

Study of friction and wear of thermoplastic vulcanizates: the correlation with abraded surfaces topology

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Abstract. The work was focused on the study of friction and wear properties of thermoplastic vulcanizates (TPV) based on polypropylene (PP), natural rubber (NR) and styrene butadiene rubber (SBR) compounds containing all common additives and curatives using ball-on-flat method. Pure materials and binary TPV blends of PP/NR, as well those of PP/SBR with the compositions 95/5, 75/25 and 50/50 (in weight %) were compounded and analysed. It is very well known that the coefficient of friction (COF), as well as wear values of pure thermoplastic matrix are significantly lower than those for pure rubber. Thus, it was found that the friction coefficient and wear of TPVs significantly increased in accordance with increased content of rubber material. Surprisingly, NR compared with SBR of similar concentrations in PP matrix, considerably affected wear of samples and the friction coefficient remained almost unaffected. Finally the topology of abraded surfaces were examined by using scanning electron microscopy (SEM) in order to understand the relationship between the COF, wear process and the composition of TPVs.

1. Introduction

Thermoplastic dynamic vulcanizates (TPV) represent the plastics and rubber blends. Such kinds of elastomers are frequently used in automotive, electric or footwear industries. They overcome other conventional materials due to combination of outstanding mechanical characteristics of elastomers and the excellent processing properties of thermoplastics. TPVs also gain substantial attention due to the simple realization of the desired physical properties by varying the blend ratios [1]. The cross-linked rubber phase in TPVs gives them a good compression behavior and a good chemical resistance against water, acids and bases and can play an essential role in recycling of “end of life” rubber products.

TPVs are produced by dynamic crosslinking of blends of thermoplastics and curable elastomers. During an intensive mixing process, fine dispersion of crosslinked, micron-size rubber particles are imbedded in a thermoplastic matrix [2]. The morphology of multiphase blends strongly depends on volume ratio, the solubility, the viscosity of components and mixing time. Usually the major phase forms the continuous matrix and governs the properties of entire blend, while the minor phase forms dispersed micro domains and contribute to certain specialized properties of blend [3].

Friction and wear characteristics of TPV materials were extensively studied for the last several decades [4-7]. Such materials require combining simultaneously, properties like durability resistance to a great number of solvents and external forces throughout the service life. The friction of products is



taken in to account directly during the designing process. Thus, understanding of friction mechanisms of polymeric materials becomes very important.

Friction is governed by the surface interaction in moving contact between both of frictional partners [6]. The real contact area depends on interfacial properties and commonly vary during sliding process because of mechanical behavior of material. Usually, interfacial properties change due to tribo-film and wear debris formation and consequently roughness evolution [7], whereas the tribo-film is the well-known transfer thin layer formation on the metallic counterface, which takes place during the friction process between metal and polymer surfaces. The friction film formed on the polymer composite itself as well plays an important role in the friction and wear behavior of polymer composites [8]. Friction variation during the test is frequently related to an increase in real contact area [9].

Up to date a major interest is dedicated to friction and wear properties of micro-nanoparticles [10, 11] and ground tire rubber (GTR) filled TPVs [12]. It has been found that an increase in COF takes place as a function of the concentration of rubber powder in PP matrix for GTR modified PP blends. This result was explained through the nature of GTR powder to form an inter-material layer with enhanced COF.

In this paper studies were done on the effect of blend ratios on friction and wear of TPVs based on polypropylene (PP) + natural rubber (NR) or styrene-butadiene rubber (SBR). PP/(NR or SBR) blends were compounded as potential materials with enriched wear resistance and toughness for possible engineering applications. The main goal of the work was the investigation of tribological properties of polymeric materials with high difference of COF, to study the relation between COF, wear and the topology of abraded surfaces. Finally the wear mechanism of the TPVs was investigated.

