Studying reactive plasticizers

An examination of the influence of reactive plasticizers on the migration of rubber ingredients and the performance in tire tread compounds

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When discussing rubber technology, the migration of rubber ingredients from uncured or vulcanized rubber compounds is often described using technical terms such as blooming and bleeding. The reasons for migration tendencies include the miscibility or compatibility and their synergistic effect, the desired volume of ingredients, and the reactivity to and interaction with fillers, polymers and many others. However, the migration of ingredients is an unwanted process that influences the performance of finished articles in many ways. For instance, in an uncured state, the migration of plasticizer leads to increased viscosities, changing the building tack and the homogeneity of the compound. In vulcanized rubber, migration may negatively affect the appearance and may worsen the performance during service conditions. Therefore, for a better understanding of the migration effect, the first step is to quantify it using a suitable test.

In the last few decades, silica/silane-based energy-efficient tires have played a major role in automotive applications due to their environmental sensitivity and safety aspects. Applying high-molecular-weight rubbers with very high loadings of precipitated silica, such as Ultrasil, requires improved processing aids. Bi-functional silanes such as Si 69, Si 266 and Si 363 reduce the compound viscosities and greatly improve the final tire performance. Nevertheless, for optimized processability, these systems require additional plasticizers. Treated distilled aromatic extract (TDAE) with lower polycyclic aromatic hydrocarbons (<3.0%) is a widely used processing aid for green tires, and is currently believed to be a non-carcinogenic substance. But modern tire technology needs environmentally friendly, high-performance, advanced processing aids. Polyvest liquid polybutadiene rubbers can serve this purpose, as they can bring additional benefits in tire performance.

