ADHESION AND HYSTERETIC FRICTION OF TIRE TREAD RUBBERS HAVING PROCESS OILS WITH DIFFERENT AROMATIC CONTENT

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ABSTRACT

The extent of modification of wet grip of tire tread rubber by safe aromatic process oils has been the subject of controversy, as this property has conventionally been judged by indirect methods such as the loss factor at 0 °C. The present work aims to directly measure the dry and wet frictional behavior of rubbers containing various loadings of distillate aromatic extract (DAE) or treated distillate aromatic extract (TDAE) and to elucidate the contributions resulting from the adhesion and the hysteretic terms of friction. Physico-mechanical tests including rubber hardness, rubber–substrate work of adhesion, rubber–oil compatibility, hysteretic properties, and the rubber glass transition temperature were evaluated to disclose the underlying friction mechanisms. Interestingly, TDAE-containing rubbers presented a comparable or even better hysteretic friction not only at low oil loadings but also at high oil levels. As the loss factor properties of DAE and TDAE are very close to each other and there is the possibility of a crossover point within the frictional zone, care must be exercised not to merely rely on the values of tanδ at 0 °C in judging the preference of DAE or TDAE with regard to the wet grip performance. [doi:10.5254/rct.22.77937]

INTRODUCTION

The special type of aromatic oils known as distillate aromatic extract (DAE) has been used as the conventional process oil for styrene–butadiene rubber (SBR)–based tire tread compounds.[1] When a tire is abraded, polycyclic aromatic (PCA) components of the DAE oil with the proven carcinogenic effects can be readily released to the environment through wear debris. Having a wear rate between 0.006 and 0.09 g·km^{-1},[2] a passenger tire, by the end of its life, may lose up to 2 kg and a truck tire up to 12 kg of its mass by abrasion.[3] Considering that the aromatic oils constitute 15% to 20% of the total tread wear debris and that the third portion of DAE oil is of the PCA type, the significance of the amount of PCA components released to the environment should be better clarified.[4] In one domestic case, pollution of Anzali wetland by PCA materials was verified, and the analysis of chemical fingerprinting showed that the pollution mostly originated from tire debris.[5] Owing to the international regulations limiting the use of DAE, attention has been drawn to alternative safe oils with mineral or bio-based origins.[6,7] Safe mineral alternatives such as treated distillate aromatic extracts (TDAE), mildly extracted solvates (MES), residual aromatic extracts (RAE), and naphthenic oils can all meet the environmental concerns. Nevertheless, for a tread application in which several conflicting properties such as wet grip, abrasion resistance, and rolling resistance must be simultaneously satisfied, finding the best safe oils to replace DAE has always been a matter of debate.[8] Based on technical data, TDAE is the best alternative to DAE, followed by MES and naphthenic oils.[6] Silica technology[9] and the use of safe oils in tire tread are important elements in future green tires.

It has been generally accepted that bulk hysteretic energy dissipation under dynamic deformation of high frequency 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 to 100 km/h is assumed to be subjected to dynamic deformations at a frequency of 10^3 and 10^7 Hz.[10,11]

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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 an average loading frequency of 10^5 could be correlated to the loss factor from dynamic viscoelasticity measurements at a frequency of about 10 Hz and a specific low temperature of 0 °C.[10,12] A tread compound with optimized wet grip properties must have a pronounced dissipative potential in the high-frequency region (kilohertz to megahertz) or equivalently around the temperature of 0 °C in normal dynamic testing.[13] The wet grip performance of tire treads with safe oils has been conventionally judged by the values of loss factor ($\tan\delta$) at zero temperature, and a lower amount of wet grip has been assumed for replacing DAE with the safe oils.[14–16] The effect of oils on the glass transition temperature of rubbers has also been considered as another criterion for discussing the wet grip performance of oil-contained rubbers. It is often said that the lower the T_g of oil, the lower the compound T_g and the lower the expected hysteresis and wet grip of rubbers.[17] Assuming a simple rule of mixture, the Fox equation calculates the combinatory T_g of a mixture of oil and rubber.[18–21] As the glass transition temperature of all safe oils is lower than conventional high aromatic oils ($T_{g\ DAE}$: −34 to −38 °C, $T_{g\ MES}$: −57 to −63 °C, $T_{g\ TDAE}$: −44 to −50° C, heavy naphthenic: −42 to −48 °C),[22] it is simply expected that wet grip is jeopardized in the presence of safe oils. Consequently, in the literature, attempts have been made to compensate for such a decline in the T_g of rubbers with safe oils by modifying the microstructure of the rubber in its chain backbone. In a patent by Weydert from Goodyear, an SBR with higher styrene content was used in cases of oils with lower T_g, such as TDAE.[23] Likewise, Bowman et al.[24] introduced the idea of "iso-T_g" and used high styrenic SBR when using MES oil. Nevertheless, it is not possible to reach a consensus over the jeopardized wet grip of rubbers with safe oils. Null[16] 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 expected wet grip and wet brake performance could be met with noncarcinogenic oils. Elsewhere, it has been claimed that for natural rubber, compounds plasticized with noncarcinogenic oils possess a slightly higher (not lower) loss factor at 0 °C than those plasticized with the DAE, signifying greater traction and wet grip for the vulcanizates.[8]

To our knowledge, the literature data on the wet grip performance of rubbers with safe oils have been merely founded on its correlation with the loss factor at low temperatures. It is shown that the friction of elastomers in engineering practices cannot be readily predicted by the loss tangent at 0 °C because the assumptions behind this correlation are not always met. Thus, full-scale friction tests, although time and money consuming, are the only acceptable method in many cases.[25] Rubber friction under dry and wet conditions is different from other solid frictions by having a coefficient of friction (COF) that is dependent on the applied load, sliding velocity and temperature, micro- and macrotexture of the substrate, and so forth.[26–29] Along with the hysteretic contributions of friction, which is dominant at high sliding velocity and on the rough substrate, it must not be forgotten that the role of adhesion friction, which is related to the amount of intermolecular interaction between the rubber and a substrate, is dominant at smooth contact under clean and dry conditions.[30–34] It is the aim of present contribution to determine the extent to which the adhesion and hysteretic frictional properties are influenced by the replacing DAE with TDAE. By evaluating the physico-mechanical properties of rubbers, the mechanisms controlling the friction will be recognized and, finally, the findings will be compared with the existing knowledge on the wet grip of oil-contained rubbers.

