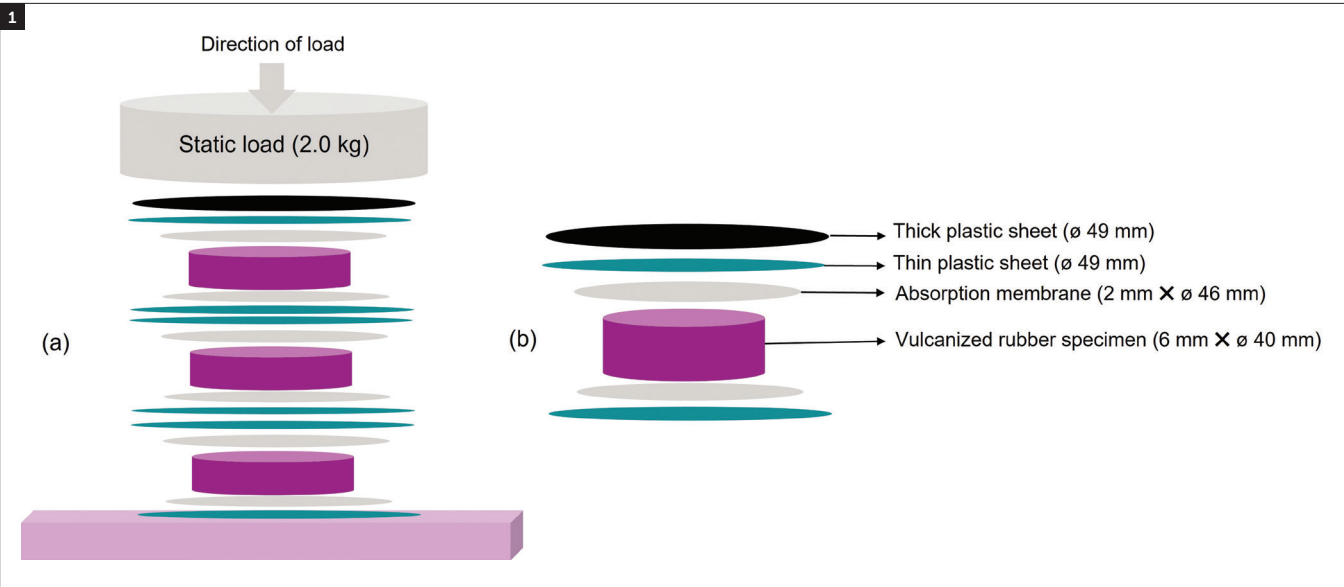


Studying plasticizer migration

Exploring the use of silane functionalized liquid polybutadienes for enhanced rubber performance and low migration in natural rubber-silica/silane systems

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The role of high-performance, functional plasticizers such as liquid polybutadienes and modified liquid polybutadienes is gaining greater importance in the tire industry. Rubber plasticizers are classified into many categories – for example, based on their reactivity to rubber they are classified as reactive and non-reactive plasticizers. Reactive plasticizers offer many advantages over non-reactive plasticizers, including processability improvements, performance enhancements and reduced migration.

Modern tire tread compounds with high amounts of silica and

Figure 1: (a) Schematic migration test setup (b) Sandwich assembly of test specimen-absorption membranes

silanes offer improved rolling resistance and wet-grip properties, but in some cases processability can be negatively affected by applying very high amounts of such filler systems. This can be overcome by adding increased quantities of plasticizers; however, a high level of these processing aids can adversely affect tire performance over time due to blooming or bleeding effects, technically referred to as migration of plasticizers. The technical reasons that cause this migration are miscibility, compatibility, synergism with ingredients, optimum dosage and others.

The migration of plasticizers is undesirable, as it may influence the rubber properties in many ways

– such as altering the compound viscosity, reducing the building tack, and modifying the homogeneity of the compound. In vulcanized rubber, migration may have a negative impact on aesthetic appearance and may worsen final performance. Such migration issues can be controlled by applying high molecular weight reactive plasticizers, because they can chemically interact with fillers or polymers or even both. Therefore it is necessary to investigate and quantify the migration characteristics via appropriate test methods.

Evonik's previous migration study was conducted on silica/silane-based passenger car tire tread formulations. This current investigation was conducted on a silica/silane-based natural rubber (NR) tread formulation with various Polyvest liquid polybutadienes (Table 1) and a TDAE reference (Table 2). To avoid the possible migration of anti-aging chemicals, they were not added to the rubber formulations.