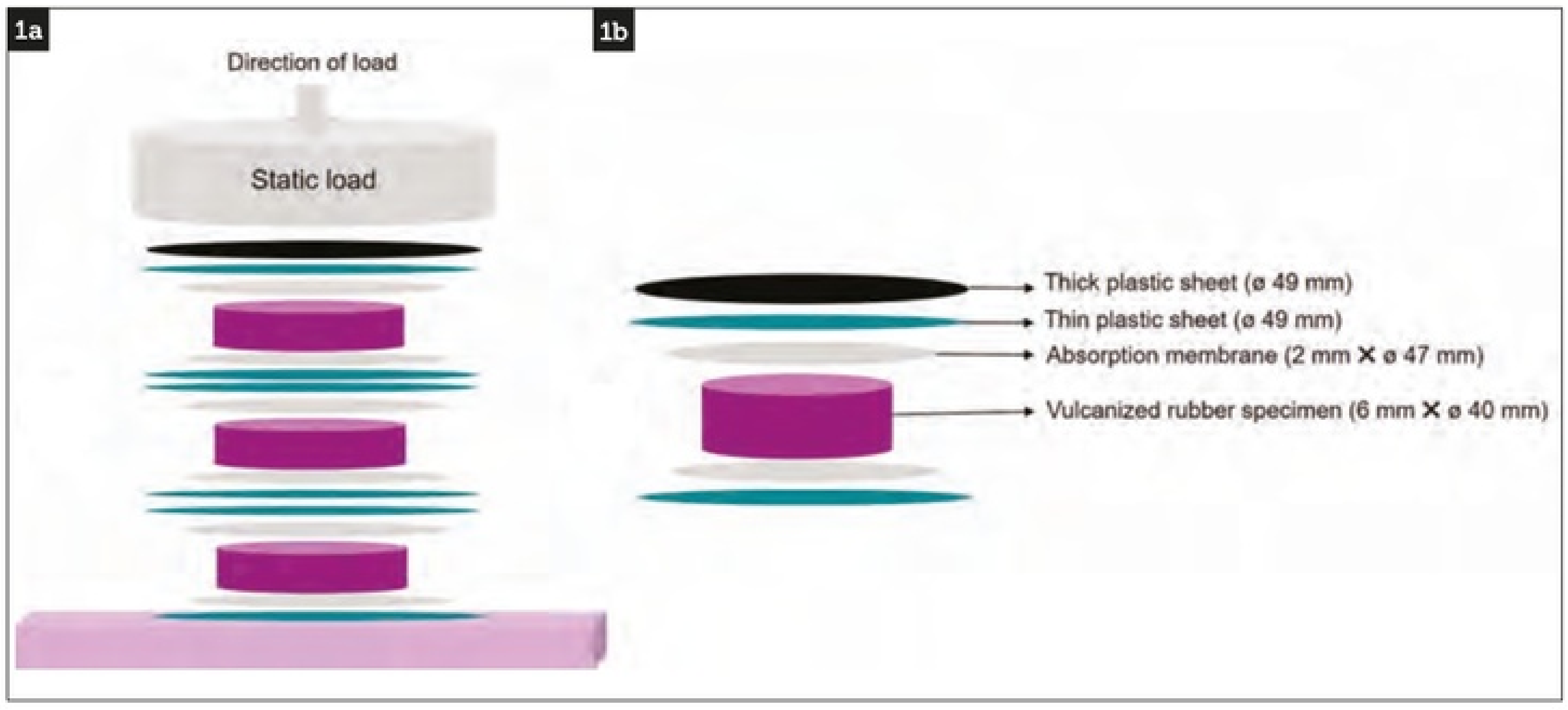


Figure 1a: Schematic diagram of migration test setup
Figure 1b: Sandwich structure of vulcanized test specimen-absorption membrane with protecting foils

Four Polyvest grades shown in Table 1 are utilized for the following investigations. A typical tread formulation and its mixing procedure are given in Table 2. Considering the migration possibilities of other rubber ingredients, anti-aging chemicals are not added into these formulations.

Migration test method

The schematic diagram of developed migration test setup is shown in Figure 1. The three migration test specimens are stamped out from a 6mm-thick vulcanized sheet with a diameter of 40mm. The absorption membranes are prepared separately based on S-SBR/BR – N330 carbon black compound and do not contain any plasticizers or anti-aging chemicals. The absorption membranes are 2mm thick with a diameter of 47mm and stamped out from the vulcanized sheets. The migration test is carried out at 60°C for 70 days under 2kg of static load on the top of the sandwich setup. The membranes are renewed every week after measuring the Shore A hardness and the mass loss of the test specimens. The concentration gradient between the test specimen and the absorption membrane is the driving force for the diffusion-induced migration process. Besides this, the elevated test temperature and static load are the physical parameters accelerating the migration process.

Migration test results

The migration weight loss during the testing period and the calculated final migration loss percentage is illustrated in Figures 2a and 2b. The test results reveal that the migration loss increases with time, and all test specimens exhibited a significant weight loss. However, the migration loss is varied regarding various plasticizer types. The highest

