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Devulcanization of Elastomers and Applications

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Abstract

In no other phase of human development was produced such amount of waste as currently. Its composition and quantity are directly related to the way the population lives, socioeconomic condition and the ease of access to consumer goods. The irregular disposition of such waste may cause harmful environmental impacts. One of the most dangerous solid wastes is the vulcanized rubber, which, besides having high natural degradation time, has many chemical additives on its formulation and the possibility to store rain water when disposed in landfills and may become a breeding place for vectors. So, recycling comes against this problem and devulcanization is a way of recycling that restores the fluidity of the rubber. One of the applications of this devulcanized rubber is in the production of polymeric blends. Devulcanization of rubbers, the application of this material in polymeric blends based on thermoplastic/recycled rubber, and the parameters involved during the processing of these materials will be addressed in this work.

Keywords: sustainability, recycling, devulcanization, revulcanization, polymer blends

1. Introduction

Elastomers consist in a class of materials widely used today in many fields of application. Their typical properties such as high levels of elasticity and damping are what make this class so important. For this, the elastomers must, first, go through a complex process known as vulcanization [1]. Chemically, it is the process in which the molecular chains of rubber, independently, are joined by chemical bonds forming primary cross-linkings, which lead to the formation of a three-dimensional network in the material. This structural organization allows to maintain or increase the elastic properties and to reduce the plastic behavior of the material. The elastomer becomes insoluble and with greater mechanical resistance, different from nonvulcanized elastomer.

However, while the vulcanization provides improvements in the properties of the elastomers and with it the possibility of a wide use as consumer goods, it brings difficulties for recycling after the use, once the vulcanized polymer becomes a thermosetting, making it impossible for subsequent molding into another product.

Presently, a key expression is the sustainable development, which refers to the responsible search for economic and material development without damaging the human being and the environment, using natural resources wisely so that future generations will not be harmed. Among the related subjects are the waste problem, and one of the possible solutions is the recycling of recyclable materials (especially postconsumer polymeric materials) [2].

Among the most harmful polymeric materials include those that contain heavy metals fillers, plasticizers and vulcanized elastomers. The latter ones, for being nonreprocessable due to the presence of cross-linkings, may cause serious public health problems, since they may be accumulators of rain water when disposed in landfills (especially tires), becoming a place able to the proliferation of vectors, such as the *aedes aegypti* mosquito, transmitter of dengue, chikungunya and zika (and day by day the scenario is getting worse, since new diseases transmitted by the same vector are being discovered) [2]. Adding, vulcanized elastomers are materials which require long periods of time to degrade naturally due to their structure of cross-linkings, presence of stabilizers and other additives in their formulation [3], making them infusible and difficult to be reprocessed. Besides, these are considered high value-added materials, due to the range of chemical additives on the formulation, making their discard a waste. According to Imbernon and Norvez [4], "Because of the scarcity and increasing prices of natural resources, and of the growing environmental awareness, waste management has become a crucial issue in today's society."

Presently, the high growth of consumption and inadequate disposal of polymeric materials have increased problems related to solid urban residues. The ideal would be that 100% of all the polymeric materials used around the world was recycled, assisting in sustainable development. However, the real scenario is quite different for bumping into numerous difficulties, which generates serious environmental, public health, economic and governmental problems [2]. In this way, devulcanization is against this serious global problem, seeking a viable reuse way of postconsumer vulcanized elastomers.

This work aims to discuss about devulcanization of vulcanized elastomers and some possible applications of this material, with focus on the preparation of polymeric blends containing recycled elastomers (based on thermoplastic and recycled rubber), and the factors that affect the properties of the final material, with the purpose of being a useful literature serving in obtaining final materials applicable in consumer goods.

2. Devulcanization of elastomers

A very prominent form of recycling is the devulcanization, which is the process of total or partial cleavage of the cross-linkings formed during the initial vulcanization [5–8]. Despite returning to the material its flow capacity, the higher the devulcanization degree, the greater

the breakage of the main polymer chain links. The effect of this degradation is the significant reduction of stiffness and other mechanical properties when the material is revulcanized (second vulcanization process). Therefore, for the choice of the parameters of the devulcanization process, must be taken into account the balance between the processability and mechanical properties of the final material [9].