2. Experimental

2.1. Materials

The PP used in this research was Polypropylene homopolymer (TITANPRO 6531, isotactic type) with a specified melt flow index of 3.5 g/10 minutes. It was supplied by Titan PP Polymers (M) Sdn. Bhd. NR of the type SMR 20 CV/BP1 was supplied by the Astlett Rubber Inc. SBR of the type Buna CB 24 was provided by TRINSEO. Sulphur was used as the curing agent, whereas zinc oxide and stearic acid were used as activators. Sulphur, zinc oxide, and stearic acid were supplied by Sigma-Aldrich®. Carbon black of the type N339 was used as the filler. CBS (N-cyclohexyl-2-benzothiazolesulfenamide) was employed as curing activator and IPPD (N-isopropyl-N'-phenyl-p-phenylenediamine) as antioxidant. The complete composition of the compounds is listed in the table 1.

Table1. Rubber composition.

	NR	SBR	Carbon Black	CBS	Sulphur	IPPD	ZnO	Stearic Acid
NR	100	-	50	2,5	1,7	1,5	3	1
SBR	-	100	50	2,5	1,7	1,5	3	1

*phr – parts per hundred rubber

2.2. Rubber compound manufacturing

The rubber blends for both NR and SBR were mixed according to ASTM D 3192 – 09 in an internal mixer Banbury (Pomini Farrel) with a total batch weight of 360 g each at 70 °C. Chemicals in proportion listed in table 1 were successively added as follows: elastomers mixed for 2 min followed by mixing of ZnO, Stearic Acid, IPPD and Carbon Black for next 5 min. Each mixing was accomplished at a rotor speed of 65 rpm. CBS and sulphur were added in the batches and further homogenized in an open two roll mixing mill (Farrel G-2603) at 60 °C for 5 min.

Each TPV batch was prepared on a Brabender Plastograph. Compounding was done at 190°C, 60 rpm and a fill factor of 80 %. PP was melted in the mixer for 2 min and then NR or SBR containing additives and curing agents were added in proportion defined in table 2 in % by weight. The mixing was continued for 3 min. Finally, the material was collected and compression molded into a 120 x 120 x 2 mm sheet. The remaining time between the collecting of the compound and molding has to be 2 minutes.

Table 2. Blend ratio of the samples

	PP	NR	SBR	PP/5NR	PP/25NR	PP/50NR	PP/5SBR	PP/25SBR	PP/50SBR
PP	100	0	0	95	75	50	95	75	50
NR	0	100	0	5	25	50	0	0	0
SBR	0	0	100	0	0	0	5	25	50

Samples of the blends were molded in an electrically heated hydraulic press upon 250 kN force. Hot-press procedures involved preheating at 200 °C for 3 min followed by compressing for 3 min at the same temperature. The final cooling of the molded sheets was performed using manual cooling press for 5 min at the maximal reached compression force.

Sheets based on pure PP were molded directly from PP granulates using aforementioned procedure. Rubber samples were cured at 150 °C in accordance with optimum curing time established by using a moving die rheometer (MDR 3000, Montech).

2.3. Testing

Dry friction tests were conducted using Bruker Universal Mechanical Tester (UMT) in a linear ball-on-flat mode at room temperature in air. The relative humidity was 28 ± 5 %. An 8 mm diameter ball, made of stainless steel, was slid against a flat sample in reciprocating mode (figure 1) under constant load $F = 0,5$ N. The ball traversed 300 cycles during 120 s at 125 mm/s sliding speed and 25 mm stroke length.

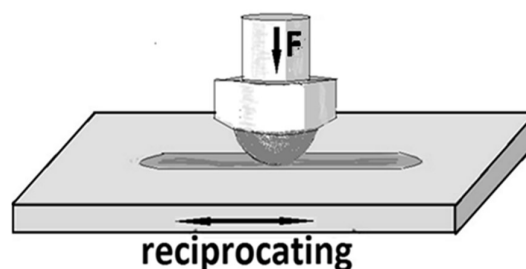


Figure 1. Scheme of ball-on –flat reciprocating friction test.

Determination of hardness was done using BAREISS HP-D - Shore D durometer. The same measuring procedure was applied for all samples including rubber samples (method SHORE, ISO 868). For rubber materials the Shore D method was used instead of the usual Shore A to maintain a consistency in comparison amongst all the samples, based on varied polymeric materials. This method measures penetration of a special shaped steel rod after a fixed time, which in the present study was 2 minutes. Frequently, hardness of materials helps to understand COF and wear evolution [13] and serves as a parameter which complements the comprehension of materials behaviors.