EXPERIMENTAL

MATERIALS AND COMPOUND PREPARATION

SBR 1502 was supplied by Takht Jamshid Petrochemical Company. Oil DAE 290 was received from Behran Oil Company (Iran), and TDAE grade EXTENSOIL 1721 was obtained from

TABLE I
SBR-BASED TIRE TREAD FORMULATION HAVING VARIOUS DAE OR TDAE OIL CONTENT[a]

Material, phr	DAE 10	DAE 20	DAE 30	TDAE 10	TDAE 20	TDAE 30
SBR	100	100	100	100	100	100
CB	80	80	80	80	80	80
ZnO	3	3	3	3	3	3
StA	2	2	2	2	2	2
IPPD	2.4	2.4	2.4	2.4	2.4	2.4
DAE Oil	10	20	30	0	0	0
TDAE Oil	0	0	0	10	20	30
CBS	1.4	1.4	1.4	1.4	1.4	1.4
MBTS	0.2	0.2	0.2	0.2	0.2	0.2
Sulfur	1.7	1.7	1.7	1.7	1.7	1.7

[a] phr, parts per hundred rubber; IPPD, N-isopropyl-N′-phenyl-1,4-phenylenediamine; CBS, n-cyclohexyl-2-benzothiazole sulfenamide; MBTS, 2,2′ dibenzothiazyl disulfide.

Repsol (Spain). Carbon black (N330) and other materials were of high-purity grades. An SBR-based tread formulation filled with 80 phr of carbon black was chosen to prepare compounds having either DAE or TDAE in three oil levels, including 10, 20, and 30 phr (Table I). The compound was mixed in two steps. First, the SBR was added to a lab-scale Banbury (capacity 1600 cc) and allowed to be softened for 1.5 min at 70 °C under a rotor speed of 70 rpm. Then, ingredients of the so-called master compound (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 adapted to guarantee the reliability and reproducibility necessary for successful tracking of the oil's effects on the vulcanizate properties. It is also worth noting that the designations selected for the rubber samples were based on the type and amount of oil they contained.

INSTRUMENTS AND TESTS

To characterize the process oils, a number of parameters including light refractive index, viscosity, density, flash point, pour point, aniline point, PCA content, viscosity gravity constant (VGC), analysis of carbon type, and so forth were measured for the two oils, DAE and TDAE. Further details of the standard test methods used for this purpose will be given later on. In addition, differential scanning calorimetry (DSC) was employed using the instrument type Netzsch-200 F3 Maia in the range of −100 to 30 °C and under a heating rate of 10 °C/min to experimentally measure the glass transition temperature of the two oils.

Tests implemented on the oil-contained rubber composites were either frictional testing or other physico-mechanical experiments required to explain the frictional behavior, such as hardness, dynamic mechanical thermal analyses (DMTA), and scanning electron microscopy (SEM). The work of adhesion between the rubber and substrate and the amount of rubber–oil compatibility were among the indexes calculated by the available theories. Measurements of hardness were performed on 6 mm thick samples using a Bareiss tester. DMTA was performed on a DMA 8000 (PerkinElmer, Waltham, MA, USA) by a temperature sweep of composites at the single cantilever bending mode under a frequency of 1 Hz and strain amplitude of 0.4%. SEM (model TeScan Mira III) was used to examine the morphology of carbon black in the rubber matrix. This was carried out on gold-coated

TABLE II
PHYSICAL AND CHEMICAL PROPERTIES OF DAE AND TDAE OILS[a]

Property	Standard Test Method	DAE	TDAE
Refractive index (at 20 °C)	ASTM D1218	1.5784	1.5249
Viscosity at 100 °C, mm^2/s	ASTM D445	23.89	16.88
Density at 15.6 °C, g/cm^3	ASTM D1481	1.018	0.941
Density at 20 °C, g/cm^3	ASTM D1481	1.015	0.938
Flash point (open cup), °C	ASTM D92	247	275
Pour point, °C	ASTM D97	9	15
Aniline point, °C	ASTM D611	36	75
VGC	ASTM D2140	0.9624	0.8705
%C_A	ASTM D2140	43	24
%C_P	ASTM D2140	31	53
%C_N	ASTM D2140	26	23
PCA content, %	IP 346	22.32	2.95
Oil T_g (DSC), °C	—	−34	−53

[a] VGC, viscosity gravity constant; PCA, polycyclic aromatic.

cryogenically fractured surfaces of samples. To calculate the rubber–substrate work of adhesion, measuring the surface energy values of the rubber and the substrate was first required. This was carried out using the sessile drop-based method and the two-component theory of Fawkes.[35] Test liquids of distilled water (with a surface energy of $\gamma_w^d = 21.8$ mJ/m^2, $\gamma_w^p = 51$ mJ/m^2) and 1-bromonaphthalene (with a surface energy of $\gamma_{Br}^d = 44.4$ mJ/m^2, $\gamma_{Br}^p = 0$) were chosen for this purpose. The parameter of the work of adhesion (W_{12}) was subsequently calculated using Eq. 1, where γ_r^d and γ_r^p are the dispersive and polar surface energy components of rubbers and γ_s^d and γ_s^p are the similar counterparts for the substrate.

$$W_{12} = 2(\sqrt{\gamma_r^p \gamma_s^p} + \sqrt{\gamma_r^d \gamma_s^d}) \tag{1}$$

The degree of compatibility between the two materials can be predicted by calculating the level of difference between the solubility parameter of the two components. In this research, the Hoy method was used to calculate the solubility parameter of the rubber and oils.[36] For mineral oils with no single specified structure, calculating the solubility parameters of the oils is rather complex and challenging. The Hoy method, which is a theoretical method for calculating the solubility parameter, is explained in full detail elsewhere.[36] To apply this method, three simple molecules can be chosen to represent the aromatic, cycloaliphatic, and linear aliphatic proportions of the complex oil structures. Therefore, as a first step, one must analyze the carbon type of each oil based on a standard test method (i.e., ASTM D2140, as presented in Table II). Subsequently, for each representative structure, the type of chemical functional group is taken into consideration, and several thermodynamic parameters are extracted for these groups from the handbooks. After some mathematics, the solubility parameter is obtained not only in its total amount but also with the separate contributions resulting from the polar, hydrogen, and dispersive interactions.[37] The solubility parameter at an arbitrary temperature (δ_T) can be readily measured from the values in room temperature (i.e., 25 °C; δ_{298}) using Eq. 2.