The literature presents several works that discuss the different methods used to devulcanize rubbers, as mechanical and chemical mechanical method [10–12], microwaves method [9, 13–19], ultrasound method [20–22], chemical method [23, 24], microbial method [25, 26], and still other methods as bioreactor and spraying for solid-state shear [27, 28]. Subsequently, when the goal is to use the recycled elastomer in the production of a blend, the role of devulcanization is to increase the interaction between the raw and recycled material, reducing the degradation of the properties of the finished product, and making it possible to increase the amount of recycled elastomer in the compound raw phase/recycled phase [29].

A well-established way of recycling vulcanized elastomers is through the production of polymeric blends, that is, physical mixes of two or more polymers that can be miscible or not. As two or more properties of the polymers can be combined, the blends have been studied widely with the aim of improving the physical properties compared to neat polymers, that is, obtain materials with additional properties, and minimal loss of original properties [30], as well as being more economically viable to unite two existing polymers to synthesize another nonexistent [31], for the creation of a new molecule.

A plethora of polymeric blends composed of elastomers can be obtained. There are basically two types of polymeric blends composed in at least one of the phases an elastomer: blends composed of two or more types of elastomers (elastomeric blends) and blends composed of a thermoplastic phase and the other elastomeric. These can be of two types: when there is a high concentration of elastomer (thermoplastic elastomers—TPEs) and when there is low concentration of elastomer (toughened plastic). In all cases, the goal is to obtain materials with desired properties, additional to the properties of the neat materials.

In addition to restore the fluidity of the rubber, devulcanization is able to chemically change the structure of the material [19]. All these changes certainly affect its revulcanization. So, revulcanization is still more complex than the vulcanization itself, since other parameters influence it. And especially in the production of dynamically revulcanized blends (blends based on thermoplastic and recycled rubber in high concentrations, in which the last phase was revulcanized during processing), beyond this, others related to processing get place, to be discussed ahead.

According to Karger-Kocsis et al. [32], among the vast number of possibilities concerning blends containing ground tire rubber (GRT), value-added application can especially be expected in thermoplastic elastomers, and rubber combinations. In the literature, several studies about elastomeric blends with satisfactory results are easily found [16, 33]. Despite the great advances obtained by this type of material, a great difficulty, or even a disadvantage, is that the rejects produced during processing are not easily recycled and reworked and may cause environmental problems due to incorrect disposal of this waste. On the other hand, rejects of TPE blends can be easily reworked, which presents some remarkable advantages,

being the most important one the ability of being processed as a thermoplastic, presenting the performance of a vulcanized elastomer. However, even today with all the progress achieved in the field of science and technology, the use of recycled elastomer in this type of blend remains a major challenge. Even so, this class of polymeric blends represents a major current trend for the use of recycled elastomers and will be addressed in more details in the following section.

3. Thermoplastic elastomers

Thermoplastic elastomers contain high concentrations of elastomeric phase (usually above 50%), combining the processability of thermoplastics and the functional performance of vulcanized rubbers at room temperature [34–37]. There are three distinct classes of thermoplastic elastomers, namely: block copolymer, thermoplastic/dynamically vulcanized elastomer blends—thermoplastic vulcanizates (TPVs) and ionic thermoplastic.

The unique combination of properties allows the processing of TPEs in conventional equipment used for processing of thermoplastics in processes such as injection and blow molding, film production and extruded profiles, keeping the elastomeric properties. Such behavior is attributed to their structures that contain both flexible and elastic fields of high extensibility with low glass transition temperature (T_g), and rigid low extensibility areas with a T_g and/or crystalline melting temperature (T_m) high [38].

The key advantages of TPEs include [38]: (i) their ability to become fluid with heat and then hardening with cooling gives manufacturers the possibility to produce articles with rubber behavior using equipments commonly used in the processing of thermoplastics. (ii) Little or no mixing of additives necessary for the production of TPEs. The majority is ready for manufacturing. Rubbers, however, require the mixture of all the additives. (iii) TPEs, once prepared, do not need vulcanization stage. Their processing consists of fewer stages than the processing for obtaining a vulcanized rubber. (iv) Scraps produced in the production process can be reprocessed. Scraps generated in processing of vulcanized rubbers, however, have their potential reuse limited, and the cost of its production is higher, due to the loss of material and disposal cost of scraps. (v) Thermoplastic processing consumes less total energy by having a more efficient processing and smaller time cycles.