The data of wear were compared using the width of friction tracks measured by optical microscope Leica DVM2500.

Studies on the morphology of friction tracks were carried out using a scanning electron microscope (SEM), model Nova NanoSEM 450 (FEI) with Schottky field emission electron source.

3. Results and discussion

The homogeneity of the studied TPV blends is a very important factor, which is dependent on the compounding procedure.

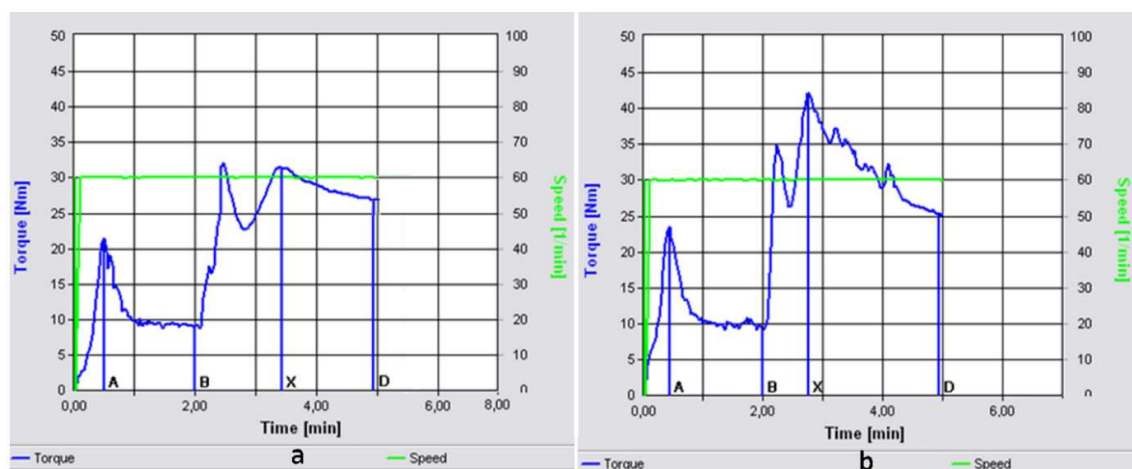


Figure 2. The torque vs time of TPV compounding a) PP/50SBR and b) PP/50NR .

In figure 2, the compounding process exemplary is shown for TPV blends, based on the highest content 50 phr of SBR (a) and NR (b). Figures 2a-b show the dependence of compounding time on torque. For all the blends, PP was inserted into the mixing chamber without preheating. The torque increased sharply due to the resistance exerted on the rotors by the un-melted PP at the first phase of the compounding process during the first 30 s, followed by a region where PP melted and got transformed from solid to liquid phase (see interval AB). After 2 min, rubber was added into the mixing chamber, which caused the next rise of torque due to the un-homogenized rubber and impregnation into PP matrix. The torque increased up to 35 Nm for NR and 32 Nm for addition of SBR. Next, the decrease in torque was due to the melting of rubber and was followed by another increase in torque due to the rubber getting cross linked at this stage as is shown on the plot. A large difference is observed between cross linking behaviours of NR and SBR. NR crosslinking (see figure 2b) started earlier than that of SBR (figure 2a) and attained the maximum in about of 30 s compared with more than 60 s for SBR (see point X). Evident fluctuation of torque during continuous decreasing on the last part of graph for NR denotes combined mechanism of crosslinking with simultaneous breaking of already existing links until final stabilization was attained. On the other hand, smooth decreasing for similar region for SBR exhibited predominantly breaking of already formed links until some kind of saturated state was reached. SBR dispersed more easily in the PP matrix compared with NR.

