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Green thermoplastic vulcanized based on recycled polyethylene and waste tire powder

Elastômeros termoplásticos vulcanizados verdes a base de polietileno recilcado e pó de pneu

Elastómeros termoplásticos vulcanizados verdes a base de polietileno reciclado y polvo de neumáticos

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Abstract

ThermoPlastic Vulcanized (TPV) is a class of polymeric materials capable of combining the high elasticity of elastomers with the recycling of thermoplastics. The production of TPV with recycled material contributes to the reduction of polymeric waste on the planet, reducing its environmental impact. In this study, recycled TPV samples were produced by combining recycled polyethylene and waste tire powder. The TPV samples were obtained in an internal mixer, changing the processing conditions, during the vulcanization and stabilization stages of the final torque. The results showed that by reducing the processing speed from 60 to 40 rpm, TPV samples were obtained with higher tensile strength and low swelling in oil. ANOVA statistical analysis confirmed that significant changes occurred due to processing speed variations. The DUNCAN mean parity statistical model was used for comparisons between pairs of TPV samples. Frequency sweeping rheological analysis confirmed the effect of adding tire powder on the samples' elastic modulus. There were no changes in the viscous and elastic modules of the samples. The absence of significant changes in the final morphology of the TPV samples was attributed to the tire powder size. The increased properties of TPV samples are attributed to new crosslinking of the elastomeric phase during dynamic vulcanization.

Keywords: Thermoplastic elastomers; Dynamic vulcanization; Recycling; Polyethylene; Waste tire.

Resumo

Os elastômeros termoplásticos vulcanizados dinamicamente (TPV) são uma classe de materiais poliméricos capazes de combinarem a alta elasticidade dos elastômeros, com a reciclagem dos termoplásticos. A produção de TPV com material reciclado contribui para redução de rejeitos poliméricos no planeta, reduzindo o impacto ambiental dos polímeros. Neste estudo, produziu-se TPV reciclados utilizando polietileno reciclado e pó de pneu. Os TPV foram obtidos em misturador interno, alterando as condições de processamento, durante as etapas de vulcanização e estabilização do torque final. Os resultados comprovam que ao reduzir a velocidade de processamento de 60 para 40 rpm, obtêm-se TPV com maior resistência à tração e menor inchamento a óleo. A análise estatística ANOVA confirmou a significância das alterações na velocidade de processamento. O modelo estatístico de paridade das médias de DUNCAN foi utilizado para comparações entre pares dos TPVs. A análise reológica de varredura de frequência confirmou o efeito da adição do pó de pneu sobre o módulo elástico. Não foram observadas alterações nos módulos viscoso e elástico entre as amostras. A ausência de modificações significativas na morfologia final dos TPVs foi atribuída ao tamanho do pó de pneu utilizado. O aumento nas propriedades dos TPV é oriundo de novas reticulações da fase elastomérica durante a vulcanização dinâmica.

Palavras-chave: Elastômeros termoplásticos; Vulcanização dinâmica; Reciclagem; Polietileno; Pó de pneu.

Resumen

Los elastómeros termoplásticos vulcanizados dinámicamente (TPV) son una clase de materiales poliméricos capaces de combinar la alta elasticidad de los elastómeros con el reciclaje de los termoplásticos. La producción de TPV con material reciclado contribuye a la reducción de residuos poliméricos en el planeta, reduciendo el impacto ambiental de los polímeros. En este estudio, el TPV reciclado se produjo utilizando polietileno reciclado y polvo de neumáticos. Los TPV se obtuvieron en un mezclador interno, cambiando las condiciones de procesamiento durante los pasos de vulcanización y estabilización final del torque. Los resultados prueban que al reducir la velocidad de procesamiento de 60 a 40 rpm, se obtienen TPV con mayor resistencia a la tracción y menor hinchazón del aceite. El análisis estadístico ANOVA confirmó la importancia de los cambios en la velocidad de procesamiento. Se utilizó el modelo estadístico de paridad media de DUNCAN para las comparaciones por pares de los TPV. El análisis reológico de barrido de frecuencia confirmó el efecto de la adición de polvo de neumáticos en el módulo de elasticidad. No se observaron cambios en el módulo viscoso y elástico entre las muestras. La ausencia de cambios significativos en la morfología final de los TPV se atribuyó al tamaño del polvo de neumático utilizado. El aumento de las propiedades del TPV proviene de nuevos entrecruzamientos de la fase elastomérica durante la vulcanización dinámica.