A particular type of TPE blend, thermoplastic vulcanizate blend, known as TPV, is largely adopted when using devulcanized elastomers, due to its typical features and properties. It will be described in more details in the following sections.

4. Thermoplastic vulcanizate blends

TPV is a type of TPE produced via dynamic vulcanization of the elastomeric phase of an immiscible blend of thermoplastic in molten state and elastomer under high shear rates [39–43]. TPVs are materials widely used in automotive [12, 44] and electronics industries, civil construction,

wiring and cables, biomedical products [12, 45–47], among others. Due to the high applicability of this kind of blend, the use of recycled rubber can be useful and worth being studied.

Dynamic vulcanization is the vulcanization of the elastomeric phase in a molten mixture with other polymer(s) [48]. The process produces a cross-linked polymer dispersion in a continuous polymer matrix phase not cross-linked [38, 40, 49–52]. The continuity of the thermoplastic phase provides the thermo-plasticity and mechanical resistance necessary to blends [53], while the dynamically vulcanized rubber particles give elasticity, flexibility and stability [36, 46, 54]. The process can be described as follows: after enough fusion-blend of thermoplastic and rubber, vulcanization agents are added. The vulcanization of rubber phase occurs with a continuation of the mixture. After the output of the mixer, the cold blend can be chopped, extruded, injected, molded, pelletized, etc [43, 52].

The literature presents a vast number of works showing the differences in the properties of polymer blends resulting from dynamic vulcanization, among them: improvement in mechanical properties [55], greater thermal stability [56], minor swelling of the extruded [43], better reprocessability [46, 57], increase in the service temperature [49, 55], greater weather resistance [12] among others, depending on the analyzed system. Several papers also feature improvements in mechanical properties as a result of the dynamic vulcanization, but through the use of compatibilizing agents [36, 48, 58–60] as a result of greater refinement of morphology [34, 61], in general. Among the improvements, it is also found reduced permanent elongation, increased fatigue resistance, greater stability of morphology and better chemical resistance.

TPV containing recycled elastomers, a special issue nowadays as a possible solution to the problem of solid urban residues, especially vulcanized rubbers, will be addressed in the following section.

5. Thermoplastic vulcanizate blends containing recycled elastomers

The reuse, recycling and recovery of waste of cross-linked rubbers are of great scientific and technological interest. As discussed previously, there is great difficulty in recycling, as they are infusible and insoluble materials, which have difficult processing [57] due to their structure of cross-linkings. In this context, many efforts have been made regarding the preparation and characterization of polymer blends containing GTR and various thermoplastics, as an alternative to recycling [62, 63].

The properties of these materials depend on the concentration of the recycled material, as well as the adhesion among phases [64, 65]. According to Zhang et al. [66], the adhesion between the GTR and the polymer matrix is usually very weak due to the three-dimensional structure of the cross-linkings, in the case of blends, in which the GTR is just ground. Cañavate et al. [63] report that the lack of adhesion among phases is due to the large particles of GTR, their superficial characteristics and structure of cross-linkings, hindering their adsorption by molecules of the thermoplastic matrix, being that the use of only ground GTR into blends makes

the processing a difficult step [67]. For Kumar et al. [68], for the production of TPVs containing recycled rubber, the addition of a raw rubber or the devulcanization (at least partial) of recycled material is prerequisites. The devulcanization improves the compatibility between GTR and the matrix [4]. However, despite all the difficulties presented by Cespedes et al., "The use of GTR is an excellent option for reducing the cost of TPVs, and GTR is an environmentally friendly alternative because of its upcycling applications" [69].

