



Wet Friction of Rubbers Containing DAE or TDAE Process Oil in ESBR and ESBR/BR Blends

Iman Abbasi Shahdehi, Mohammad Alimardani,* and Hossein Roshanaei

The inevitable need to replace conventional high aromatic process oils with new safe ones has made it critically important to investigate the extent of tire wet grip modification by process oils' aromatic content. Here, direct measurement of wet friction is conducted on emulsion styrene butadiene rubber (ESBR) and ESBR/butadiene rubber (BR) rubber blends containing either safe treated distillate aromatic extract (TDAE) or the conventional distillate aromatic extract (DAE) oils. Interestingly, the results reveal that the wet coefficient of friction for rubbers with TDAE is comparable or even better than rubbers with the DAE. This stands in contrast with previous predictions founded on indirect methods such as the values of loss factor $\tan \delta$ at 0°C. Analysis of temperature dependent dynamic properties exhibits similar values of $\tan \delta$ at 0°C for two oil types; however, a higher level of loss tangent for TDAE is found near the glass transition temperature. It is hypothesized that the frequency of loading imposed by the microtexture of the concrete counterface may have dictated the temperature range in which the TDAE can surpass the DAE in terms of the wet grip performance. The difference in the wet grip of rubbers having two oils is more pronounced for the ESBR/BR blend system.

lower T_g could expectedly decrease both the compound glass transition temperature and the viscoelastic energy dissipation, which is good for rolling resistance but is undesirable for frictional properties. As the glass transition temperature of all safe oils is lower than conventional high aromatic oils (i.e., $T_{g,DAE}$: -34°C to -38°C, $T_{g,MES}$: -57°C to -63°C, $T_{g,TDAE}$: -44- to -50°C, heavy naphthenic: -42°C to -48°C),^[6] it is reasonably expected that wet the grip is jeopardized at the presence of safe oils. Keeping it in mind, Bowman et al. employed an "iso- T_g " concept and developed a type of ESBR having styrene content higher than the commercial grades, which could present a higher compensating T_g when it is utilized in formulations containing mildly extracted solvate (MES) or treated distillate aromatic extract (TDAE) oils.^[7] Other researchers prefer to compare the values of loss tangent at the common temperature of "zero" to find out the desired oil in terms of the frictional properties.^[8-10] However, it must not be forgotten that choosing the temperature of zero as a point of comparison is based on several assumptions

1. Introduction

Environmental regulations banning the use of process oils with high levels of polycyclic aromatic hydrocarbons have made it critically important to thoroughly investigate the impact of new safe process oils on frictional properties of tire tread.^[1,2] The "magic triangle" properties of a tire tread (rolling resistance, frictional properties, and the wear resistance) could be roughly related to the glass transition temperature (T_g) of the tread compound.^[3,4] Therefore, rubber process oils can alter the tire performance by changing the glass transition temperature of the tread compound.^[5] Oils with

that have to be preliminarily met. It is generally accepted that bulk hysteretic energy dissipation under dynamic high-frequency deformations is responsible for wet-sliding friction. On a road surface with asperities of length scales between 1 μm and 1 mm a car tire with a sliding speed of 10–100 km h⁻¹ may be subjected to dynamic deformations at the frequency of 10³ and 10⁷ Hz.^[11,12] Employing the time-temperature superposition principle (William, Landel, and Ferry [WLF]), the performance of a tire operating at a temperature of about 40°C and on the average loading frequency of 10⁵ Hz could be correlated to the loss tangent from dynamic viscoelasticity measurements at the frequency of about 10 Hz and the temperature of 0°C.^[11,13] It is therefore said that a tread compound with preferred wet grip properties must have a pronounced dissipative potential at temperatures close to 0°C.^[14] While there are reports exhibiting a lower loss tangent and a lower wet grip for safe oils such as TDAE, Null argued that the wet grip performance indicated by the $\tan \delta$ at 0°C is only slightly poorer for MES and TDAE oil contained rubbers and that with some modifications in tire formulations, the desired wet grip and wet brake performance of tires could be reachable by noncarcinogenic oils.^[10] Elsewhere, it has been claimed that for natural rubber, the compounds plasticized with noncarcinogenic oils possess a slightly higher loss factor at 0°C than those plasticized

I. Abbasi Shahdehi, M. Alimardani
Polymer Engineering Department
Tarbiat Modares University
14115-114, Tehran Iran
E-mail: M.Alimardani@modares.ac.ir

H. Roshanaei
Department of Research and Development
Iran Yasa Tire and Rubber Company
13185-1753, Tehran Iran

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/masy.202200010>

DOI: 10.1002/masy.202200010

Table 1. Recipe utilized for the preparation of rubber compounds.