$$\ln\delta_T = \ln\delta_{298} - 1.25\alpha(T - 298) \tag{2}$$

where T is the temperature (K) and α is the coefficient of the linear thermal expansion of the oils and
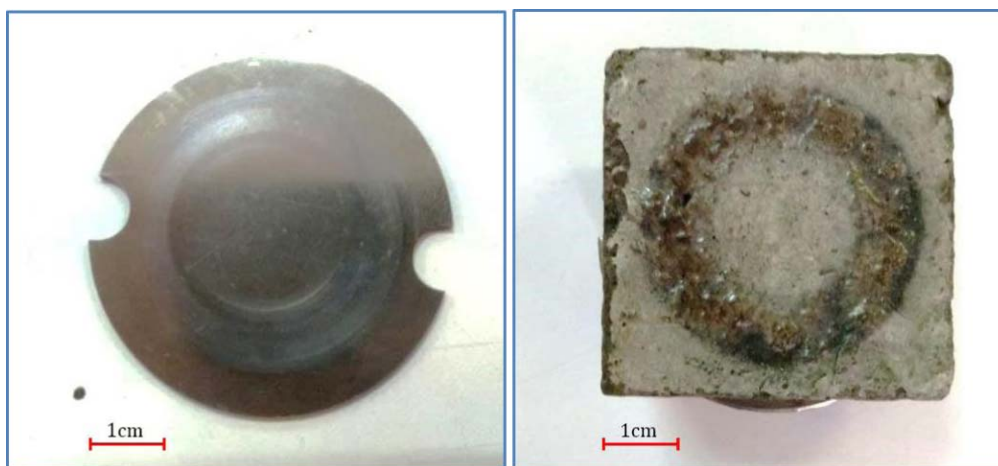
FIG. 1. — Metal (left) and concrete (right) substrate used for the friction test; the imprint of the rubber ring could be seen on the substrate plates.

rubbers. The α values for the oils were estimated from their density change in a range of 15 to 140 °C: 6.55×10^{-4} K^{-1} for DAE and 6.94×10^{-4} K^{-1} for TDAE. The linear thermal expansion coefficient of SBR was estimated to be equal to a value of 4.80×10^{-4} K^{-1}.

A frictional tester previously designed in our lab was used for the purpose of measuring the coefficient of friction. It is a "ring on plate" type instrument working at a normal load of 30 kg and an angular velocity of 300 rpm that is equivalent to a linear sliding velocity of 0.0967 m/s.[38] To differentiate between the hysteretic and adhesion terms of friction, two substrates, including metal and concrete (Figure 1), were used, and the experiment was implemented under either dry or wet conditions. The geometry of the rubber sample in the ring form for frictional testing is given in Figure 2. During the test, the temperature was kept almost constant at about 25 °C (ambient temperature). For the
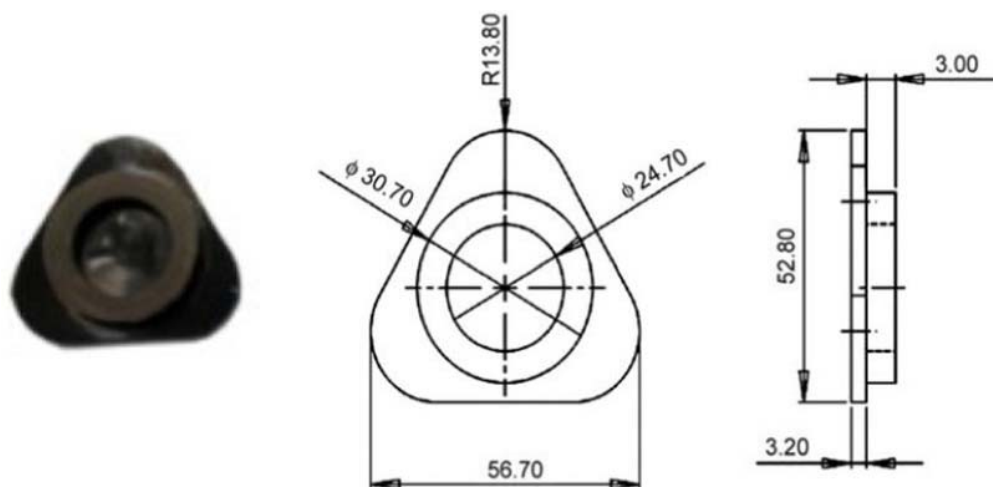

FIG. 2. — Ring form of rubber samples selected for the frictional testing (left) as well as the dimensions in millimeters (right).
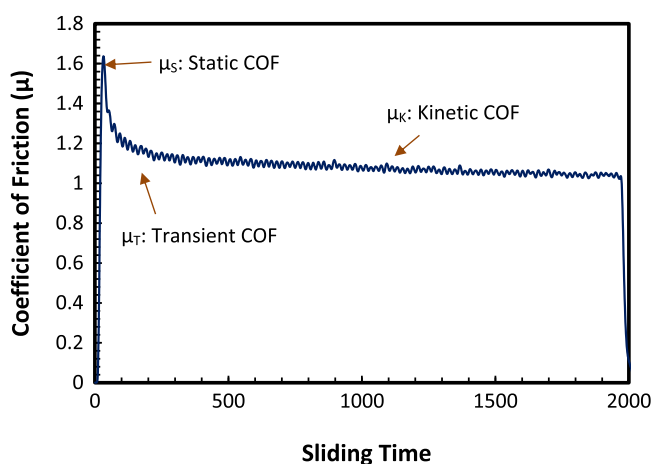
FIG. 3. — Typical graph depicting the parameters related to the coefficient of friction (COF).

latter case of wet friction testing, a 2% water/soap solution was placed at the interface of the rubber and substrate prior to testing. The best condition for the adhesion friction is achieved with a dry contact with the metal substrate and for the hysteretic friction, with wet contact with the concrete substrate. A typical graph of the frictional testing used to measure the static and kinetic coefficient of friction (hereafter COF) is displayed in Figure 3. The static friction coefficient is recorded from the peak value, and the kinetic friction coefficient is calculated by averaging the values in the plateau range of the curve.