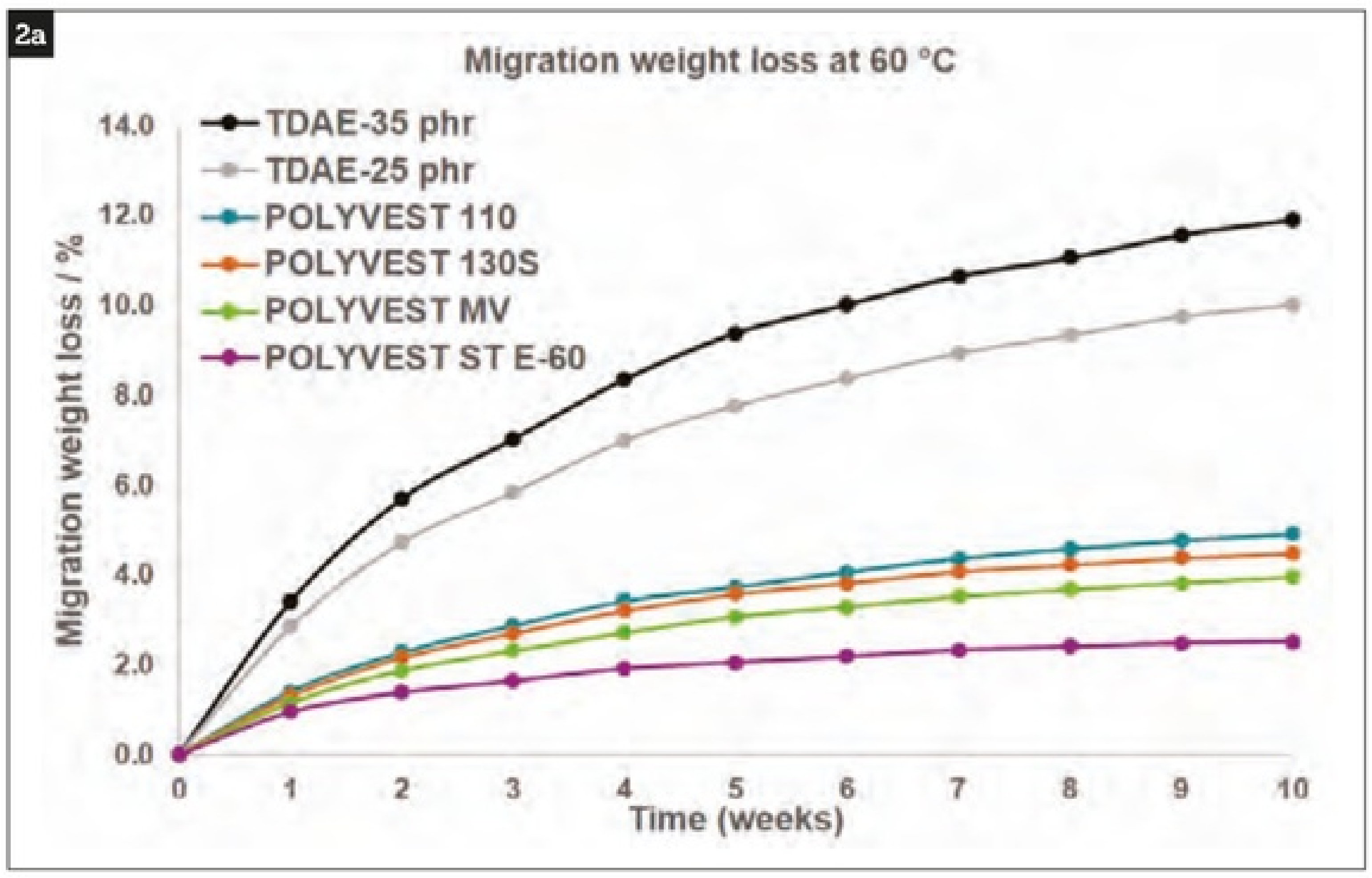
Table 1: Polyvest grades for the tire and rubber industry

Grade	Functionalization	Vinyl content (%)	Molecular weight range
Polyvest 110	-	1	Low
Polyvest EP 130 S	-	1	Medium, high
Polyvest EP MV	-	61	Low, medium
Polyvest EP ST-E 60	Silane	22	Medium, high

migration loss is observed for TDAE vulcanizates and, as expected, the higher the concentration of TDAE, the higher the migration tendency. The amount of TDAE used in the vulcanizates is around 11.0% (25.0phr) and 15.0% (35.0phr) and the migration weight loss noticed for the TDAE vulcanizates is around 10.0% and 12.0%. It proves that around 80-90% of TDAE is lost within 10 weeks. Next, the average migration loss observed for Polyvest 110 and Polyvest 130 S are approximately 4.9% and 4.5% respectively, which is nearly two times lower than the migration tendency of TDAE. The migration loss difference between Polyvest 130 S and Polyvest 110 is only 0.4% and reveals that the molecular weight has only a minor impact. Polyvest MV vulcanizate exhibits only 3.9% migration loss, probably due to the restricted diffusion tendency of the bulky vinyl group and enhanced compatibility with high-vinyl S-SBR. Finally, the lowest migration loss of 2.5% is observed for the Polyvest ST-E 60 vulcanizate, which is nearly four times lower than the TDAE reference. The chemical interaction of the functionalized Polyvest ST-E 60 and its high affinity toward the silica/silane system is the key factor for this favorable behavior.