Palabras clave: Elastómeros termoplásticos; Vulcanización dinámica; Reciclaje; Polietileno; Polvo de neumáticos.

1. Introduction

Vulcanized elastomers are materials with specific mechanical properties, such as high elasticity and low modulus. However, the vulcanized material cannot be reprocessed, since there are sulfidic bonds, which makes them insoluble and infusible. To minimize this problem, researchers in the areas of thermoplastics and elastomers have joined efforts in the development of dynamically vulcanized thermoplastic elastomers (TPV). These materials have synergistic properties of elastomers and thermoplastics. They are elastic materials capable of reprocessing (Soares, 2008; Mondal, 2008, Ranjbar, 2012; Carvalho, 2016;).

The first industrially produced TPV were based on polypropylene (PP) and ethylene-propylene-diene rubber (EPDM), due to the good compatibility between the two polymers. This material presented excellent dispersion of the vulcanized phase in the thermoplastic matrix, without compatibilizers (Coran, 1980; Naskar, 2004). Other compositions of TPVs, however, need compatibilizing agents in the formulations due to differences in polymer polarity like PP / nitrile rubber (NBR) (Naderi, 1999 Soares, 2006; Soares 2008), Polyamide (PA) / NBR (Chatterjee *et. al*., 2016) and PP / acrylic rubber (ACM) (Soares, 2008b; Celestino *et. al.*, 2009. For the development of TPV with good mechanical properties, it is necessary to observe the compatibility between the polymers and the process of production (Lyer, 2021).

Recently, a TPV was produced based on the swelling of the vulcanized elastomeric phase, using tire powder and styrene monomer (Lima, 2016). The polystyrene polymerization was carried out in suspension, but the thermoplastic phase had low molecular weight, drastically reducing the mechanical properties of the TPV. The swelling methodology of the elastomeric phase is not economically advantageous, in addition to the usage of organic solvents. The use of these solvents should be avoided in synthetic routes. The development of new products and reuse of materials are recommended by the principles of green chemistry. Another methodology used in the production of TPV was by electron radiation, absence of solvents. As a result, the elastomeric phase crosslinking occurs by radiation, combining the breaking of the polymeric chain with the formation of lattices (Shen, 2013). This technique does not require vulcanization additives, such as zinc oxide, synthetic plasticizers, accelerators, and sulfur. However, the TPV has low mechanical performance and tendency of aging. Among the processes to produce TPV samples, the physical mixture is considered the most versatile, due to the ease of processing and to the countless possibilities of polymeric combinations.

The physical mixtures of the TPV samples are performed on internal mixers and extruders. The most used internal mixers are Banbury and Kneader models, which are capable of producing multiphase polymeric mixtures with excellent dispersion (Silva, 2007). The stress-strain profile in the Banbury mixing chamber is high for the TPV production. TPV samples consume high energy during processing, due to the disruption of the elastomer chains and to misorientation of the vulcanized particles in the thermoplastic matrix. The dispersion process involves the separation of the vulcanized particles from the solid, where there is a mechanical work on the cohesive forces that maintain the particles agglomerated (Ning, 2018). The multiphase polymeric systems of TPV samples consist of two phases: dispersed phase and matrix phase (Moreira, 2002; Zhao, 2015). The formation of the dispersed phase occurs in two stages, the first one is the dispersion of the thermoplastic phase in the elastomeric matrix. The division of a drop of immiscible polymeric fluid involves the generation of stresses in the interphase space and requires high mechanical work. This division will occur in the presence of the elastomeric matrix, where the cohesive forces of the viscous polymeric fluid (interfacial tension) will agglomerate the macromolecules of the thermoplastic (Minale, 2010). Then, the second dispersion stage occurs: there is the dynamic vulcanization process of the elastomeric phase, the matrix being the thermoplastic and the dispersed phase being the vulcanized elastomer. The inversion phase is decisive to obtaining TPV with increased mechanical properties (Magioli, 2010; Tian, 2012; Li, 2017).