Figure 3 exhibits the variation of COF during the 120 s or 300 cycles for PP, pure NR and SBR samples as well as for their blends. For all the samples, a fast increase of COF can be observed in the course of the first 5-20 s of test followed by slight and continuous decrease for rubbers, increasing for pure PP and blends with lower (5%) rubber concentration in PP matrix. Blends with 25 % and 50 % rubbers represented more or less stable COF with fluctuations caused by wear debris formation. Generally, it is well known that COF in rubber-steel interaction is high [14]. The results show the COF ranged between 2,00 and 2,25 for rubbers used in the investigation (NR and SBR). Noticeable

differences in COF are observed in the first 40 s or 75 cycles of ball sliding, followed by continuous and sluggish decrease. It can be the witness about the different wear mechanisms, which at initial stage play an important role in COF values.

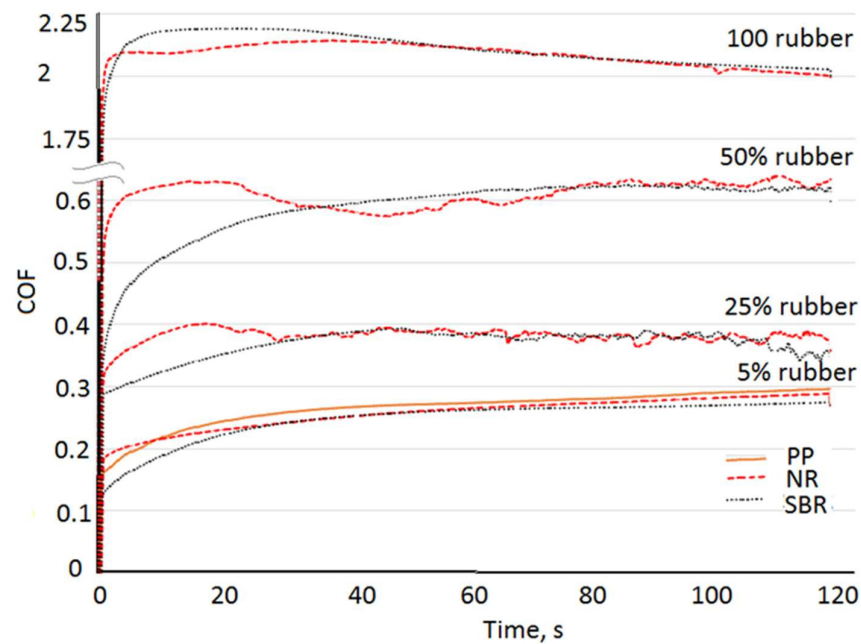


Figure 3. Evolution of COF of PP/rubber blends and their components.

Due to different mechanical properties of NR and SBR such as hardness, elastic modulus, fracture toughness etc., initial abrasion and topology inside of friction tracks are quite different, which directly affect COF through the contact surface. COF usually is governed by surface adhesion, surface roughness, surface deformation, and surface contamination. Continuously increasing number of ball passes creates a specific surface topology (figure 4) which can be compared with waves on water surface, with certain amplitude, periodicity and width for certain applied COF (load and speed) and rubber (different for NR or SBR). This particular surface kept more or less constant morphology due to permanent creation of new “waves” instead of abraded ones. COF on waved surfaces was lower than on pristine rubber surfaces.

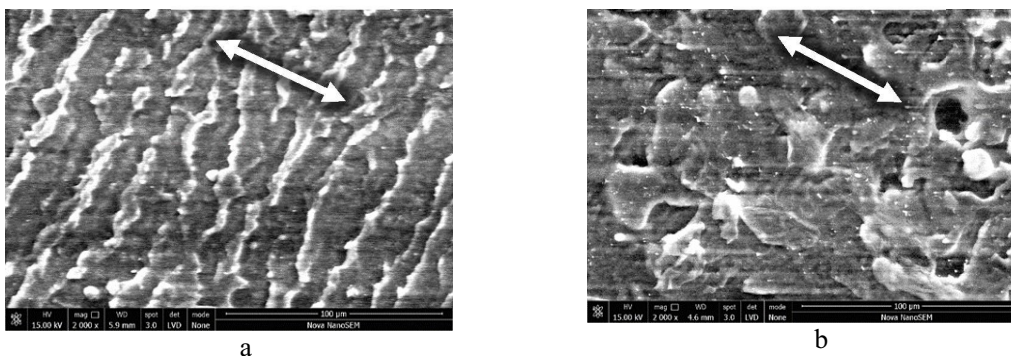


Figure 4. Morphology of friction tracks: a) NR, b) SBR. Arrows show the sliding direction.