In order to improve adhesion and interaction among phases, many authors have used compatibilization techniques [48, 66, 70], devulcanization of elastomeric phase [12, 20, 57, 66, 71–74], addition of a third elastomeric phase or replacing part of recycled rubber for a raw one [53, 63, 68, 69], functionalization [75], filler addition [47, 70, 74], among others, beyond the dynamic vulcanization, which notoriously increases the adhesion and interaction among phases of the blends [20, 34, 55, 57, 68, 76]. Additionally, the dynamic vulcanization in blends containing recycled material gives them greater added value [37].

The next section will present the stages involved during the evolution of morphology of thermoplastic vulcanizate blends and some important parameters able to influence the development of the final morphology of these blends.

6. Evolution of the morphology of thermoplastic vulcanizate blends during processing and important parameters

The final morphology of a blend is achieved during its processing, so it is a crucial stage in getting the final desired properties, since they are consequence of its morphology.

Many factors can change the morphology of polymer blends during processing such as temperature, residence time (processing on extruders), intensity of the mixture (speed of the extruder and setting of the screw), composition of the blend, viscosities and elasticities ratio, and interfacial tension among the phases [77]. In this way, the final morphology of immiscible polymer blends depends on the properties of the individual components, as well as processing conditions [78, 79].

Regarding the parameters related to the processing, the literature presents several works in which the processing variables are changed and analyzed [44, 55, 57, 72, 80–89].

As an important example of processing variable, temperature should be close to the T_m of the thermoplastic phase (or a little greater) [44] and be able to activate the vulcanization reaction of the elastomeric phase [46]. It is known that the behavior of vulcanization of the elastomeric phase varies according to the adopted temperature, besides that it should not be high enough so that, combined with the high shear rates involved in the process (especially in twin screw extruders), promotes high level of degradation in both phases of the blend. However, no matter the studied parameter, all of them are very important, since they are able to directly affect the final morphology of blends and, then, their final properties.

Figure 1 shows in a schematic way the transformation of the morphology of thermoplastic vulcanizate blends during processing. According to the schema, initially a rubber-thermoplastic blend is formed, with co-continuous morphology and rubber phase non-cross-linked (stage A). In the next stage, rubber phase becomes stretched and strongly deformed due to the beginning of dynamic vulcanization. A rubber-thermoplastic blend is formed, with cocontinuous morphology as well (stage B). Due to dynamic vulcanization, rubber phase is able to break up in the following stage (stage C). So, a TPV is formed, the rubber phase is cross-linked and is dispersed in thermoplastic phase. In the last stages (stages D and E), rubber particles have the distribution improved on the matrix phase.

On the whole, the blend completely changes its morphology, from co-continuous to dispersed phase. However, so that the blend presents typical final properties for noble uses, the processing must be carefully analyzed and optimized. In the case of using an extruder, the analysis becomes more complex because of the large number of variables involved, but at the same time, it becomes a big advantage in the improvement of the technique. A good example of possible parameter change in an extruder is the number of feeders.

When producing a thermoplastic vulcanizate blend in an extruder containing two feeders, it is possible to introduce independently each phase through each one of the feeders. In the case of blends in which the elastomeric phase was previously mixed to vulcanization additives, this can be added in the second feeder, whereas, in the case of elastomeric phase not be previously mixed to additives, the two phases of the blend can be added together in the same feeder, while the additives can be added in the second one.

The change of some processing parameters was deeply studied by de Sousa et al. [61]. The authors produced dynamically revulcanized blends based on 60 wt% of devulcanized GTR (GTR5.5) and 40 wt% of high density polyethylene (HDPE), by using a twin screw extruder. Processing parameters such as screw speed and feeding mode were varied. In the production of blends using only one feeder, both HDPE and devulcanized rubber were added together. For blends produced with two feeders, the HDPE phase was added in the first feeder and the GTR phase in the second one. Vulcanization additives were previously added to the GTR phase. The authors proved the importance of knowing previously the rheological properties of the rubber phase, as well as matching these properties to the processing conditions.