Figure 2a: Percentage of migration weight loss during testing period

Figure 2b: Percentage of plasticizer loss in vulcanizates after 10 weeks at 60°C



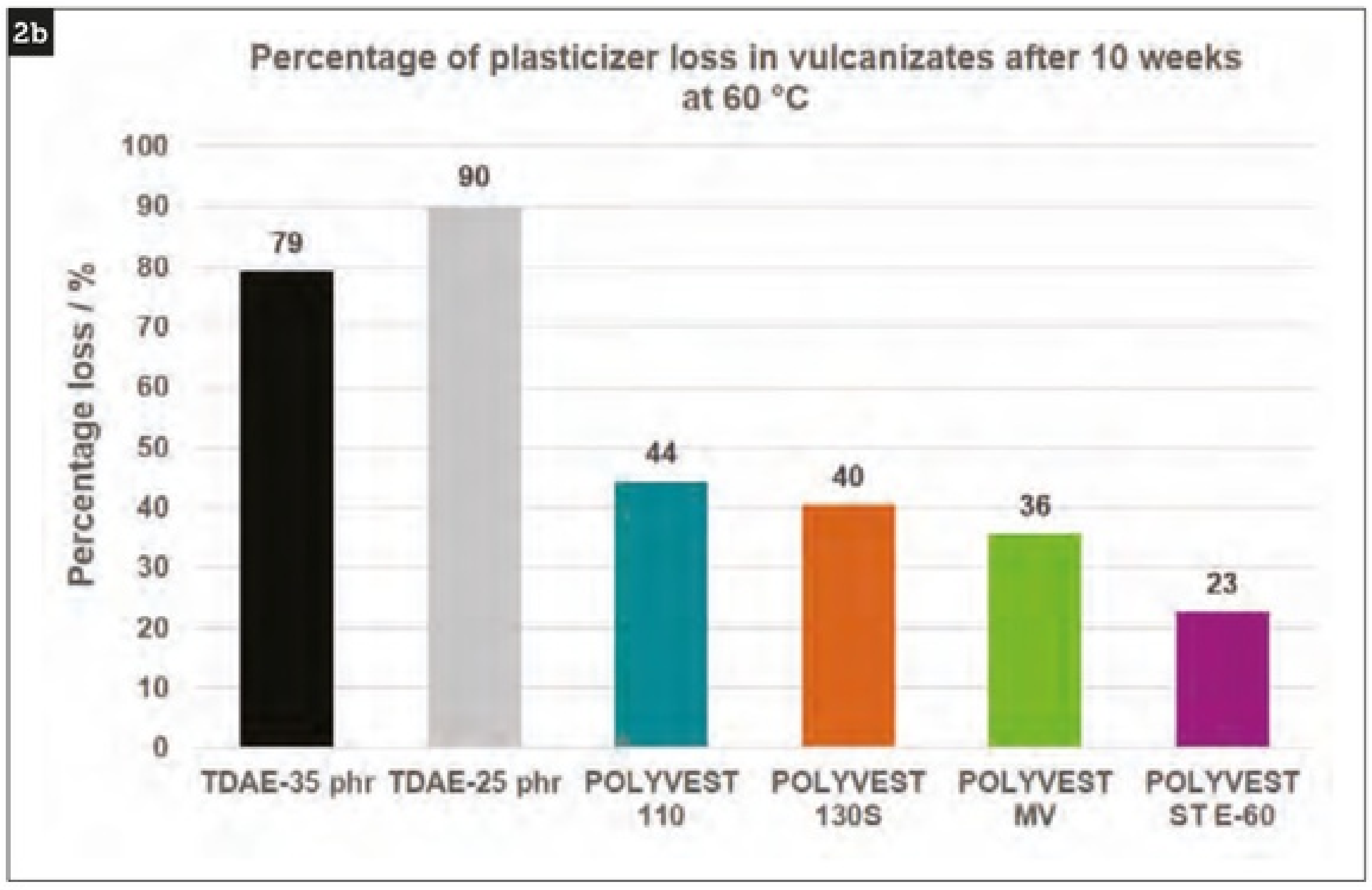


Table 2a: Compounding formulation		
	TDAE (phr)	Polyvest (phr)
First stage		
Europrene SOL R 72613	70.0	70.0
Buna CB 24	30.0	30.0
Ultrasil 7000 GR	80.0	80.0
Si 266	5.8	5.8
TDAE	**35.0, 25.0**	**-**
Polyvest	**-**	**25.0**
Carbon black – N330	5.0	5.0
Zinc oxide	2.0	2.0
Stearic acid	2.0	2.0
Second stage		
Batch first stage		
Rhenogran DPG	2.5	2.5
Third stage		
Batch second stage		
Ricon TBzTD OP	0.2	0.2
Vulkacit CZ/EG-C	1.6	1.6
Sulfur	2.0	2.0

Plasticizer loss and aging