The mechanism of COF variation versus time can be illustrated assuming the instantaneous presence of two regions inside of friction track. One is the waved area (zone 1) located along the middle of track and the second (zone 2) surrounding the zone 1 and has the COF higher than that of the waved area. Abrasion process changed the ratio between the widths of the aforementioned areas

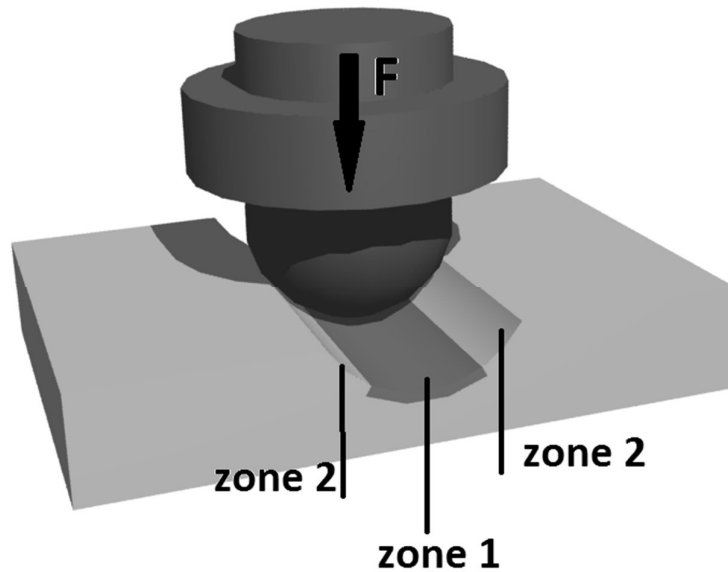


Figure 5. Scheme of bi-zonal mechanism of friction in ball-on-plate mode.

(see figure 5) and led to slight decrease in COF. On the opposite side, COF of PP slightly increased from 0,15 to 0,30 during 300 cycles (figure 3). Noticeably, it is almost 10 times lower than COF of studied rubbers. Adding of 5 % of rubber in PP matrix did not affect significantly the COF as well as the topology of the abraded surfaces (figure 6). Friction tracks topology is characterized by small cracks formed in PP matrix, which are aligned perpendicular to the sliding direction of counterbody. It was noticed that adding of small quantity of rubber (5 %) decreased the crack formation and propagation in PP matrix.

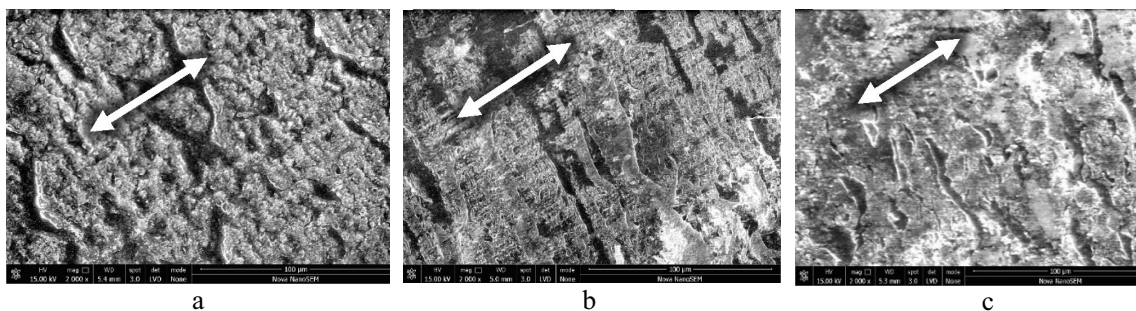


Figure 6. Topology of tracks. a) PP, b) PP/5NR, c) PP/5SBR. Arrows show the sliding direction.