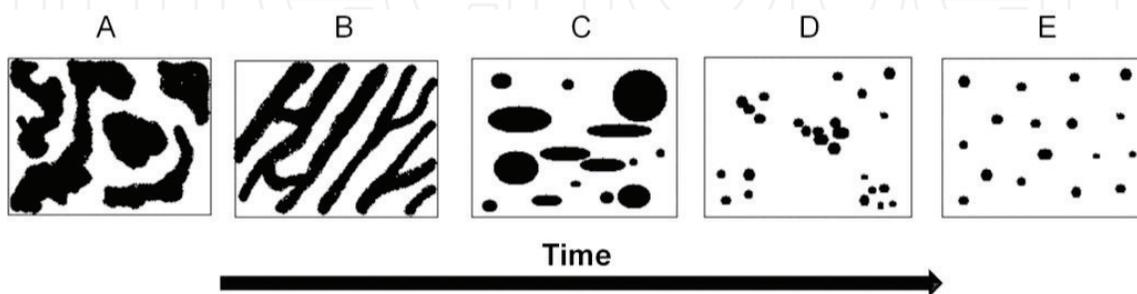


Figure 1. Schematic morphology transformation during the dynamic vulcanization of polymeric blends. The black part represents the elastomeric phase, and the white represents the thermoplastic phase.

According to de Sousa et al. [61], overall, the effects of screw speed on the mechanical properties were not significant. Furthermore, the mechanical properties of the blends were far below those of classical TPVs, probably because of the poor compatibility and adhesion between GTR5.5 and HDPE. In general, the blends produced by using the second feeding mode obtained a finer morphology.

Figure 2 shows some vulcanization parameters involved in the processing of dynamically revulcanized blends, as well as the scheme of a probable evolution of morphology during processing. The screw profile is for feeding mode 2, since it produced finer morphology and consequently slightly higher mechanical properties.

According to **Figure 2**, at point 1 of the extruder, there is only physical mixing among the phases and there is no revulcanization of the GTR5.5. At the beginning of the second high shear zone (point 2), the revulcanization reaction gets place (the residence time of the rubber from its introduction in the extruder to this point is about the same of ts_1 (scorch time of the reaction)) and, around this point, the blend presents a cocontinuous morphology, in which the elastomeric phase is stretched in the flow direction [61].

Due to the high elongational flow in this zone (use of mixing or kneading blocks), the rubber along vulcanization process can deform (due precisely to the three-dimensional structure formation of cross-linkings and consequent increase in viscosity of the blend [76]) enough for