The influence of migration loss in rubber is studied by hardness measurements, and the ΔShore A hardness values are shown in Figure 3. The Shore A hardness is increased for all vulcanizates due to the loss of plasticizers and thermal aging. Both TDAE vulcanizates show a drastic increase in Shore A hardness of 16 and 19 points. All unfunctionalized Polyvest grades exhibit ΔShore A values in the range of 9-11 points, which is approximately two times lower than TDAE. Polyvest ST-E 60 exhibits the lowest ΔShore A hardness value. The flexibility and performance of tread compounds can be maintained for a longer period when using these reactive plasticizers with the lowest migration tendency.

Performance analysis

Incorporation of Polyvest products in green tread formulations is extending

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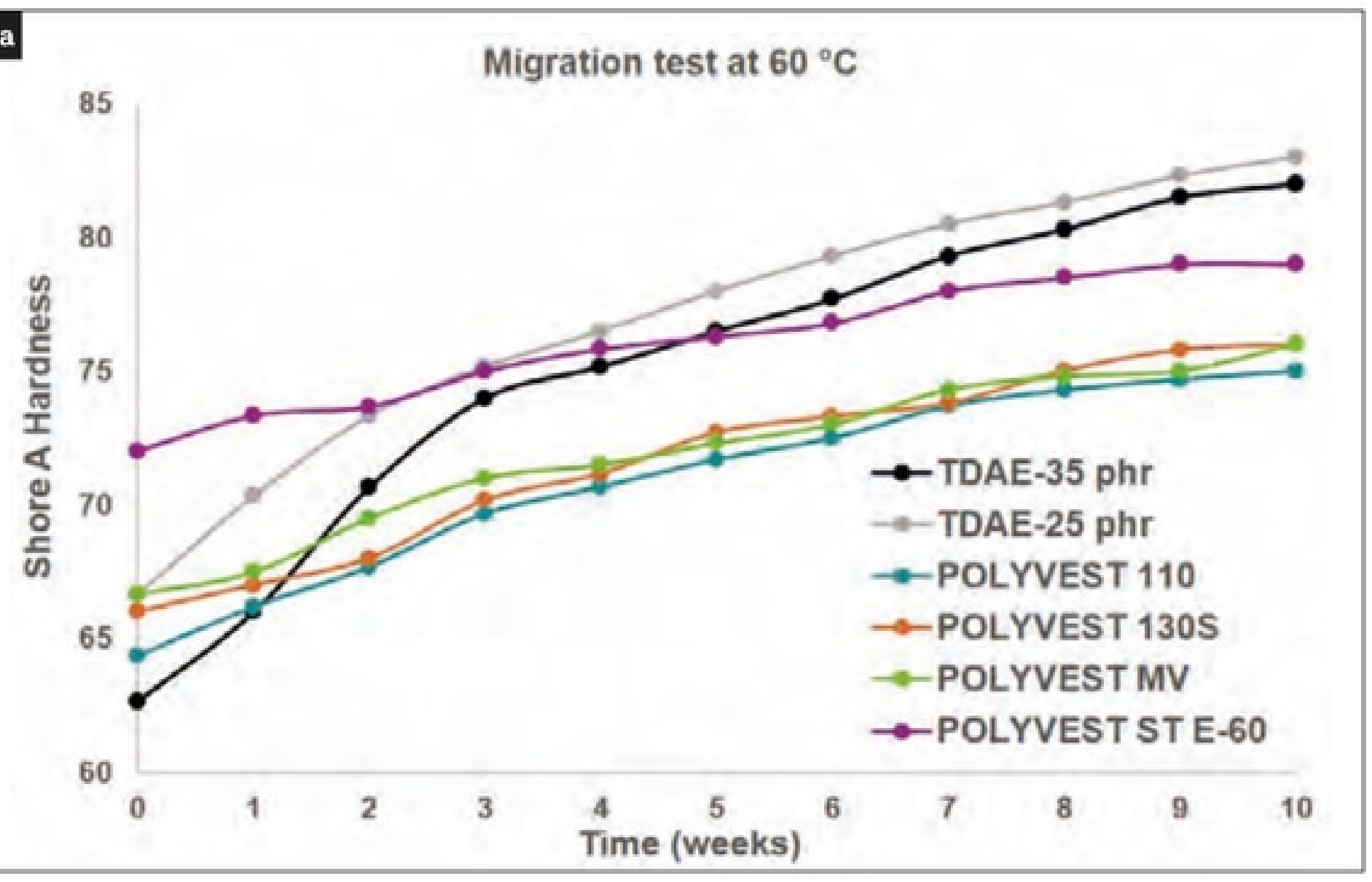