Migration test method

The schematic diagram of the laboratory migration test setup is shown in Figure 1. Three test

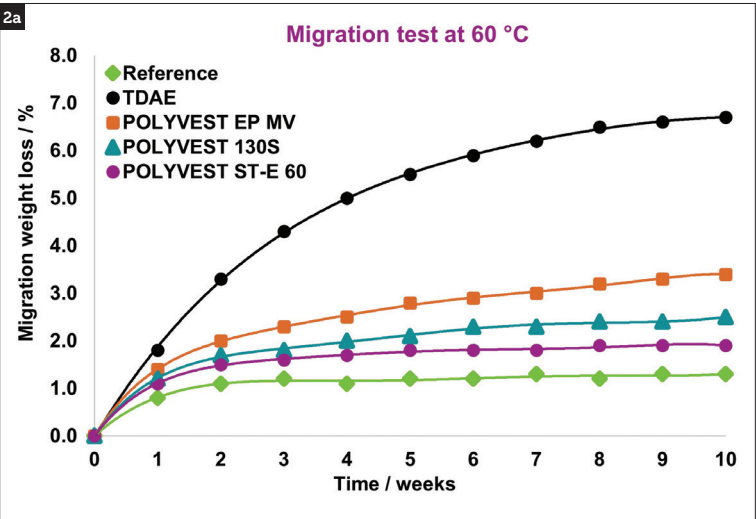
Table 1: Selected Polyvest grades for the tire and rubber industry			
Grades	Functionalization	Vinyl content (%)	Molecular weight (M _n)/g/mol
Polyvest 130S	-	1	Approximately 4,600*
Polyvest EP MV	-	61	1,700-2,700*
Polyvest ST-E 60	Silane	22	Approximately 3,200**
*GPC: Polystyrene standard			
**GPC: Polybutadiene standard			

Table 2: Compounding formulations			
	Reference	TDAE	Polyvest
	phr	phr	phr

First stage			
SMR 10	100.0	100.0	100.0
Ultrasil 7000 GR	55.0	55.0	55.0
Si 266	7.7	7.7	7.7
TDAE	-	15.0	-
Polyvest variables	-	-	15.0
Zinc oxide	3.0	3.0	3.0
Stearic acid	3.0	3.0	3.0

Second stage			
Batch first stage	-	-	-

Third stage			
Batch second stage	-	-	-
Sulfur	2.0	2.0	2.0
Vulkacit CZ/EG-C/CBS	1.0	1.0	1.0
Rhenogran DPG-80	2.5	2.5	2.5



specimens are stamped out from a 6mm thick vulcanized sheet and have a diameter of 40mm. The absorption membranes are prepared separately based on NR-N330 carbon black compounds and do not contain any plasticizers or anti-aging chemicals. The absorption membranes are 2mm thick with a diameter of 46mm and are stamped out from the vulcanized sheets.

The migration test is conducted at 60°C for 70 days under 2kg of static load on the top of the sandwich setup. The absorption membranes are renewed every week after measuring the mass loss and Shore A hardness

of the test specimens. The concentration gradient between the test specimen and the absorption membrane is the physical driving force for the diffusion-induced migration process. In addition, the elevated test temperature and applied static load further accelerate the migration process.

Migration results

The migration weight loss during the experimental period and the final migration loss percentage is shown in Figures 2a and 2b. All vulcanizates show a significant migration mass loss, as does the reference vulcanizate,

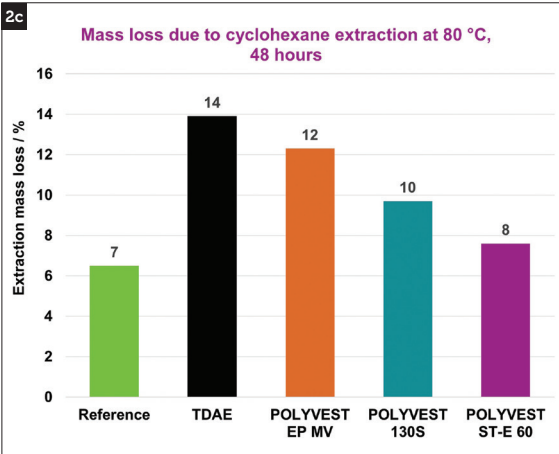
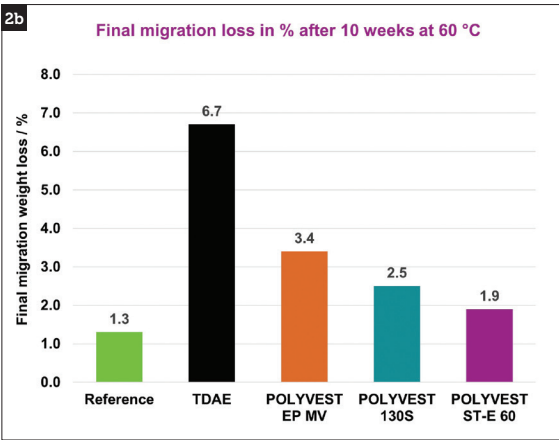
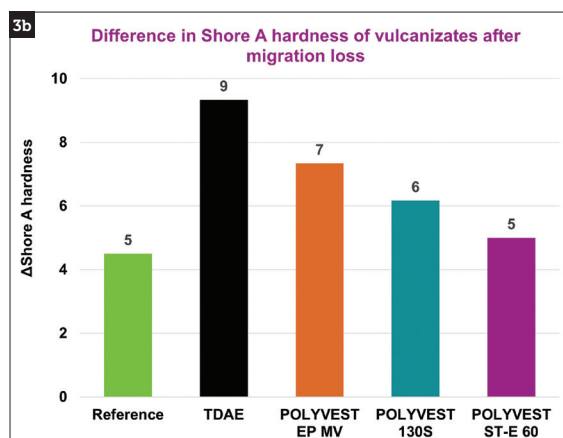
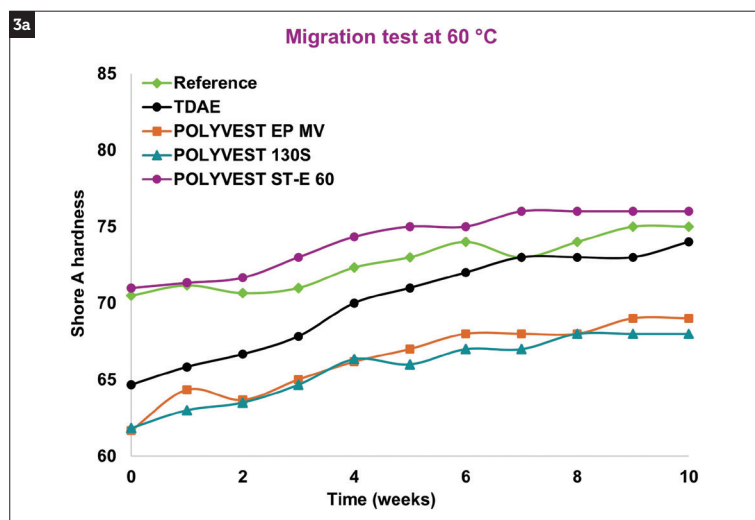


