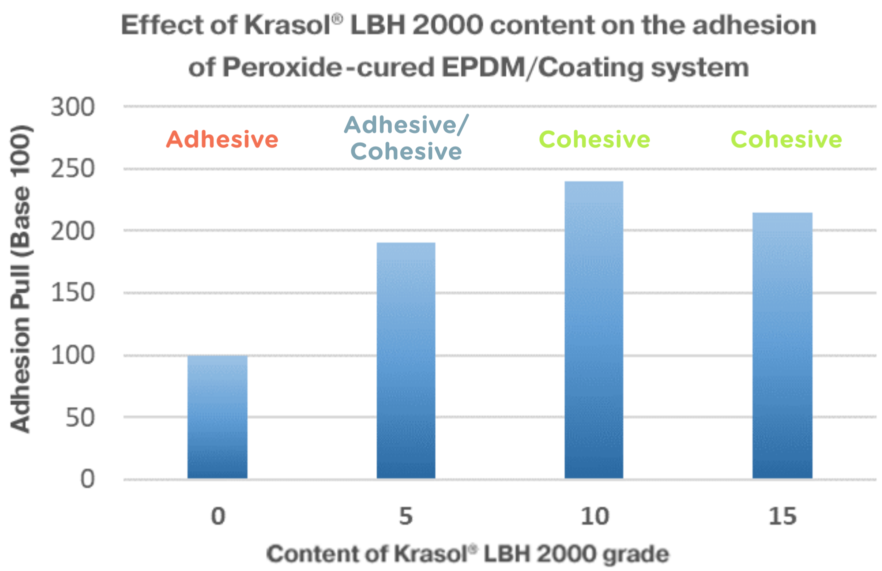

Figure 4: Results of T-peel tests with peroxide-cured EPDM compound and PU binder

Thanks to bulky modification of sulfur- and peroxide-cured EPDM rubber compounds by Krasol® LBH 2000 grade, it is possible to improve considerably their adhesion performances with a standard polyurethane composition (at ISO hardness). Due to the fact that the failure mode evolves in both cases, it can be notified that:

- The surface energy of EPDM rubbers is modified due to the incorporation of hydroxyl-terminated polybutadiene;
- Interactions are increased between the hydroxyl end groups of Krasol® LBH 2000 chains and the functionalities of the polyurethane system.

Summary

The incorporation of a functionalized liquid polybutadiene, such as Krasol® LBH 2000 grade, in EPDM rubber compounds, crosslinked either by sulfur-based systems or organic peroxides, improves their processability and their adhesion strength significantly with polyurethane coating composition. These improvements are observed at ISO hardness, in the case of both rubber compounds, and with no real impact on their mechanical properties.

The results of T-peel testing highlight an evolution of failure mode, in particular from 10 phr of Krasol® LBH 2000 grade introduced in model EPDM rubber compounds used for the study. It can be considered that some hydroxyl end groups of Krasol® LBH 2000 grade interact strongly with polyurethane coating applied on the surface of EPDM rubber compound.

Cray Valley develops and manufactures other functionalized liquid butadiene homopolymers and copolymers, such as maleinized polybutadienes. According to our technical knowledge, the latter can be introduced in vulcanized rubber compounds to enhance their adhesion performance to adhesive or coating compositions.

About Cray Valley

Cray Valley is the premier global supplier of specialty chemical additives, hydrocarbon specialty chemicals, and liquid and powder tackifying resins used as ingredients in adhesives, rubbers, polymers, coatings, and other materials. Cray Valley has pioneered the development of these advanced technologies, introducing hundreds of products that enhance the performance of products in energy, printing, packaging, construction, tire manufacturing, electronics, and other demanding applications.

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