Our research group has studied the PP / NBR TPV samples. This polymeric pair, due to the difference in polarity, requires the use of compatibilizing agents: the addition of PP grafted with maleic anhydride (PPgMA) reduces the size of the vulcanized rubber domains in the PP phase, improving the final properties (Soares, 2008; Soares, 2007; Carvalho, 2018;). Another TPV developed in the group involves PP, residues of vulcanized elastomers (tire powder) and the styrene-butadiene-polymer cup (SBR) (Cossa, 2009; Leite, 2011). The results showed the successful replacement of the virgin elastomer by tire powder. The production of TPV with industrial application using polymeric material totally recycled is new. This research is in line with the principles of green chemistry, which advocates the reuse of materials. In this work, the recycled TPV was developed from the physical mixture of recycled polyethylene, from irregularly discarded plastic bags, and tire powder. This pair does not require compatibilizing agents, the studies were focused on the processing speed of the TPV, to improve its mechanical performance.

2. Methodology

The raw materials used to study the processing conditions of recycled vulcanized thermoplastic elastomers were: recycled high density polyethylene supplied by Peterlu®, fluidity index (IF) of 15 g/10 minutes, waste tire powder supplied by Artgoma do Brasil, AG 40 (particle size between 100 and 700 microns), dicumyl peroxide with 40% calcium carbonate, supplied by Retilox and liquid from the cashew nut shell (CNSL) provided by Irmãos Fontenele S.A. Ceará. CNSL was used as a vegetable plasticizer between waste tire powder and recycled HDPE.

Table 1 show the formulation used to obtain the TPV samples. Processing was carried out in an internal Haake mixer, equipped with Banbury-type rotors, with a temperature of 185 °C and 85% of mixer chamber occupation. The processing speed was changed during processing, during dynamic vulcanization and during final torque stabilization of the recycled TPV samples (Carvalho, 2018).

Table 1. Formulation.

Raw material	Weight (%)	Mass (gr.)	Volume (cm^3)
Waste tire	34.3	19.77	21.68
Recycled HDPE	51.5	29.66	29.66
CNSL	12.9	7.42	7.42
Peroxide	1.3	0.74	0.74
Total	100.0	57.59	59.50

Source: Authors.

The speed profile during processing is shown in Table 2. The mixtures were prepared in triplicates, where mixtures with final mass variation greater than 5% were rejected, keeping strict mass control of the suitable formulation.

Table 2. Speed profile used to manufacture the TPV samples.

	Time (min)				
	HDPE	Waste tire	CNSL	Vulcanization	Stabilization
	(0—2)	(2—4)	(4—6)	(6—8)	(8—10)
Samples	**Rotation (rpm)**				
1	60			60	
2	40			40	
3	60			40	
4	60			40	60
5	60			20	60
6	60			80	60

Source: Authors.

After processing, the TPV samples were ground in a knife mill, and stored in the dark for up to 7 days. The determination of melt flow index (MFI) of the TPV samples was performed in MFI equipment, manufacturer Ceast. The analysis conditions were temperature of 190 °C, mass of 2.16 kg and cutting time of 3 minutes.

The samples for tensile test were obtained by compression, using a hydraulic press heated to 200 °C, pressure of 3 tons and pressing time of 3 minutes. The tensile strength of the TPV samples was determined in an EMIC universal testing machine, equipped with a 500N load cell, speed of 10 mm / min, rectangular specimens, in accordance with the Standard ASTM M882-2016. The results were evaluated by the ANOVA excel statistical package.

The swelling test was performed in SAE 5 engine oil, at 75 °C for 70 hours. The samples were weighed before and after the swelling test and the percentage difference was calculated.