A PP film was developed from rupture within the polymer and adhered to the friction track. This process as well as the film transfer to the counterbody are characteristic for most of the polymers except the highly cross linked and some glassy polymers [9]. According to article [10], the transfer film from polymers has a tendency to adhere on metal surfaces and influence the friction and wear. In

the present study, PP film creation inside of tracks, decreased the influence of rubber filler on COF and wear in PP/rubber blends. Due to weaker crosslinking between rubber particles and PP matrix relative to crosslinking inside of rubber particles and inside of PP, such particles were easily rubbed or compressed comparatively with PP matrix and facilitated the PP film creation. Blends containing 25 % of rubber show COF ranged between 0.3 and 0.4. 50 % of rubber in PP matrix increased COF up to 0.63, which was still almost 3.5 times lower than COF of pure rubbers. Morphology of tracks was still dominated by PP film creation (figure 7), but was quite different for blends containing NR (figures 7 a, c) and blends containing SBR (figures 7 b, d). For ball-on-flat contact the initial conditions changed over time, due to changes in the topography, microstructure and composition of the material.

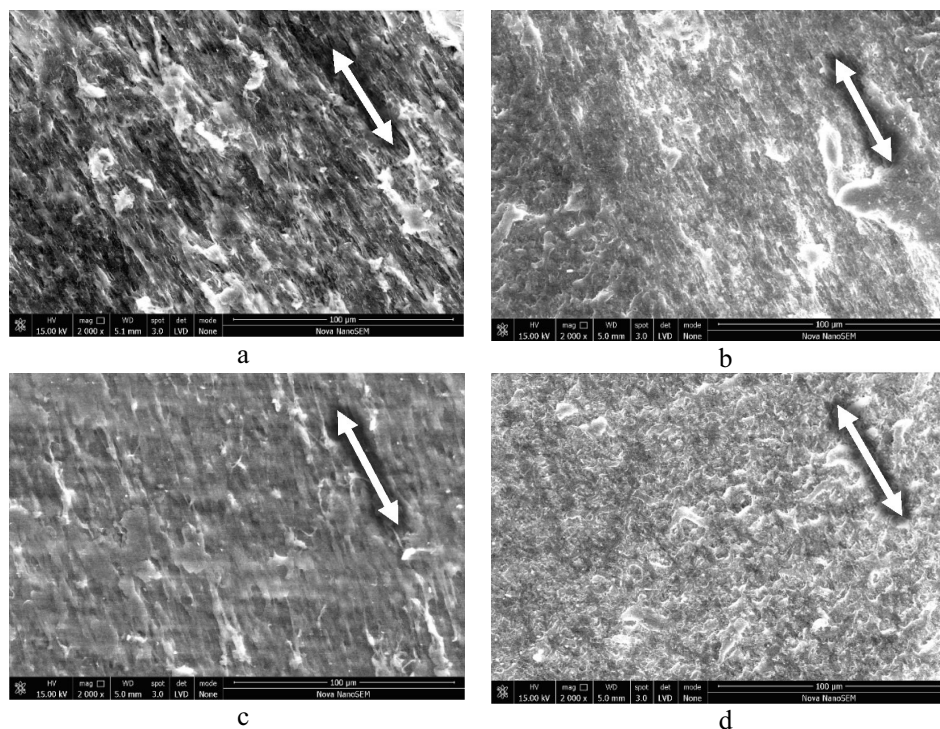


Figure 7. SEM images of friction tracks. a) PP/25 NR, b) PP/25 SBR, c) PP/50 NR, d) PP50/SBR. Arrows show the sliding direction.

The analyses of average value of COF during the last 5 cycles from 300 cycles exhibited a general trend of friction variation dependent on rubber concentration in TPVs as well as the nature of rubber (figure 8). An increase of rubber concentration in PP matrix showed a continuous increase of COF, the differences between NR and SBR filled samples being insignificant.