	Rubber	CB	ZnO	StA	IPPD*	DAE/TDAE	CBS*	MBTS*	Sulfur
ESBR	100	80	3	2	2.4	30	1.4	0.2	1.7
ESBR/BR	100 (50/50)	80	3	2	2.4	30	1.4	0.2	1.7

Parts per hundred rubber (phr). BR, butadiene rubber; CBS, *n*-cyclohexyl-2-benzothiazole sulfonamide; DAE, distillate aromatic extract; ESBR, emulsion styrene butadiene rubber; IPPD, *N*-isopropyl-*N'*-phenyl-1,4-phenylenediamine; MBTS, 2,2'-dibenzothiazyl disulfide; TDAE, treated distillate aromatic extract.

with the DAE, signifying greater traction and wet grip for these vulcanizates.^[15]

It is concluded that within the literature, a lack of consensus over the role of the aromatic content of the process oils on frictional properties of tire tread can be felt. The validity of previous estimations made by indirect methods such as analysis of dynamic mechanical behavior is here explored by using a direct frictional tester. Two rubber systems including a carbon black filled ESBR and an ESBR/BR blend were chosen to evaluate the generality of findings. Also, physico-mechanical tests from hardness to oil-rubber compatibility and work of adhesion are adopted to find the roots behind the friction modification by oil type.

2. Experimental Section

Emulsion styrene-butadiene rubber ESBR 1502 was supplied by Takht Jamshid Petrochemical Company. The oil DAE 290 was received from Behran Oil Company (Iran) and the TDAE grade EXTENSOIL 1721 was obtained from Repsol (Spain). The carbon black was N330 type. Other materials were of high purity grades. An ESBR or an ESBR/BR based tread formulation filled with 80 phr of carbon black was chosen to prepare compounds having 30 phr of DAE or TDAE (Table 1). The mixing of the two rubber systems was similar and it was performed in two steps. First, the polymer (ESBR or ESBR/BR) was added to a lab-scale Banbury (capacity 1600 cc) and it was allowed to be softened for 1.5 min at 70°C under the rotor speed of 70 rpm. Then, all materials except the curing system were incorporated and the mixing was continued for 7 min. Subsequently, the master compound was transferred to a two-roll mill and the curing system was added. The samples were finally cured using a hot press at a temperature of 160°C and under a pressure of 345 bar. Precise control over the whole mixing process was taken into consideration to guarantee the reliability and reproducibility necessary for successful tracking of the oil impacts on the vulcanizate properties.

Dynamic mechanical thermal analysis (DMTA) was performed on DMA 8000 Perkin Elmer by a temperature sweep of composites at tension mode under a frequency of 1 Hz and a strain amplitude of 0.4%. The temperature range of the test was from -100°C to 100°C, where the results from -100°C to 0°C have been selected for precise analysis of the rubber pairs.

A frictional tester previously designed in the lab was employed to measure the coefficient of friction. It was a type of "ring on plate" type instrument working at room temperature and under a normal load of 30 kg and an angular velocity of 300 rpm (equivalent to a linear sliding velocity of $(0.0967 \text{ m s}^{-1})$).^[16] The ring has inner and outer diameters of 24.7 and 30.7 mm, respectively, and a contact surface area of 260.93 mm².