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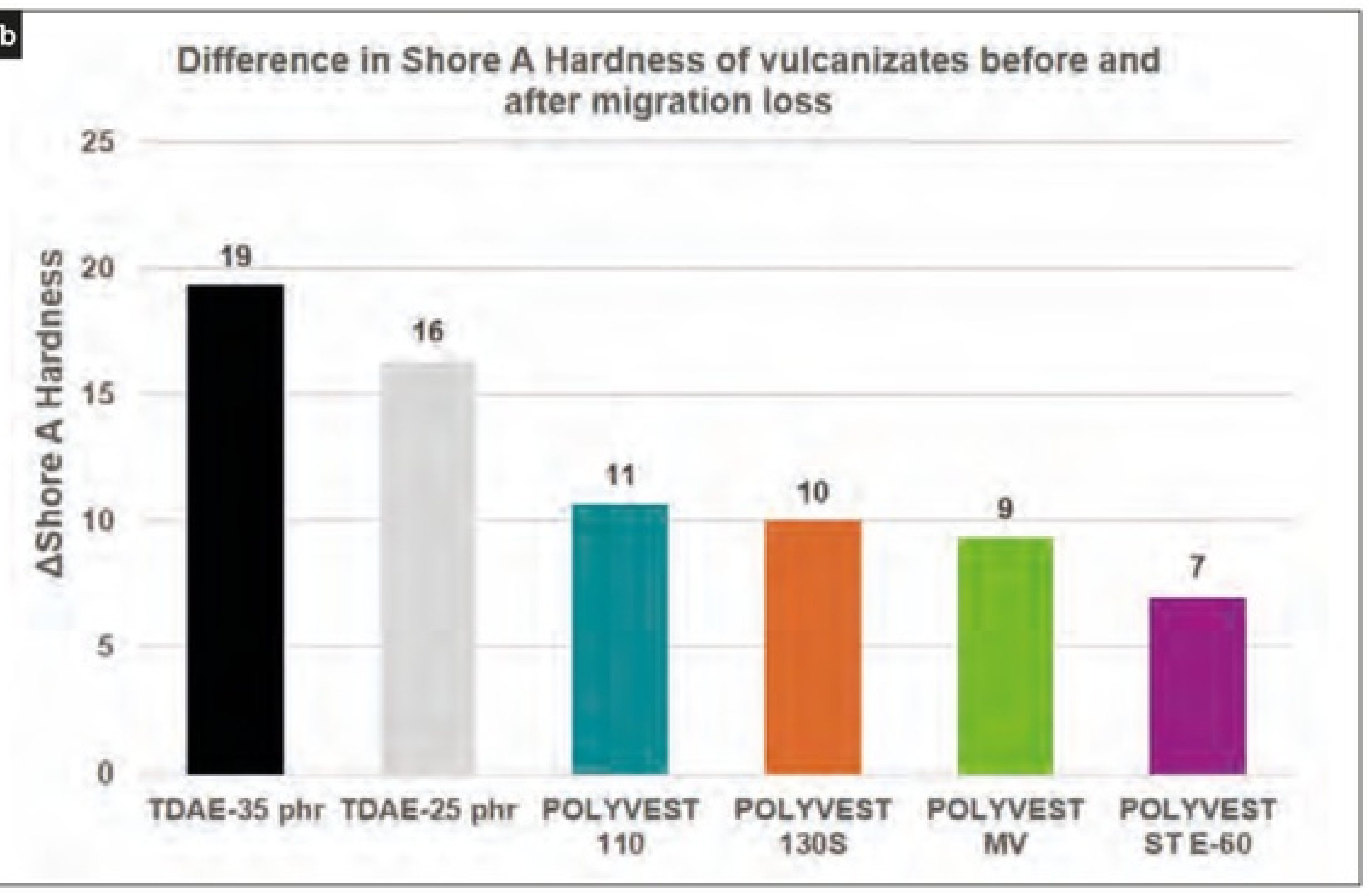