RESULTS AND DISCUSSION

OIL CHARACTERIZATION

The physical and chemical attributes of the DAE and TDAE oils were determined as shown in Table II. The difference in the aromatic contents of the two oils was well reflected in all the tests, and the values were in the typical range. For instance, the aniline point, which is the temperature at which a mixture of aniline and oil form a single-phase mixture, exhibited higher values for TDAE (with less aromatic content) and lower values for DAE (with high aromatic content).[16] Having calculated the factors VGC and RI, the analysis of carbon type could be performed based on the instructions in ASTM D2140, and we observed that aromatic carbon in DAE and TDAE was 43% and 24%, respectively.

The percentage of PCA components was measured following the standard test method IP346, and values of 22% and 3% were obtained for DAE and TDAE, respectively. Because of the significance of oil T_g in understanding the effect of oil on rubbers, the glass transition temperature of DAE and TDAE was measured by DSC, and values of −34 °C and −53 °C were attained, respectively. The lower value of T_g for TDAE is expected to bring a lower T_g for the resulting oil-contained rubber.

RUBBER PHYSICO-CHEMICAL CHARACTERIZATIONS

Rubber Hardness. — Adhesion friction can be defined by $F_{Adhesion} = \tau \times A_{real}$, where τ denotes the level of intermolecular interactions between the two interacting surfaces in friction, and A_{real} is the true area of contact, which is inversely related to the rubber stiffness or hardness.[39] Therefore,
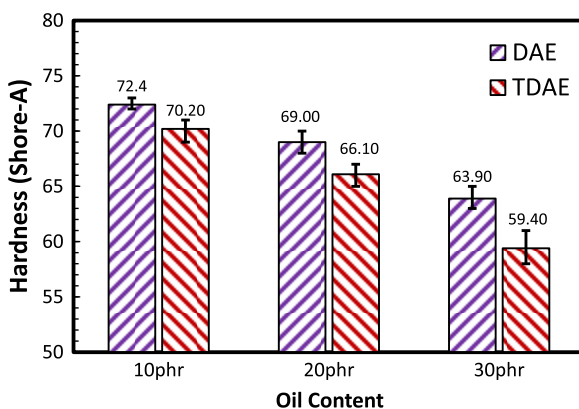
FIG. 4. — Values of hardness measured for samples containing DAE or TDAE at various oil levels.

measuring the rubber hardness is crucial in understanding the mechanisms behind the rubber friction. As illustrated in Figure 4, the hardness of the composites is expectedly decreased by increasing the oil content for both DAE and TDAE. This is in part due to the natural softening role of oils in lowering rubber intermolecular frictions and also in part due to the lower curing efficiency and crosslink density of oil-contained rubbers. Rheometric data and analysis of swelling crosslink density, which are not presented for brevity reasons, prove that the curing efficiency is lowered by increasing oil content. In addition, the state of filler dispersion and the amount of filler–polymer and filler–filler interactions may contribute to the observed hardness trend. It will be demonstrated later that for the TDAE composites, the filler–filler interaction is lower than DAE, which could also contribute to a lower hardness of the TDAE. Regardless of the reasons behind the hardness trend, what matters most for frictional points of view is that TDAE is capable of offering better adhesion friction, because of the possibility of imparting a higher true area of content. Assuming hardness is the single factor defining the friction, it is expected that increasing the oil content may augment the adhesion term of friction.

Rubber–Substrate Work of Adhesion. — The index τ ($F_{\mathrm{friction}} = \tau \times A_{\mathrm{real}}$) introduced earlier as the intermolecular interaction between the interacting bodies can be quantified by the work of adhesion. The results of the contact angles and surface energies calculated for the rubbers and the substrates are listed in Table III. Increasing oil content lowers the dispersive but augments the polar component of the surface energy of the DAE rubber series. The trend is revered for the TDAE, creating lower polar and higher dispersive components for samples with higher oil content.

The presence of heterocyclic polar compounds, generally aromatic groups that include sulfur, nitrogen, or oxygen, is principally responsible for the higher polar nature of DAE rubbers. At the same time, the polar component of surface energy for both concrete and steel is lower than the dispersive part, and it is expected that the two substrates generate more intermolecular interactions with TDAE, which also has a higher ratio of dispersive to polar surface energy. The calculated values of the work of adhesion in Figure 5 lend support to the claim. Therefore, from the perspective of work of adhesion, TDAE can be projected to have a greater τ and therefore greater adhesion friction, although, the other factor A_{real} must still be taken into account. With an increase in oil content, the superiority of TDAE is even further enlarged, for both the steel and concrete substrates, suggesting again an increasing trend for the adhesion term of friction with oil loading.

TABLE III
POLAR AND DISPERSIVE COMPONENTS OF SURFACE ENERGY FOR RUBBER SAMPLES AND FOR THE STEEL AND CONCRETE SUBSTRATES

	DAE 10	DAE 20	DAE 30	TDAE 10	TDAE 20	TDAE 30	Steel
1-Bromo naphthalene angle, °	66	72.25	73.25	61.00	48.50	46.75	30.8
Water angle, °	94	95	93	103.5	97.25	91.5	82
γ_s^d	21.97	19.02	18.06	24.47	30.68	31.52	38.36
γ_s^p	2.89	3.17	4.30	0.45	0.69	1.67	3.09
$\gamma_s^t = \gamma_s^d + \gamma_s^p$	24.85	22.19	22.36	24.92	31.38	33.19	41.45

OIL–RUBBER COMPATIBILITY

Compatibility between the oil and rubber is another factor that may influence the adhesion term of friction. Any possibility for oil bleeding from the bulk rubber to the surface that may be caused by the lack of compatibility transforms the dry friction to lubricated friction with an abrupt fall in the values of the friction coefficient. The effect is particularly prominent when the long-term performance of oils is to be tackled. Based on the difference in the solubility parameter of oil and rubber, it is anticipated (Table IV) that DAE reveals better compatibility toward SBR than TDAE, and the compatibility at room temperature is higher than the processing temperature for both cases. Generally speaking, for good compatibility, the difference between the solubility parameters of the two substances should be less than 5 $(MJ/m^3)^{1/2}$.[18] Although the two oils are rather compatible, a higher chance of oil bleeding may be devised for TDAE, which needs to be considered in describing the frictional behavior of the TDAE composites.