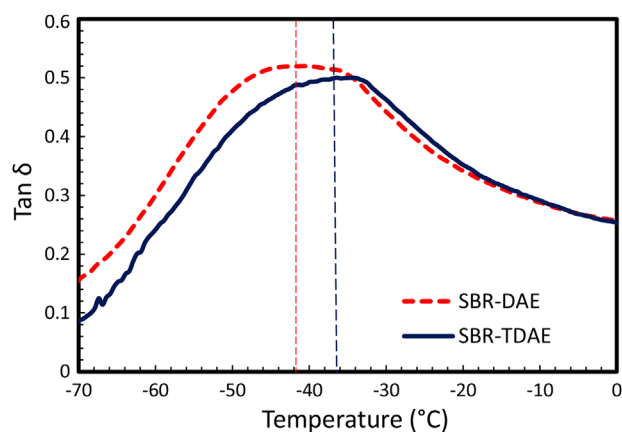


Figure 1. Variation of loss tangent versus temperature for ESBR having 30 phr of DAE or TDAE; index lines show the position of the glass transition temperature. DAE, distillate aromatic extract; ESBR, emulsion styrene butadiene rubber; TDAE, treated distillate aromatic extract.

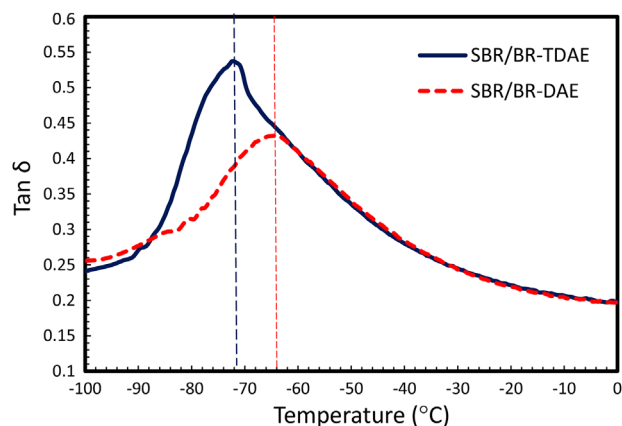


Figure 2. Variation of loss tangent versus temperature for ESBR/BR blends having 30 phr of DAE and TDAE; index lines show the position of the glass transition temperature. BR, butadiene rubber; DAE, distillate aromatic extract; ESBR, emulsion styrene butadiene rubber; TDAE, treated distillate aromatic extract.

3. Results and Discussion

Temperature dependency of loss factor for ESBR and ESBR/BR blends containing 80 phr of carbon black and 30 phr of either DAE or TDAE have been presented in Figures 1 and 2. For ESBR compounds it is observed that the TDAE has a lower loss factor both at low and high-temperature ranges. There is an intermediate region, however, between temperatures -38°C to -23°C where rubber with TDAE exhibits a higher amount of energy dis-

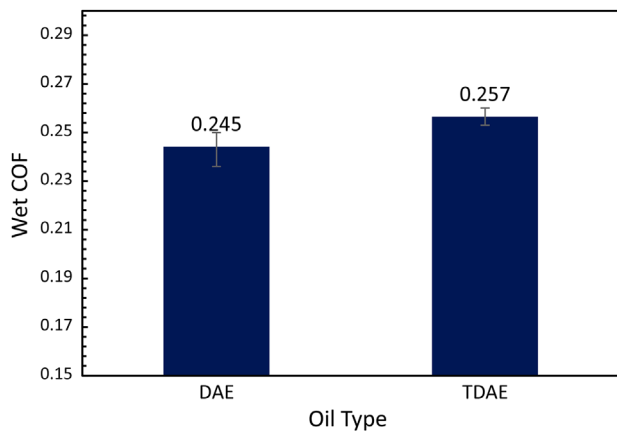


Figure 3. The wet coefficient of friction for ESBR having 30 phr of DAE and TDAE. DAE, distillate aromatic extract; ESBR, emulsion styrene butadiene rubber; TDAE, treated distillate aromatic extract.

sipation than DAE. Interestingly, TDAE rubber here has a higher T_g than DAE. This finding which was reproducible was not initially expected because the TDAE oil had a lower T_g than the DAE. It is presumed that this increase in T_g is a result of better filler dispersion and a higher amount of rubbers with restricted mobility that has shifted the rubber glass transition temperature to a level that has hidden the role played by the initial oil T_g . For a 50/50 blend of ESBR/BR, it is immediately seen that the glass transition temperature of the rubber is moved dramatically to the lower temperatures because of the presence of polybutadiene with $T_g = -100^\circ\text{C}$. As illustrated in Figure 2, the difference between the glass transition temperature of rubbers with DAE and TDAE is -63.5°C and -73°C , respectively, which is more pronounced than that observed for ESBR. It is also interesting to note that the peak of loss factor which is associated with the glass transition temperature is here higher for the TDAE rubber. It indicates that the influence of oils on various rubber matrices is unique and therefore the glass transition temperature cannot be simply judged by considering the T_g of rubber and the T_g of oil. More importantly, prediction of wet grip performance by mere knowledge of the T_g of initial oils is strongly criticized. A higher amount of energy dissipation around the glass transition temperature of the rubber blend is also exhibited. Both two graphs represent very similar energy dissipation characteristics at the temperature of 0°C .