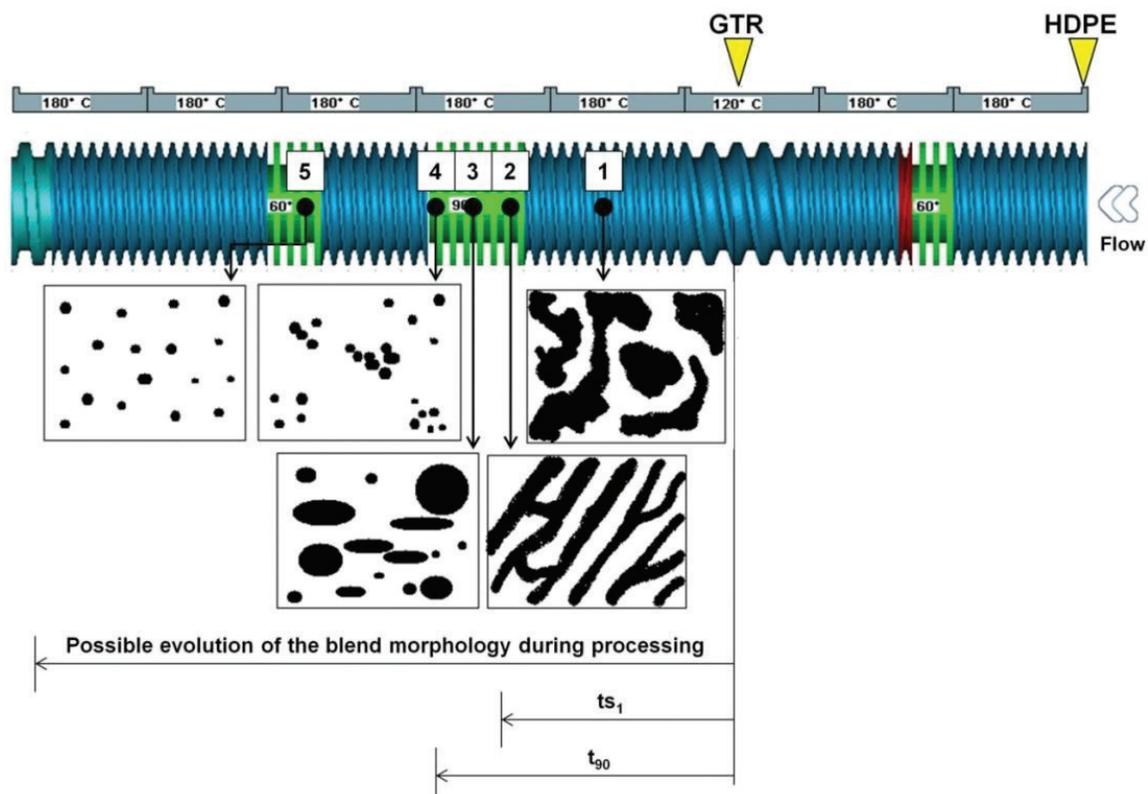


Figure 2. Screw profile relative to feeding mode 2 used in the preparation of the blends, showing the schema of the possible evolution of the morphology and rheology of the elastomeric phase involved during processing. Reprinted with permission from Ref. [61]. Copyright 2017, John Wiley and Sons.

break of their particles in other smaller than the ones before [60] and phase inversion may occur. At this stage, the overall viscosity is increased (the elastomeric phase with high elasticity is stretched and breaks into smaller particles due to high shear rates, intense elongational flow and high elasticity generated by cross-linkings (point 3), resulting in high mechanical stresses [61]. The elastomeric phase deforms until it reaches a critical tension, when it breaks up into small particles [90]. The biggest changes of morphology occur in the first high-shear region, in which both phases are together [39, 91–93].

At point 4, still under the effect of high shear rates, rubber particles break into smaller particles, and at point 5, there is a better distribution in the thermoplastic matrix. The end of the second shear zone (point 4) refers approximately to the optimum cure time (t_{90}) of the elastomeric phase which, in the case of GTR5.5, is 44 s. The residence time of rubber from its introduction in the extruder to the end point of the reaction must be equivalent to t_{90} , and this point should be in a high shear zone of the extruder for breakage of rubber particles in micrometric dimensions [61].

In the point 5, cross-linked rubber particles, at this moment, have a very high viscosity and elasticity, and it occurs only the distribution of the particles in the matrix, improving macroscopic homogeneity, being necessary the use of mixing elements. It must be pointed out that the dispersion process occurs instantly with the vulcanization reaction, and both processes are influencing each other. The rapid increase in the cross-linkings of rubber also leads to an increase in the surface tension of the elastomeric phase. Cross-linkings and the high superficial tension will reduce the driving force for the coalescence and, therefore, the characteristic of the particles of vulcanized rubber phase will be preserved, even in a new mixture after the completion of the cross-linking process [67, 90].

The increase of interfacial tension as a result of cross-linkings and the high elasticity of the particles produce the relaxation of the deformed structures; in an ideal case, spherical particles are formed. Due to the high viscosities ratio, elastomeric cross-linked particles can only be distributed, and no longer dispersed on a new mixing cycle [90]. In agreement, some results [94] revealed that the developed microstructure is highly affected by the type of the melt compounding process, as well as the feeding mode.

It is important to address here that, for both screw profiles used, the first mixing zone served to melt the HDPE, the second one to dynamically revulcanize the GTR and the last one to improve the distribution of the rubber particles in the HDPE. In the case of the blends produced through feeding mode 1, the high shear rate in the first mixing zone could bring about premature revulcanization of the rubber phase, since the components were added together. As the length of this zone and the corresponding residence time were short, the time for the reaction to go to completion was longer than the residence time on the zone, which probably happened in the second transport zone. Thus, the rubber domains were not satisfactorily well dispersed and distributed in the HDPE matrix. However, in the case of the blends produced through feeding mode 2, the residence time of the rubber phase inside the extruder from its introduction to the end of the second mixing zone was closer to the optimum cure time of the GTR5.5 at 180°C (43.8 s). Therefore, the mixing zone was long enough for the revulcanization reaction to go to completion and the dispersed rubber domains to have its size reduced in the HDPE matrix [61].