Rubber Viscoelastic Dissipation and T_g. — Temperature dependency of loss factor for each pair of DAE and TDAE composites is presented in Figure 6. For such properly mixed composites that have disparity in only either oil type or oil loadings, the level of difference among the dynamic behavior is expectedly minor, and therefore, to establish the discussions on a more solid and reliable base, reproducibility of the results was evaluated by repeating the test by another instrument and on other separately prepared samples. The two experiments were in principle similar but hereafter, the discussions are built only on the common aspects of the two testing trials.
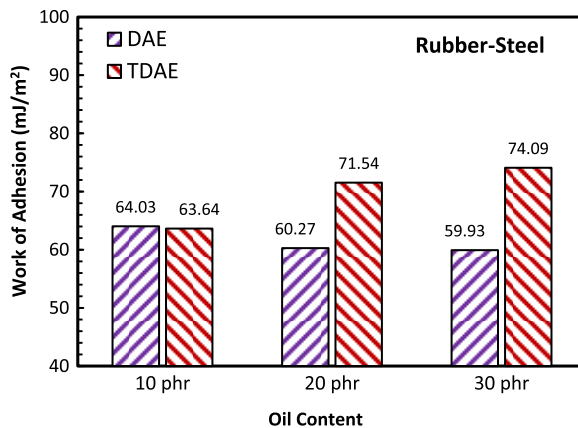

FIG. 5. — Calculated values of work of adhesion for the rubber–steel pair.

TABLE IV

VALUES OF SOLUBILITY PARAMETERS FOR THE OILS DAE AND TDAE AND FOR SBR AT AMBIENT AND PROCESSING TEMPERATURES[a]

	Temperature, °C	
Parameter and oil	25	140
δ_t in varying temperatures, $J^{1/2}/cm^{3/2}$		
DAE	17.37	15.81
TDAE	17.21	15.58
SBR	18.74	17.73
$\Delta\delta_t$ (SBR–oil)		
DAE–SBR	1.37	1.53
TDAE–SBR	1.92	2.16

[a] Difference in solubility parameter for oil–rubber pair has also been indicated.

From the loss factor at a 0 °C point of view, TDAE is expected to have a lower friction than DAE at 10 and 30 phr loading. For samples containing 30 phr of oil, which is very important in this study because of its sufficiently large oil content, there is a crossover point within the graph at the temperatures below 0 °C, where TDAE depicts a higher loss tangent over the DAE. Therefore, it is very critical to know the exact temperature that could be considered as a point of comparison for analyzing the wet grip performance. Based on the WLF, the equivalent temperature depends heavily on the texture of the counterface. If one considers the friction a result of loading by the
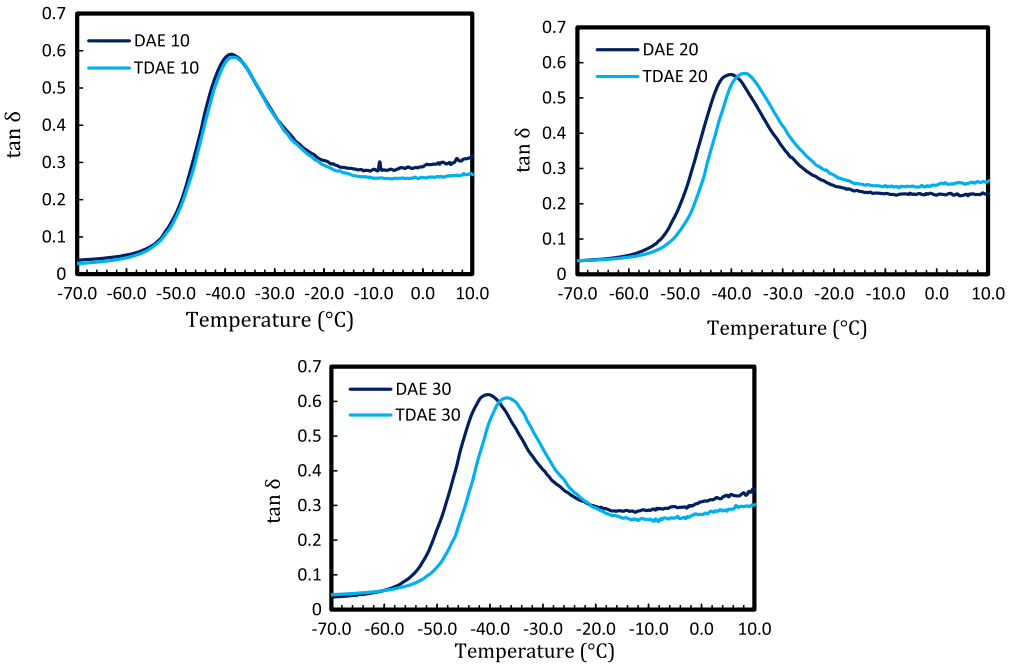

FIG. 6. — Comparing the values of loss factor measured at "single cantilever bending" mode for DAE (a) and TDAE (b) composites at various oil loadings.

macrotexture of asperities, the obtained WLF temperature will be higher, and if the microtexture is responsible for frictional dynamic loading, then the obtained WLF temperature would be much less than 0 °C. As a result, for comparing the wet grip performance of samples with close dynamic behavior, it is much more reliable to analyze the trend in a temperature zone and not a single temperature point. The width of the frictional zone also depends heavily on the operating conditions of friction. It has been said that at sufficiently high normal force or low sliding velocities, the contribution of microtexture appears to be more relevant.[13,40] Considering the sliding velocity of 96.7 mm/s of the friction test, which is a low to moderate velocity, and the intense normal pressure of 1.2 MPa, the significance of the substrate microtexture on frictional behavior cannot be neglected; therefore, it is possible that the actual friction test is correlated with the temperatures close or below the crossover point.

One of the other interesting findings of the DMTA results is the higher glass transition temperature obtained for the TDAE compounds compared with the DAE. This was completely different from expectations, because the T_g of the oil as shown in Table II was lower than DAE, and therefore, from a simple rule of mixture equation (Fox equation, for instance), it is anticipated that the compounds with TDAE present a lower T_g than those with DAE. The reproducibility and reliability of these results were verified during the two testing trials. These findings, however, question the simple belief that assumes a lower wet grip performance for TDAE-contained rubbers simply because the TDAE oil by itself has a lower glass transition temperature than the DAE oil does. A higher T_g for the TDAE compounds seems to be rooted in its filler dispersion and the role played by filler dispersion on the mobility restriction of rubber surface layers known as "shell rubber."[41] A better state of filler dispersion for TDAE brings about a higher surface area for the filler and a higher amount of shell rubber, which will be reflected by higher values of rubber T_g. This increase in T_g has been large enough to cover the effect of lower T_g of the TDAE oil. SEM and the strain-dependent dynamic test (Payne effect) were performed on TDAE and DAE samples to seek further evidence for this behavior (Figure 7). A lower amount of Payne effect is associated with more uniform dispersion and a lower amount of aggregate. From both the nonlinear test and SEM images, it can be proved that TDAE has a better state of filler dispersion compared with DAE and is therefore capable of imparting a higher glass transition temperature.