Friction wear usually is a combination of several parameters which include the contact pressure, temperature, and sliding velocity [11]. The wear of polymers is a complex process which clearly is related to the formation of the transfer film. Chemical reactions in the contact spots and additives in the polymer composition affect the tribological properties [10]. The wear of samples was analysed measuring widths of tracks in optical microscope. The obtained results are presented in figure 9. In order to compare the wear of samples, the simple width of track measurements were used on optical microscope. The determination of wear in viscoelastoplastic materials like TPVs is sometimes very difficult. If the wear is defined like a volume of material which has lost its initial properties during friction process, then the calculation of the real volume of such a material may be a great challenge. This is because besides detached material there is also present abraded surface with unknown depth. In

this case, according to the authors of the present study, the most suitable method was found to be the widths of track measurement. The leading wear mechanism in the prepared blends was adhesive wear related to the formation, shearing and rupture of the adhesive junction in the contact spots and the material transfer from one surfaces to another. The film transfer from the polymer was continuously created and smeared out. With increasing of rubber concentration wear increased, but contradictory to COF, wear changed drastically depending on nature of fillers. For example, in case of 50 % rubber in PP, width of track for NR blend was two times larger than that for SBR blend.

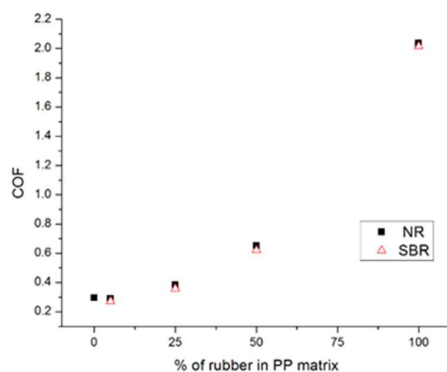


Figure 8. COF of TPVs versus rubber concentration in TPVs.

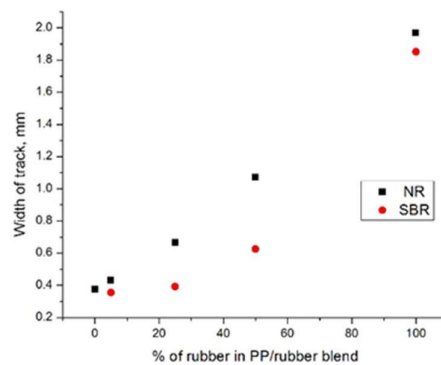


Figure 9. Width of tracks after 300 cycles vs rubber concentration in TPVs.

Hardness measurements usually supplement the tests which determine the mechanical properties of materials. Hardness is the property of a material to resist to scratching, perforation or deformation and usually expresses the deformability of materials under concentrated load action. The Shore hardness was quantified by penetration of steel rod, shaped like a truncated cone, into surface and is related to the modulus of elasticity and viscoelastic properties of the material. The adding of rubbers in PP matrix commonly modifies physical and mechanical properties of blends. There are the results of Shore D hardness measurements for investigated samples in figure10. Hardness almost linearly decreased with increasing of rubber concentration, showing the maximum of 64 Shore degree for pure PP, where the minimum was found for pure rubbers: 30 for NR and 32 for SBR. The difference of hardness between NR and SBR filled blends having the same rubber concentration was stated by slight decreasing in hardness for PP/NR blends.

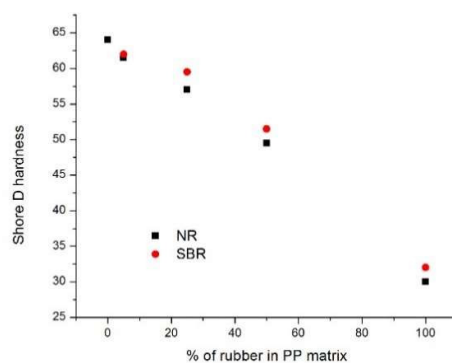


Figure 10. Shore D hardness vs rubber concentration in the PP matrix.

The relationship between hardness and wear are quite difficult to be computed. It was observed that samples having higher hardness showed lower values of wear.

4. Conclusions

Friction coefficient of PP/NR, PP/SBR TPV materials increased with increasing of rubber concentration in PP matrix.

Wear of investigated materials increased with increasing content of rubber and also depended of the rubber type.

Even a small quantity of rubber decreased the crack formation and propagation in PP matrix during the friction process.

Hardness results contributed to the understanding of wear trends in investigated materials, where samples having higher hardness showed lower values of wear.

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