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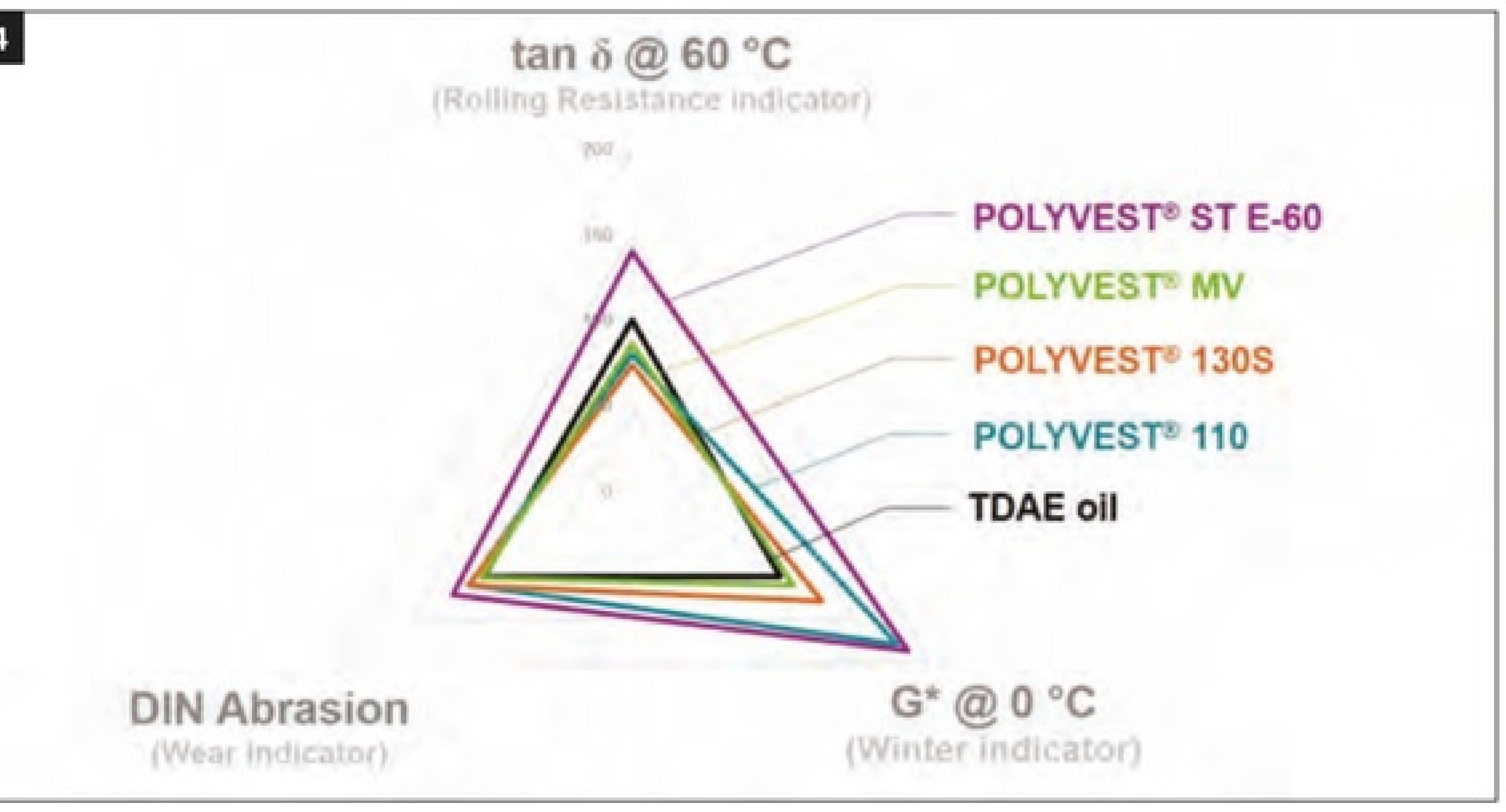