RUBBER FRICTIONAL BEHAVIOR

Adhesion Friction. — To determine the extent to which previous predictions by physico-mechanical tests are correlated with direct measurements of frictional behavior, the static and kinetic COFs of rubber composites were measured on the steel substrate. Figure 8 shows the static coefficient of the friction of rubbers on steel substrate and under dry conditions. It can be seen that TDAE has a lower COF than DAE does and that, with increasing oil loading, the COF decreases for both oils. Nevertheless, the error bar indicates that, except for 30 phr oil-loaded samples, the level of difference between DAE and TDAE is not significant or meaningful. However, as the average values in the three oil levels are lower than DAE, it is worth looking for an operating mechanism. Under the dry conditions, where the adhesion term of the friction is dominant, a small chance of the oils bleeding to the rubber surface may play a significant role in defining the COF. Because of the lower viscosity and lower rubber–oil compatibility of TDAE, a higher chance of oil penetration can be presumed for this oil type. The trend of increasing the oil content may be explained by a similar mechanism. It will be proved later that such a minor penetration can be valid only under an initial sliding motion (i.e., static condition). It must not be forgotten, however, that although the friction experiment was always conducted on clean samples that were free of contamination, there may still be a chance of oil bleeding once the two interacting surfaces are in contact under applied pressure.
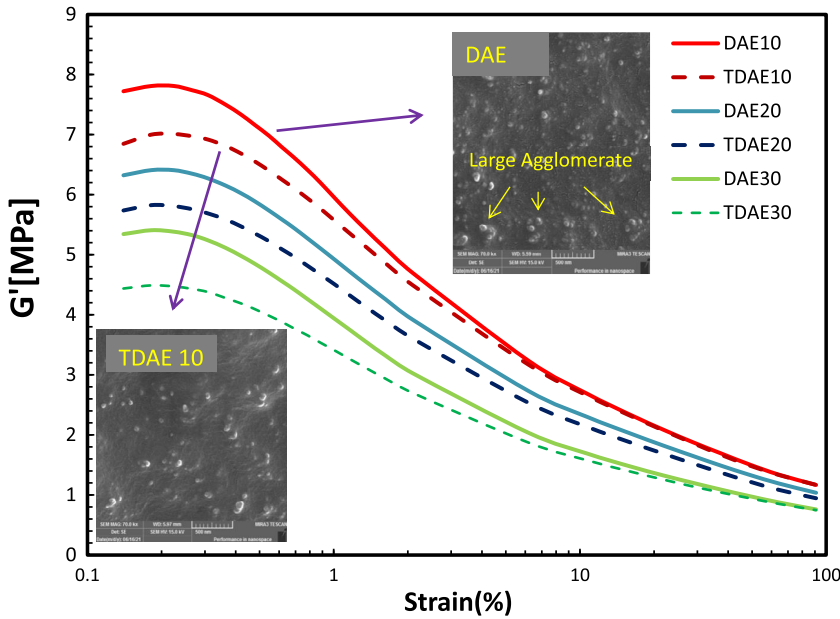
FIG. 7. — Strain dependency of storage modulus (Payne effect) for all composites and selected SEM images for DAE and TDAE samples. It is to be noted that the magnification of SEM images is 70 000, and the scale-bar represents a distance of 500 nm.

Although the static coefficient of friction clarified some of the underlying mechanisms of friction, it is the kinetic COF that is of significance for a rolling tire. The average values of COF within the plateau region of the friction curve were calculated for this purpose, as illustrated in Figure 9. With the elimination of any initial contamination of the rubber surface by oil during the sliding motion, the advantageous aspects of TDAE in terms of hardness and work of adhesion come to play their roles on the steel substrate. Therefore, the difference between the frictional properties
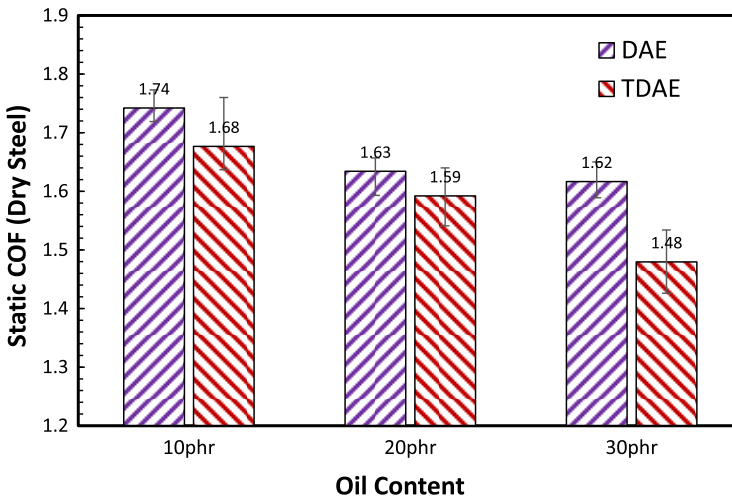

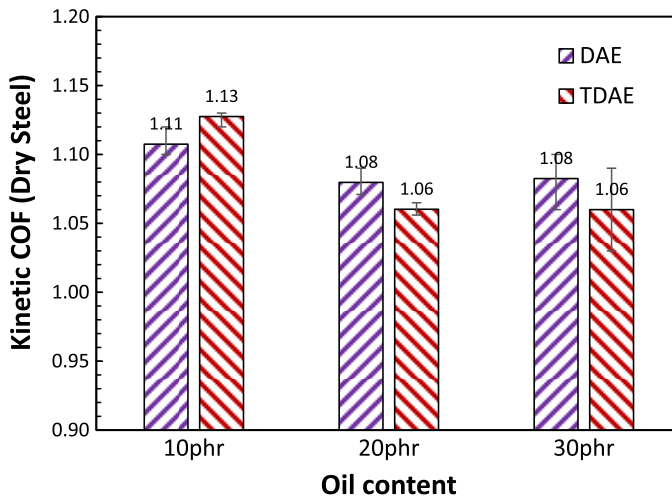FIG. 8. — Static coefficient of friction of rubbers on the steel substrate and under dry condition.