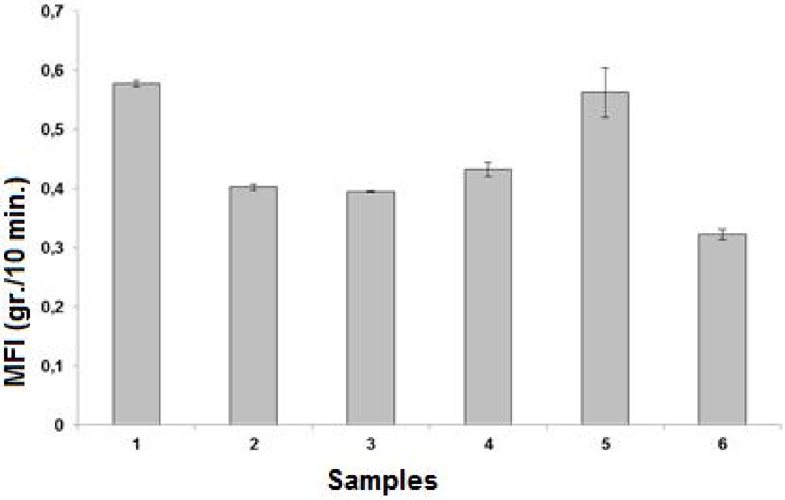
The fractured samples, after the tensile test, were metallized with carbon using the actuator LEICA ACE200 (CETEM-UFRJ). The samples were morphologically characterized by scanning electron microscopy, TM3030 Plus Hitachi equipment, operating under vacuum, voltage of 15 kV.

The rheological characterization was performed using an Anton Paar oscillatory rheometer equipment, model Physica Paar MCR 302. The frequency scan was carried out from 1 to 300 Hz. The parallel plates geometry was used, diameter of 25 mm and distance between plates of 1 mm.

3. Results and Discussion

The MFI is a direct measure of the viscosity of melted polymers, widely used in the industry for quality control of the raw material, classification according to the processing ability and application of the final product. Comparing the samples obtained with the same speed in all processing steps, the samples TPV 1 (60 rpm) and TPV 2 (40 rpm) presented a reduction in MFI. Reducing the processing speed results is a more effective dynamic vulcanization, leading to high crosslinking. This behavior can also be observed in TPV 3 (reduction from 60 to 40 rpm during vulcanization). However, by reducing the rotation speed from 60 to 20 rpm (TPV 5), the MFI value increases, matching the MFI value of TPV 1 (60 rpm). The increase of polymer viscosity or the MFI reduction is the result of polymer presenting, high degree of chemical interactions, high molar mass or strong physical bonds (Yuliestyan, 2016). It is expected that TPV samples with low MFI values present high mechanical strength. The effect of increasing processing speed was also assessed. In TPV 6, the processing speed was the highest one, 80 rpm, resulting in the lowest MFI value. The analysis of the fluidity index is inaccurate to fully understand the behavior of the TPV samples, where the frequency sweep test was performed on an oscillatory disc rheometer for further information regarding TPV's elastic and viscous modulus.

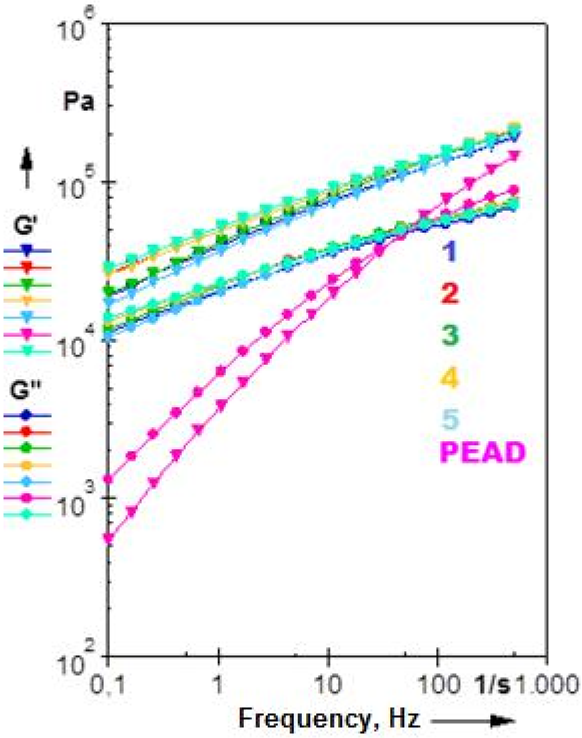
Figure 1. Flow Index of TPV samples based on recycled HDPE / tire powder.