Values of wet coefficient of friction for ESBR and ESBR/BR rubber blends have also been demonstrated in Figures 3 and 4. The wet coefficient of friction is measured on a concrete counterface where a soap solution (2%) is constantly injected into the rubber–concrete interface. Under these circumstances, the friction is almost of the hysteretic (dissipation) type, and the contribution of adhesion friction is minor. It is evident that samples with TDAE have a comparable or even higher coefficient of friction for both the ESBR and the ESBR/BR blends. The superiority of TDAE in wet grip is however more significant for the blend system. Again, the experiment has been repeated several times to ensure the reproducibility of the results. Although there are regions below the temperature of 0°C where loss tangent is higher for TDAE, it is difficult to allocate a specific temperature range in

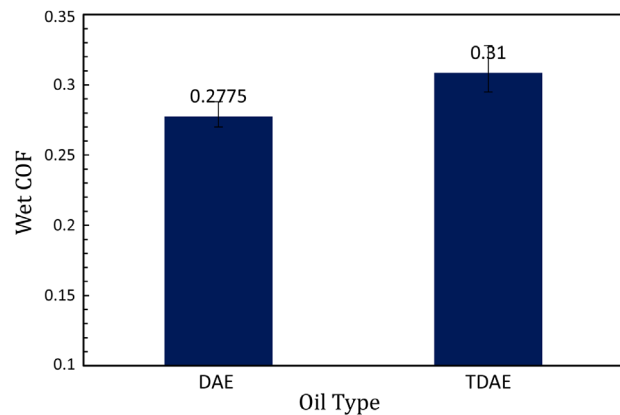


Figure 4. The wet coefficient of friction for ESBR/BR blends having 30 phr of DAE and TDAE. BR, butadiene rubber; DAE, distillate aromatic extract; ESBR, emulsion styrene butadiene rubber; TDAE, treated distillate aromatic extract.

Table 2. Physicochemical parameters related to the adhesion friction for the SBR and SBR/BR rubber systems, hardness values are average among several replicates.

Samples	Work of adhesion [mJ m ⁻²]	Hardness (shore A)	δt SBR/BR@25°C
ESBR/BR-DAE	60.29	64 ± 1	1.39
ESBR/BR-TDAE	68.09	61 ± 1	1.55
ESBR-DAE	59.93	63 ± 1	1.37
ESBR-TDAE	74.09	59 ± 1	1.53

BR, butadiene rubber; DAE, distillate aromatic extract; ESBR, emulsion styrene butadiene rubber; SBR, styrene butadiene rubber; TDAE, treated distillate aromatic extract.

dynamic tests to explain the observed frictional test, and further investigation is still required. One point to consider is the role played by the microtexture of the concrete counterface. It seems that there are asperities on the concrete counterface at the micron and submicron scales where applying the time–temperature superposition (as done in the introduction part) would result in temperatures much below 0°C in the dynamic experiment. This point of comparison that is obtained by applying the WLF equation is certainly affected by the glass transition temperature of rubbers, and therefore it is logical to have dissimilar temperature regions for ESBR and ESBR/BR blends.

The presence of a soap solution at the rubber–concrete interface and operating the test at a very high sliding speed can fully activate the hysteresis contribution of friction and completely eliminate the adhesion term of friction. However, as the sliding speed in the current test experiment is not at the maximum possible rate because of the instrumental limitations, one may imagine that the adhesion term of friction is slightly contributing to the total friction force. This may be another reason for the discrepancy between the prediction in graphs of Figures 1 and 2, and the field results reported in graphs of Figures 3 and 4. Table 2 summarizes the physicochemical parameters that routinely dictate the rubber adhesion friction. This includes the work of adhesion as a measure of interaction between the concrete and rubber, the rubber hardness which defines the deformability of rubber