Figure 2: (a) Migration loss during the test period (b) Final migration loss (c) Mass loss due to cyclohexane extraction

which does not contain plasticizers. About 1.3% of the migration loss noted for the reference vulcanizate represents a certain amount of unknown migrating substances, possibly stearic acid, accelerators and some impurities of the natural rubber. Various Polyvest grades and TDAE vulcanizates show higher migration loss compared with the reference vulcanizate. This confirms that the incorporated plasticizers exhibit diffusion-induced migration loss.

As expected, TDAE vulcanizates reveal the highest migration loss of 6.7% due to their low molecular



weight and non-reactive nature – toward the polymer as well as the silica/silane system. The Polyvest EP MV- and Polyvest 130S-based vulcanizates show a migration loss of 3.4% and 2.5% respectively, which is 50-60% lower than the TDAE-based formulation. Polyvest ST-E 60 vulcanizates exhibit the lowest migration loss of only 1.9%, due to its high silica affinity (interaction of its silane functionalization) and the high polymer affinity (interaction of its optimized microstructure).

To verify the reactivity of various Polyvest and TDAE systems, a cyclohexane extraction test is performed at 80°C for 48 hours, with results shown in Figure 2. As expected, TDAE vulcanizates show the highest extraction loss of 14.0% and the extraction loss gradually reduces with application of Polyvest EP MV and Polyvest 130S. Remarkably,

Figure 3: (a) Shore A hardness during the test period (b) ΔShore A hardness (final hardness- initial hardness)

Figure 4: Performance indicators enhancement by using various Polyvest grades

Polyvest ST-E 60 vulcanizates reveal the lowest extraction loss of only 8.0%, close to the reference vulcanizates, which evidences good affinity toward silica and polymers.

Influence of plasticizer loss and thermal aging

The influence of migration loss on Shore A hardness and the change in Shore A hardness values are reported in Figures 3a and 3b respectively. Shore A hardness increases for all vulcanizates due to the loss of plasticizers and thermal aging (Figure 3a). TDAE vulcanizates display a higher ΔShore A hardness of 9 points due to the higher migration loss (Figure 3b). Both unfunctionalized Polyvest products exhibit a ΔShore A hardness of 6 and 7 points. The

Polyvest ST-E 60-based vulcanizate provides the lowest ΔShore A of 5 points due to its lower migration tendency. The flexibility and performances of tire tread can therefore be maintained by using low-migrating Polyvest-based liquid polybutadiene rubbers.

The incorporation of Polyvest products can improve processability and the magic triangle performance indicators as depicted in Figure 4. Polyvest 130S and Polyvest EP MV grades are mostly suitable for winter performance enhancement. Polyvest ST-E 60 is highly recommended to simultaneously improve rolling resistance, winter performance and abrasion resistance.

Conclusions

This study reveals that the migration behavior of plasticizers is dependent on various parameters such as their molecular weight (TDAE versus all Polyvest grades), the microstructure, their respective compatibility with the main polymer matrices (Polyvest EP MV vs Polyvest 130S) and the reactivity of the plasticizer to silica/silane/polymer (Polyvest ST-E 60 vs TDAE and non-functionalized Polyvest grades). The tire magic triangle performance of natural rubber tread compounds can be greatly improved by the addition of Polyvest products. Polyvest ST-E 60 is also available as a more sustainable liquid polybutadiene – Polyvest eCO ST-E 60 Bio. **tire**