Source: Authors

The rheological frequency sweep test was performed on samples of TPV with recycled material, Figure 2. The experimental conditions used were within the regime of linear viscoelasticity, deformation of 1%. The rheological curve behavior, for recycled HDPE, is typical of molten thermoplastic (Magioli, 2010). The recycled HDPE, at low oscillation frequencies, has viscous modulus (G") superior to the elastic modulus (G'), the dissipated energy is greater than the stored modulus. Then, the material has viscous fluid behavior. However, at frequencies above 100 Hz, the inversion of the modulus occurs, the stored energy is higher than the dissipated energy and the material has viscous-solid behavior (Schramm, 2006). However, with the addition of tire powder in the recycled HDPE, the cross over point of the modulus absented. The TPV samples present values of elastic modulus superior to the viscous modulus, behavior characteristic of elastic polymeric materials, elastic solids (Tian, 2012). There were no significant variations in the values of modulus with the change in processing speed, the determining factor in this analysis was the tire powder content used. The presence of 34% of crosslinked material did not reveal changes in the modulus trend, regardless of processing variations.

Figure 2. Rheological frequency scan for recycled TPV and HDPE samples.



Source: Authors.

The tensile strength of polymeric materials, especially TPV, is particularly important, especially because the final application. The statistical analysis of variance (ANOVA) was performed on the tensile data, Table 3. The values of the mean tensile strength at break are different ($p < 0.05$, 95% level of confidence). The change in processing speed is a determining factor in the mechanical performance of TPV fracture strength. If p-calculated (3.4x10-10) is lower than p-tabulated (0.05), or, if F (34.5) > critical F (2.62), it can be said that the mean values are different. The mean tensile strength values are different, ranging from 4.84 MPa to 7.09 MPa. TPV1, constant speed of 60 rpm, can be considered a reference, as TPV samples are produced with constant speed. Note that by reducing the processing speed to 40 rpm (TPV 2), the fracture strength is increased of, approximately, 25%. Therefore, it can be deduced that the simple reduction in processing speed results in TPV samples with higher tensile strength. Studies involving PP / NBR-based TPV samples showed an increase in mechanical properties by reducing the processing speed (Ning, 2018). This behavior was similar to that one observed for TPV3, TPV4 and TPV5, where the processing speed was reduced during dynamic vulcanization. It is important to highlight the increase in tensile strength by reducing the speed during the vulcanization of the mixture.

Table 3. Tensile strength's ANOVA test for TPV samples of recycled HDPE / waste of tire.

Group	*Count*	*Sum*	*Mean value*	*Variance*		
TPV 1	5	24.22	4.84	0.029		
TPV 2	5	29.80	5.96	0.053		
TPV 3	5	35.49	7.09	0.056		
TPV 4	5	32.30	6.46	0.198		
TPV 5	5	30.30	6.06	0.113		
TPV 6	5	31.90	6.38	0.037		
Source of variation	*Quadratic Sum*	*Degrees of freedom*	*MQ*	*F*	*P-value*	*Critical F*
Between groups	13.9797	5	2.796	34.468	3.37E-10	2.621
Within groups	1.9468	24	0.081			
Total	15.9265	29				

Source: Authors.

The analysis of the p-values validates the hypotheses corresponding to the significance level of 0.05: comparing the values according to the standard deviation, or the variance, it is not possible to ensure with statistical precision if there is a significant change in the mean value. The analysis of variance indicates that there is a significant difference between the mean values of the factor levels. There are numerous statistical tests that find the differences between the mean values. The Duncan method is widely used procedure for comparisons between all pairs of mean values, regarding the analysis of variance, allowing the maintenance of 95% level of significance (Montgomery & Runger, 199). The results in Table 4 indicate the statistical differences between the samples evaluated by the DUNCAN test. There is a statistical difference between the mean values of the pairs, $p < 0.05$. However, among the samples TPV 5 (20 rpm) x TPV 6 (80 rpm), TPV 6 (80 rpm) x TPV 3 (speed of 40 rpm in torque stabilization), TPV 3 (speed of 40 rpm in torque stabilization) x TPV 5 (20 rpm), TPV 5 (20 rpm) x TPV 4 (40 rpm in vulcanization), there is no statistical difference between the mean values, $p > 0.05$.