FIG. 9. — Kinetic COF of rubbers on steel substrate and under dry condition.

of the two oils is lowered, and TDAE finds a better place. At 10 phr of oil loading, the TDAE exceeds the DAE for frictional properties, but at higher oil loadings, the existing possible chance of oil bleeding has not been able to fully cover the positive aspects of the TDAE. Nevertheless, even for these highly oil-loaded samples, the dissimilarity between the TDAE and the DAE has declined compared with the static COF. Such a kind of oil bleeding may be quantitatively small and negligible, but during the preparation of the samples, it was visually noticed that the paper sheet used for storing the vulcanizate samples showed signs of discoloration after a certain amount of time. It is believed that such a small chance of oil penetration is sufficient to slightly alter the frictional behavior of the rubber.

The smooth surface of the metal plate can best reflect the conditions of dry adhesion friction. However, because the hysteresis friction will subsequently be studied on the wet surface of the concrete counterface, it is worthwhile to evaluate the state of dry friction of the rubber with the concrete counterface. It is evident that this friction case is not a perfect one for studying adhesion friction, but it would certainly provide further insights into rubber friction in general. Figure 10
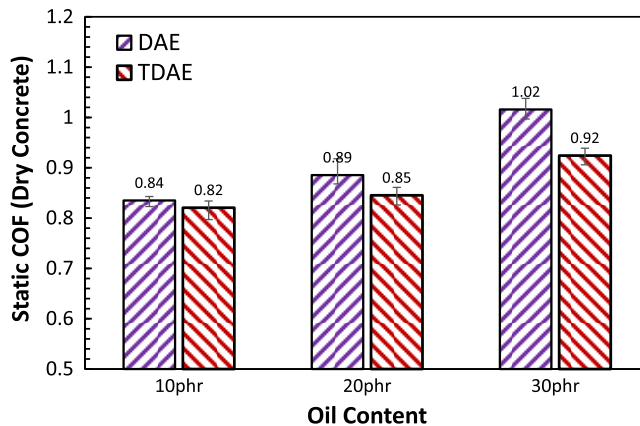

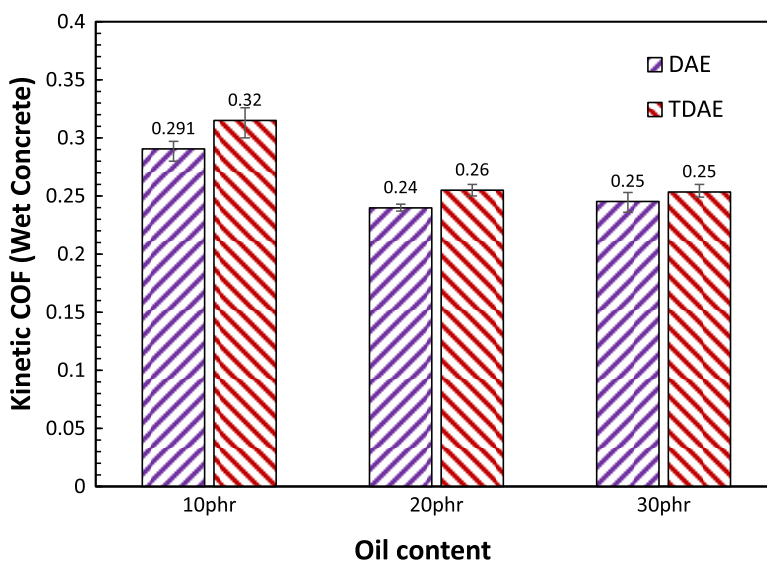FIG. 10. — Static COF of rubbers on the concrete as the counterface under dry condition.

Fig. 11. — Kinetic COF of rubbers on concrete as the counterface and under wet condition.

presents the data of the static coefficient of rubber friction on dry concrete. The previous trend is again observed, and DAE is favored over TDAE. However, as the oil content increases, a rise in the value of the coefficient of friction is observed, which is in contradiction to the previous trend reported in Figures 8 and 9. Another important point is that the adhesion friction value is lowered because of the increase in the counterface roughness and the reduced true area of contact. Under such circumstances, it seems that the reduction in rubber hardness due to oil loading has been strong enough to reflect a positive effect on enhancing the COF. However, the lower hardness of TDAE compared with DAE still could not cancel out the negative effects associated with the compatibility-related issues in the TDAE-rubber systems.

Hysteretic Friction. — Under the rough contact of rubber with the concrete surface contaminated by a soap–water solution, the hysteretic term of friction is predominant. To obtain a true state of wet frictional condition, only the kinetic COF was considered, as exhibited in Figure 11. It can be seen that values of COF have decreased remarkably for both oils, as several adhesion-related mechanisms have disappeared due to the presence of the soap–water solution at the interface. Interestingly enough, it is observed here that at not only lower oil loading but also high oil levels, TDAE has a comparable or even a better COF than DAE. This reproducible result may be related to the higher amount of loss factor and energy dissipation of TDAE within a specific temperature zone, which is different with the trend of the loss tangent at 0 °C. The results for the samples with 30 phr oils are in line with the previous findings finding that, under severe applied loading conditions and at low to moderate sliding velocities, the role of the microtexture on frictional properties is intensified. The trend observed for the wet frictional condition may be due in part to the fact that the sliding velocity of the instrument was not sufficiently large to fully activate the roles played by the viscoelastic loss. In other words, it is logical to assume that wet friction may still be affected by the adhesion friction, where TDAE has an intrinsic capability for enhancing COF. Although ongoing research on the rubber blend of SBR/BR led to the same findings, further research is still required to determine the actual reason behind the discrepancy in loss tangent data and frictional properties.

CONCLUSION

From the obtained results, it is concluded that the level of difference in the frictional properties of the two oils is rather minor, and therefore, the two oils could be used interchangeably with a simple formulation adjustment. The TDAE samples exhibited a lower hardness and a greater wok of adhesion to the steel and concrete substrates that could potentially impart better adhesion friction. However, the reduced viscosity of TDAE as well as its higher incompatibility with SBR could finally lead to a lower adhesion COF for TDAE than for DAE under dry contact with a smooth (steel) substrate. With increasing oil content, the adhesion COF falls regardless of the oil type. Interestingly, TDAE compounds have better or comparable hysteretic COF, at both low and high oil loading. Care must be taken to use a temperature of 0 °C as a point of comparison for frictional properties, as this temperature is deeply connected to factors such as temperature, substrate roughness, sliding velocity, pressure, and so forth. This is particularly important when the comparison of samples shows a crossover point within the frictional zone of their loss factor curve.