The blend produced by using the second feeding mode and at 250 rpm presented higher finer morphology and consequently better mechanical properties, despite the fact that the compatibility and adhesion between the phases were poor. The finer morphology is due to good match between processing conditions and rheological properties of the GTR5.5. The residence times of the GTR5.5 inside the extruder from its introduction to the respective points shown in **Figure 2** were approximately 50 and 30 s, respectively, which were very close to the values of t_{90} and t_{s1} (44 and 27 s, respectively) [61].

At this point, the presentation of some equations can be useful to understand all the modification occurred to the blends during the processing. The elongation and breakage of polymeric particles suspended in another polymer under shearing flow were first studied by Taylor [95]. According to the author, two dimensionless parameters that enable the prediction of morphology in the molten state are the number of Capillarity [Eq. (1)] and the viscosities ratio [Eq. (2)]:

$$C_a = \frac{\sigma R}{\alpha} \quad (1)$$

where σ represents the shear stress, R is the radius of the particle or drop, and α is the interfacial tension between the phases of the blend.

$$p = \frac{\eta_d}{\eta_m} \quad (2)$$

where η_d and η_m are the viscosities of the dispersed phase and the matrix phase, respectively.

If the value of C_a is small, interfacial forces dominate and the particles acquire the shape of ellipsoids. Above a critical value $C_{a\text{crit}}$ the particles become unstable and break down [96].

When two immiscible polymers are mixed to form a blend, in accordance with the principle of minimum dissipation of energy, it is expected that the most viscous polymer forms the dispersed phase and the less viscous forms the matrix phase. When this principle is satisfied, it means that the viscosities ratio [Eq. (2)] was the predominant factor in determining the state of dispersion of the blend [97]. The viscosities ratio strongly affects the development of morphology during the reaction [52].

Additionally, in order to study the development of the phase morphology and predict the inversion phase region in immiscible polymer blends, Avgeropoulos et al. [98] developed an empirical model based on torque ratio in internal mixer and volumetric fraction of each phase [Eq. (3)]. Jordhamo et al. [99] proposed a similar equation [Eq. (4)], based on the viscosities ratio:

$$\frac{\phi_1}{\phi_2} \cdot \frac{T_2}{T_1} = X \quad (3)$$

$$\frac{\phi_1}{\phi_2} \cdot \frac{\eta_2}{\eta_1} = Y \quad (4)$$

which results in the following variants morphologies:

$X, Y > 1$ —Phase 1 is continuous or matrix and phase 2 is dispersed.

$X, Y < 1$ —Phase 2 is continuous or matrix and phase 1 is dispersed.

$X, Y = 1$ —Two phases are continuous or region of phase inversion.

Where ϕ_1 , ϕ_2 are volumetric fractions, T_1 , T_2 are measures of torques at a same temperature, and η_1 , η_2 are viscosity values for phases 1 and 2, respectively [50].

According to Zhang et al. [57], soon after the end of the dynamic vulcanization, vulcanized rubber particles present a high surface tension, which agglomerate them. Therefore, it is necessary the application of high shear rates, which are generated due to the presence of mixing blocks in processing performed in extruder, as in point 5 (**Figure 2**). Also, Yao et al. [100] deeply studied the morphology evolution of bromo-isobutylene-isoprene rubber (BIIR)/polypropylene (PP) TPV blends. It was depicted that the dynamic vulcanization increases the compatibility among the phases, demonstrated by the increase in interfacial phase thickness and the decrease in interfacial tension. During the processing, single nanoparticles of elastomeric phase are being formed, and their agglomeration is getting lesser as dynamic vulcanization advances. Thus, Sararoudi et al. [101] concluded that the extent of agglomerations among the vulcanized rubber particles in the twin screw extruder not only depends on the rubber content, but also are controlled by a common agglomeration and disagglomeration mechanism which is, in turn, governed by the screw speed.