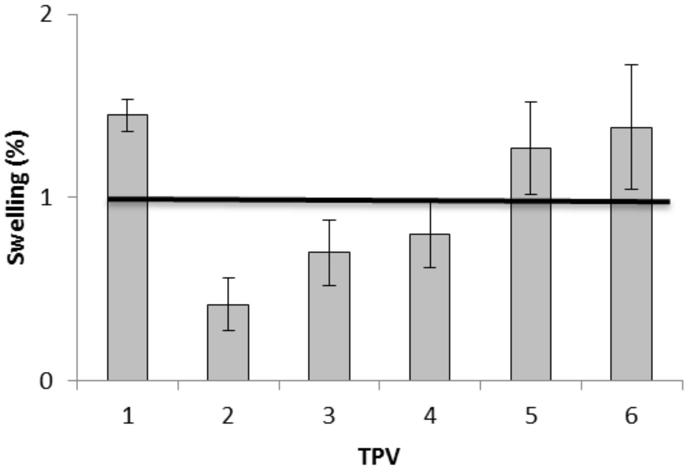
Table 4. DUNCAN test for fracture strength.

Samples	Difference between mean values	p	p < 0.05
6 vs. 2	2.124	<0.001	Yes
6 vs. 4	1.250	0.002	Yes
6 vs. 1	1.250	0.002	Yes
6 vs. 5	0.348	0.332	No
6 vs. 3	0.326	0.335	No
3 vs. 2	1.798	<0.001	Yes
3 vs. 4	0.924	0.016	Yes
3 vs. 1	0.924	0.013	Yes
3 vs. 5	0.022	0.948	No
5 vs. 2	1.776	<0.001	Yes
5 vs. 4	0.902	0.016	No
5 vs. 1	0.902	0.012	Yes
1 vs. 2	0.874	0.019	Yes
1 vs. 4	0.901	0.008	Yes
4 vs. 2	0.874	0.015	Yes

Source: Authors.

The results of swelling in oil are shown in Figure 3. In the TPV 2, TPV 3 and TPV4, the lowest values of swelling are observed; the amount of solvent absorbed in these samples was reduced. This result is important for automotive applications, since smaller the swelling, more resistant the material will be when exposed to oils and solvents. TPV samples with a degree of swelling above 1% were considered inadequate for the automobile industry (Carvalho, 2016).

Figure 3. Swelling of TPV samples in engine oil at 70 ° C / 70 h.



Source: Authors.

The ANOVA test was applied to the swelling results, Table 5, where the mean values presented statistical differences. Table 5 shows the results of parity of TPV samples. There is no statistical difference between samples 1x6, 1x5, 2x3, 2x4 and 3x4 indicating that these pairs are similar. The lowest values of swelling were found for samples 2 and 3, where there is no difference between them. The crosslink density of these samples was relevant for the processing speed.