and the amount of true area of contact under the applied load, and the oil-rubber compatibility which quantifies the possibility of oil leakage from the bulk rubber to the rubber–concrete counterface. Work of adhesion was measured using the available well-defined formulas.^[17] The compatibility has been assessed by calculating the difference between the solubility parameter of the oil and rubber where a lower value means a higher degree of compatibility.^[18] It can be seen that the parameters of work of adhesion and hardness are in favor of TDAE, but the oil-rubber compatibility index is in favor of DAE (i.e., it is lower for DAE). This scenario holds for both the ESBR case and the ESBR/BR blend system. As the topic of compatibility is prominent only at long times, one may consider a better adhesion friction performance for TDAE than DAE.

Conclusion

Direct measurement of friction on rubber compounds having either DAE or TDAE was conducted for the first time to understand whether or not the use of safe aromatic oils could jeopardize the wet grip performance of the tire tread compound. Under the experimental situation studied, no loss in frictional properties was found for rubber with safe TDAE oil. Even, the average values of coefficient of friction for rubbers with TDAE were higher than the counterparts with DAE. Also, no concrete correlation between the loss tangent at 0°C and the values of frictional properties was found. It was concluded that the routine use of loss tangent value at the temperature of 0°C as a point of comparison for wet grip performance must be done with caution as it is an estimate that may come true if several presumptions are preliminarily met.

Acknowledgements

The authors would like to express their gratitude to Tarbiat Modares University and Iran Yasa Tire and Rubber Company for their contribution to the financial support of the work.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

coefficient of friction, DAE oil, TDAE oil, tire tread rubber, wet grip

Received: January 5, 2022

Revised: March 23, 2022

- [1] C. Bergmann, J. Trimbach, M. Haase-Held, *KGK Kautsch. Gummi Kunstst.* **2011**, *64*, 24.
- [2] M. Weydert, G. M. V. Thielen, Pneumatic tire having a component containing low PCA oil, in, Google Patents, **2007**.
- [3] B. Rodgers, *Rubber Compounding: Chemistry and Applications*, CRC Press, **2004**.
- [4] S. K. Henning, M. Weydert, G. M. V. Thielen, E. L. Johnson, M. L. Kerns, Oil extended rubber and composition containing low PCA oil, in, Google Patents, **2005**.
- [5] G. Heinrich, *Physics of Polymer Networks*, Springer, **1992**, pp. 16–26.
- [6] A. Petchkaew, *Implications of Non-carcinogenic Pah-free Extender Oils in Natural Rubber Based Tire Compounds*, University of Twente, **2015**.
- [7] L. Dai, M. Chi, H. Gao, J. Sun, *Shock Vibrat.* **2020**, *2020*, 8814332.
- [8] A. Kuta, Z. Hrdlicka, J. Voldanova, J. Brejcha, J. Pokorny, J. Plitz, *KGK Kautsch. Gummi Kunstst.* **2010**, *63*, 120.
- [9] G. Liu, J. Cong, P. Wang, S. Du, L. Wang, R. Chen, *Constr. Build. Mater.* **2022**, 316.
- [10] V. Null, *KGK Kautsch. Gummi Kunstst.* **1999**, *52*, 6.
- [11] X. D. Pan, E. D. Kelley, M. W. Hayes, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 757.
- [12] X.-D. Pan, *Wear* **2007**, *262*, 707.
- [13] H. Takino, R. Nakayama, Y. Yamada, S. Kohjiya, T. Matsuo, *Rubber Chem. Technol.* **1997**, *70*, 584.
- [14] A. L. Gal, L. Guy, G. Orange, Y. Bomal, M. Klüppel, *Wear* **2008**, *264*, 606.
- [15] Y. Chokanandsombat, C. Sirisinha, *Polym. Polym. Compos.* **2014**, *22*, 599.
- [16] M. R. Kashani, E. Behazin, A. Fakhar, *Polym. Test.* **2011**, *30*, 271.
- [17] B. Natarajan, Y. Li, H. Deng, L. C. Brinson, L. S. Schadler, *Macromolecules* **2013**, *46*, 2833.
- [18] S. L'Heveder, F. Sportelli, N. Isitman, *Plast. Rubber Compos.* **2016**, *45*, 319.