For the case of blends in which all phases are added together in the extruder in one feeder, studies show that as soon as the complete melting of the thermoplastic phase is reached, the blend reaches quickly its final morphology [39, 85] due to generated interfaces among phases. According to Covas et al. [102], the increase in the interfacial area raised soon after the melting of the thermoplastic, which induced chemical conversion and the evolution of morphology. Therefore, the choice of the parameters of the processing, the number of feeders to be used depending on the screw profile adopted is a factor of great importance. Van Duin and Machado [39] studied the dynamic vulcanization reaction of ethylene-propylene-diene rubber (EPDM)/HDPE blend through the withdrawal of peer-to-peer samples on twin screw extruder during processing. According to the authors, the cross-linking of EPDM phase began when the HDPE still was not fully melted, and the final morphology of blends was reached very quickly. The phase inversion occurred due to formation of cross-linkings. Machado and van Duin [103] analyzed the properties of EPDM/HDPE TPV blends and found that, the higher the content of EPDM, the greater the viscous dissipation, the higher the melting and, consequently, the greater the rate of cross-linkings.

The type of equipment can also alter the particle size distribution of rubber, in the case of morphology of dispersed phase. Studies show that blends produced on extruder tend to have smaller particle sizes compared to blends produced in internal mixer [20, 71, 104–106] due to the higher shear rate during processing in extruders and intensive flow field [105]. The elastomeric phase of the blends produced on extruder can also present greater cross-linking density, as verified by Sengupta and Noordermeer [104]. However, the distribution of sizes of particles is more uniform in the blends produced in internal mixer due to longer residence time and greater total shear stress, promoting the breakdown of particles [104]. According to Shahbikian et al. [105], that produced EPDM/PP blends in internal mixer and extruder, even with the shortest residence time for processing in extruders, the cure reaction occurred quickly, resulting in EPDM particles of sizes more heterogeneous and with greater cross-linking density. By combining the effects of time, temperature and shearing, the matrix phase acquires elasticity, and it is extruded into sheets. At the same time, there is a break of these

sheets due to elongational and shear forces generated in the mixing equipment. So, there is a dynamic balance between the process of breakdown of phases and coalescence.

Among other factors mentioned, the final morphology is the result of processes of coalescence and breakage of the elastomeric phase particles (in the case of blends with the morphology of dispersed phases) during processing. In the case of TPV blends containing devulcanized rubber, the devulcanization acts on the process of break, while the dynamic revulcanization acts on the reduction of the coalescence process of particles [73].

In short, the process of devulcanization makes the rubber fluid, aiding in the process of breaking what, consequently, helps in reducing the size of the particles, increases the contact area among the phases and increases the transmission of tensions. Dynamic revulcanization helps in stabilizing the morphology by inhibition of coalescence process among the particles of the dispersed phase [73]. According to Goharpey et al. [107], dynamic vulcanization can prevent the coalescence of the rubber particles from the early stage of the dynamic vulcanization.

As a conclusion, the stage of processing (dynamic vulcanization) is of extreme importance, and all aspects involved should be carefully analyzed and optimized, as they may change the final morphology of blends and, with it, completely alter their final properties [108].

7. Conclusion

The irregular disposition of solid urban residues, especially vulcanized elastomers like tires, may bring together dangerous environmental impacts. In this way, a very outstanding form of vulcanized elastomers recycling is the devulcanization. Along with a variety of possible uses, the devulcanized elastomer can be used in the formation of polymeric blends. Among a vast number of polymeric blends composed of elastomers, TPV is largely adopted when using devulcanized elastomers, due to its typical features and properties. However, parameters of processing as well as the devulcanization process itself must be considered and carefully analyzed, since they are able to dictate the final morphology of the polymeric blend and, consequently, its properties as a whole.

TPV is considered a “green” polymer, since its recyclability promotes the environmental protection and resource saving. When it is composed by a recycled elastomeric phase, it aids the petroleum sources saving, saves raw materials and energy, not harming the environment, and still being a source of income for many families who survive from the collection of recyclable materials. The production of blends composed of recycled rubber is still a major challenge for the academic community, since its final properties need to justify all energy expenditures necessary for production, in addition to being economically viable. However, attention should be given to the subject, since it is a possible solution to the problem of final disposal of urban solid waste. On the other hand, it is observed that the subject is still little explored in literature, possibly due to difficulties encountered in the production and final properties obtained.

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