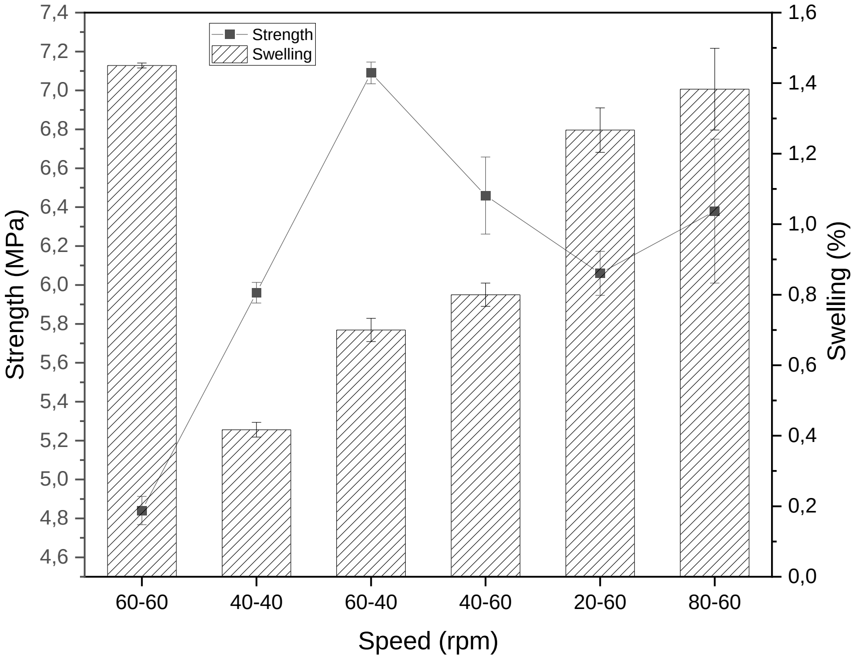
Table 5. ANOVA and DUNCAN tests for swelling in engine oil.

Group	Count	Sum	Mean value	Variance		
TPV 1	3	4.35	1.450	0.007		
TPV 2	3	1.25	0.417	0.021		
TPV 3	3	2.1	0.700	0.033		
TPV 4	3	2.4	0.800	0.033		
TPV 5	3	3.8	1.267	0.063		
TPV 6	3	4.15	1.383	0.116		
Source of variation	Quadratic Sum	Degrees of freedom	MQ	F	P-value	Critical F
Between groups	2.672361	5	0.534	11.7682	0.000274	3.1059
Within groups	0.545	12	0.045			
Total	3.217361	17				
DUNCAN TEST						
Samples	Difference between mean values		p	p < 0.05		
6 vs. 2	0.0260		<0.001	Yes		
6 vs. 3	0.0203		<0.001	Yes		
6 vs. 4	0.0183		<0.001	Yes		
6 vs. 5	0.0090		0.036	Yes		
6 vs. 1	0.0076		0.057	No		
1 vs. 2	0.0183		<0.001	Yes		
1 vs. 3	0.0127		0.007	Yes		
1 vs. 4	0.0107		0.016	Yes		
1 vs. 5	0.0013		0.721	No		
5 vs. 2	0.0170		<0.001	Yes		
5 vs. 3	0.0113		0.011	Yes		
5 vs. 4	0.0093		0.025	Yes		
4 vs. 2	0.0076		0.068	No		
4 vs. 3	0.0020		0.593	No		
3 vs. 2	0.0056		0.146	No		

Source: Authors.

In Figure 4 is observed the behavior in the swelling and strength, both properties increased with the processing speed. Therefore, the reduction in processing speed during the dynamic vulcanization process results in TPV with higher mechanical performance (Carvalho, 2018).