Figure 3a: Shore A hardness measured during migration test

Figure 3b: ΔShore A hardness (change in Shore A hardness = Shore A hardness at 10th week minus Shore A hardness at start)

Figure 4: Performance indicators enhancement by using various Polyvest grades

the magic triangle performance indicators as depicted in Figure 4. Polyvest 110 and Polyvest 130 S grades are suitable for abrasion resistance and winter performance enhancement. Polyvest MV with high Tg is mostly suitable for achieving performances equivalent to the TDAE system. Polyvest ST-E 60 is most favorable for achieving excellent rolling resistance, winter performance and abrasion resistance.

Summary

This study reveals that the migration behavior of plasticizers is dependent on various parameters, including concentration of plasticizer (35.0phr versus 25.0phr of TDAE); molecular weight of plasticizers (TDAE versus all Polyvest grades); microstructure of plasticizer and the respective compatibility with main polymer matrices (Polyvest 110, 130 S versus Polyvest MV); and the reactivity of the plasticizer to silica/silane/polymer (Polyvest ST-E 60 versus TDAE, non-functionalized Polyvest). The magic triangle performances of tire treads can be extended further by the addition of Polyvest. **tire**

Table 2b: Mixing procedure

First stage		GK 1.5 E, fill factor 0.66, 65rpm, chamber temperature 70°C
		Batch temperature 140-155°C
1	0.0-0.5′	Polymer, TDAE/Polyvest (5phr)
2	0.5-1.0′	TDAE/Polyvest (5phr)
3	1.0-2.0′	1/2 silica, silane, ZnO, stearic acid, TDAE/Polyvest (5phr)
4	2.0-2.0′	Clean
5	2.0-3.0′	a) Add CB, 1/2 silica, TDAE/Polyvest (5phr)
		b) Add remaining chemicals
6	3.0-7.0′	TDAE/Polyvest (5phr)
		Mix and keep temperature at 140-155°C by adjusting rpm
		Dump, check weight
		Mill temperature 60°C, front speed 25rpm, rear speed 18rpm
		45 seconds on open mill (4mm nip), sheet out
		Weigh compound for second stage, storage 24 hours at 23°C
Second stage		GK 1.5 E, fill factor 0.63, 70rpm, chamber temperature 75°C
		Batch temperature 140-155°C
1	0.0-1.0′	Batch stage 1 plasticize
2	1.0-3.0′	Add DPG-80, mix and keep temperature at 140-155°C by adjusting rpm
3	3.0-3.0′	Dump, check weight
		Mill temperature 60°C, front speed 25rpm, rear speed 18rpm
		45 seconds on open mill (4mm nip), sheet out
		Weigh compound for third stage, storage 4-24 hours at 23°C
Third stage		GK 1.5 E, fill factor 0.60, 55rpm, chamber temperature 50°C
		Batch temperature 90-110°C
1	0.0-2.0′	Batch stage 2, add accelerators, sulfur
2	2.0-2.0′	Dump batch and process on mill
		Mill temperature 80°C, front speed 16rpm, rear speed 11.5rpm
		20 seconds with 3-4mm nip
		Cut 3 x left, 3 x right with 3mm nip
		Roll up and pass through a 3mm nip three times, sheet off 5-6mm