ACKNOWLEDGEMENTS

REFERENCES

[1]J. G. Sommer, *Engineered Rubber Products*, Hanser, Liberty Twp, Ohio, 2009.

[2]A. Wik and G. Dave, *Environ. Pollut*. **157**, 1 (2009).

[3]S. Dasgupta, S. L. Agrawal, S. Bandyopadhyay, R. Mukhopadhyay, R. K. Malkani, and S. C. Ameta, *Polym. Test*. **28**, 251 (2009).

[4]Aatmeeyata and M. Sharma, *Polycyclic aromatic hydrocarbons, elemental and organic carbon emissions from tire-wear*. *Sci. Total Environ*. **408**, 4563 (2010).

[5]A. Azimi, A. R. Bakhtiari, and R. Tauler, *Environ. Pollut*. **243**, 374 (2018).

[6]C. Bergmann, J. Trimbach, and M. Haase-Held, *KGK Kautsch. Gummi Kunsts*. **64**, 24 (2011).

[7]M. Öter and V. Deniz, KGK *Kautsch. Gummi Kunsts*. **64**, 48 (2011).

[8]Y. Chokanandsombat and C. Sirisinha, *Polym. Polym. Compos*. **22**, 599 (2014).

[9]L. Qu, G. Yu, L. Wang, C. Li, Q. Zhao, and J. Li, *J. Appl. Polym. Sci*. **126**, 116 (2012).

[10]X. D. Pan, E. D. Kelley, and M. W. Hayes, *J. Polym. Sci. B Polym. Phys*. **41**, 757 (2003).

[11]X.-D. Pan, *Wear* **262**, 707 (2007).

[12]H. Takino, R. Nakayama, Y. Yamada, S. Kohjiya, and T. Matsuo, RUBBER CHEM. TECHNOL. **70**, 584 (1997).

[13]A. Le Gal, L. Guy, G. Orange, Y. Bomal, and M. Klüppel, *Wear* **264**, 606 (2008).

[14]A. Kuta, Z. Hrdlička, J. Voldánová, J. Brejcha, J. Pokorný, and J. Plitz, *KGK Kautsch. Gummi Kunsts*. **63**, 120 (2010).

[15]S. Ezzoddin, A. Abbasian, M. Aman-Alikhani, and S. Taghvaei, *Iran. Polym. J*. **22**, 697 (2013).

[16]V. Null, *KGK Kautsch. Gummi Kunst*. **52**, 6 (1999).

[17]R. Rahalkar, RUBBER CHEM. TECHNOL. **62**, 246 (1989).

[18]A. Petchkaew, K. Sahakaro, and J. W. Noordermeer, *KGK Kautsch. Gummi Kunsts*. **66**, 43 (2013).

[19]A. Rathi, W. k. Dierkes, A. Blume, and M. Hernandez, *KGK Kautsch. Gummi Kunsts*. **69**, 22 (2016).

[20]A. Petchkaew, K. Sahakaro, and J. W. Noordermeer, *KGK Kautsch. Gummi Kunsts*. **66**, 21 (2013).

[21]A. Rathi, M. Hernández, W. K. Dierkes, J. W. M. Noordermeer, C. Bergmann, J. Trimbach, and A. Blume, "Effect of Aromatic Oil on Phase Dynamics of S-SBR/BR Blends for Passenger Car Tire Treads," presented at the 190th Fall Technical Meeting of the Rubber Division, ACS, Pittsburgh, October 12, 2016.

[22]A. Petchkaew, *Implications of Non-carcinogenic Pah-free Extender Oils in Natural Rubber Based Tire Compounds*, University of Twente, 2015.

[23]M. Weydert and G. M. V. Thielen, U.S. Patent 7193004B2 (to Goodyear Tire and Rubber Co.), March 20, 2007.

[24]J. Bowman, M. D. Via, M. E. Pattnelli, and P. Tortoreto, *KGK Kautsch. Gummi Kunsts*. **57**, 31 (2004).

[25]M. Klüppel and G. Heinrich, RUBBER CHEM TECHNOL. **73**, 578 (2000).

[26]J. Q. Yao, M. P. Laurent, T. S. Johnson, C. R. Blanchard, and R. D. Crowninshield, Wear **255**, 780 (2003).

[27]M.-R. Pourhossaini and M. Razzaghi-Kashani, *Polymer* **55**, 2279 (2014).

[28]H. Luo, J. Wu, F. Teng, B. Su, H. Li, A. Lin, Z. Li, and Y. Wang, *J. Appl. Polym. Sci.* **138**, 50453 (2021).

[29]X. Yang, J. Tian, and J. Dong, *J. Appl. Polym. Sci.* **138**, 50120 (2021).

[30]M. Mokhtari and D. J. Schipper, *Tribol. Int*. **96**, 382 (2016).

[31]M. Al-Assi and E. Kassem, *Appl. Sci*. **7**, 1029 (2017).

[32]D. Tabor, RUBBER CHEM. TECHNOL. **33**, 142 (1960).

[33]K. Grosch, *Proc. R. Soc. Lond. Ser. A. Math. Phys. Sci.* **274**, 21 (1963).

[34]B. N. Persson, *Surf. Sci*. **401**, 445 (1998).

[35]C. Rulison 1998, *So You Want to Measure Surface Energy,* Kruss USA, Charlotte, NC, 1999.

[36]D. W. Van Krevelen and K. Te Nijenhuis, *Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*, Elsevier, Amsterdam, 2009.

[37]S. L'Heveder, F. Sportelli, and N. A. Isitman, *Plast. Rubber Compos*. **45**, 319 (2016).

[38]M. R. Kashani, E. Behazin, and A. Fakhar, *Polym. Test*. **30**, 271 (2011).

[39]S. Maegawa, F. Itoigawa, and T. Nakamura, *Tribol. Int*. **92**, 335 (2015).

[40]S. Kawasaki, T. Tada, and B. Persson, *Soft Matter* **4**, 5428 (2018).

[41]J. L. Leblanc, *Prog. Polym. Sci*. **27**, 627 (2002).