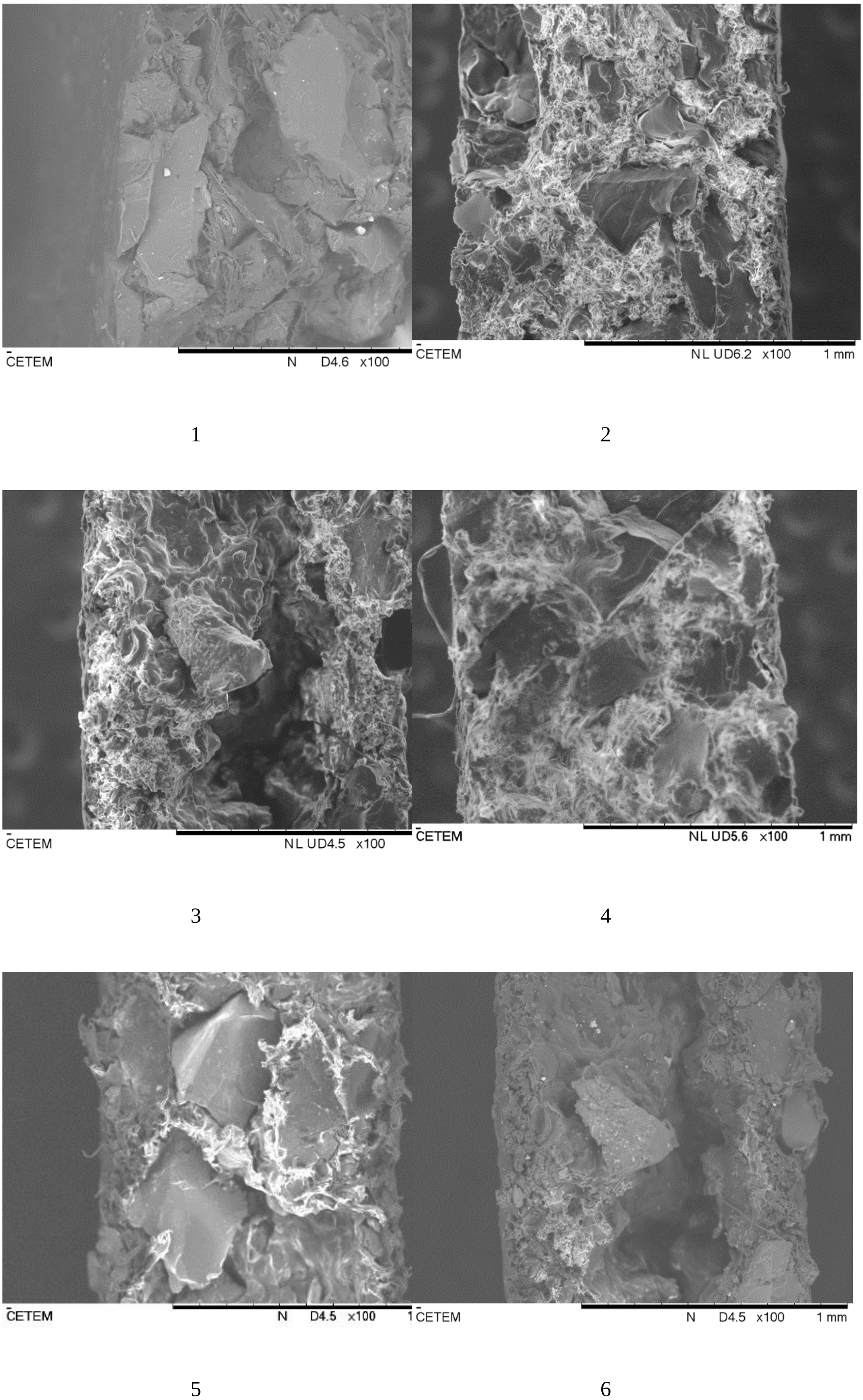
Figure 4. Fracture strength and swelling in oil vs processing speed.



Source: Authors.

The scanning electron microscopy analysis was performed on the samples after the tensile test; the images were obtained to evaluate the influence of the processing speed on the final morphology of the TPV samples, Figure 5. There were no considerable variations in the final morphology of the fractured samples. Araújo et. al. (1997) analyzed the effect of the granulometry of vulcanized residues in mixtures with thermoplastics, observing little or no change in their mechanical properties and morphology. The increase in tensile strength of TPV samples with the change in speed is due to the increase in crosslinking density, not to changes in final morphology.

Figure 5. Micrographs of TPV samples.



Source: Authors.

4. Conclusion

Variations in processing speeds (during vulcanization and torque stabilization) directly affect the final properties of the TPV samples. The reduction in processing speed during vulcanization increases the viscosity of the material, lowering the flow rate. By reducing the processing speed, the tensile strength increases. The low swelling was caused by the increase in crosslinking. The TPV samples present values of elastic modulus superior to the viscous one, due to the presence of tire powder which alters the rheological behavior. Among the values elastic modulus, no variation was observed between the samples studied, as the material's morphology was not modified. The increased properties of TPV samples are attributed to new crosslinking of the elastomeric phase during dynamic vulcanization. News processing will be done to characterize the morphology before, during and after the dynamic vulcanization.

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