SPECIAL SYMPOSIA | CIRCULAR ECONOMY OF POLYMERS

The Effect of Clays on the Mechanical Properties of Dynamically Revulcanized Blends Composed of Ground Tire Rubber/High-Density Polyethylene

Fabiula Danielli Bastos de Sousa

DOI: https://doi.org/10.51573/Andes.PPS39.SS.CEP.5

December 2024

View Online

Export Citation

The Effect of Clays on the Mechanical Properties of Dynamically Revulcanized Blends Composed of Ground Tire Rubber/High-Density Polyethylene

Fabiula Danielli Bastos de Sousa[1]

Abstract: This study examines the impact of adding Cloisite 20A and Halloysite clay on the mechanical properties of dynamically revulcanized blends composed of high-density polyethylene (HDPE) and ground tire rubber (GTR), which have been previously devulcanized via microwaves. Blends were prepared, containing different concentrations of the phases. Halloysite clay seems to have acted as a compatibilizer agent between the phases of the blends, whereas Cloisite 20A clay seems to have acted as a reinforcement in the revulcanized blends. However, slight deviations were noticed in the variations in the phases' concentrations. This study explored the possibility of utilizing end-of-life tires in polymeric blends.

Keywords: Clays, Cloisite 20A, Halloysite, Mechanical Properties, Morphology

1 The author Fabiula Danielli Bastos de Sousa (fabiuladesousa@gmail.com) is affiliated with the Technology Development Center at the Universidade Federal de Pelotas-UFPel in Brazil.:

DOI: https://doi.org/10.51573/Andes.PPS39.SS.CEP.5

Introduction

As a result of growing ecological consciousness and global concern about the continuous accumulation of end-of-life tires, the scientific community is encouraged to research alternative methods of recycling them [1]. Microwave devulcanization is a method of recycling ground tire rubber (GTR) using microwave energy to break down the cross-links. However, this method may degrade the material, so a thorough understanding of the process and its variables is crucial. When GTR is a phase of a polymeric blend, devulcanization improves the interaction between the polymeric phases. This helps reduce the deterioration of the final product's properties and increases the concentration of recycled elastomer in the blend [2].

Thermoplastic vulcanized polymeric blends require sufficient adhesion between the phases to achieve mechanical behavior similar to an elastomer. The revulcanization of the GTR phase is beneficial, but researchers have incorporated nanofillers such as nanoclays to enhance adhesion between the blend phases [3,4]. A substantial lack of literature on the issue still exists.

This work aims to analyze the influence of Cloisite 20A and Halloysite clays on the mechanical properties of dynamically revulcanized blends composed of high-density polyethylene (HDPE) and GTR. The results indicate that each clay behaved differently with Halloysite acting as a compatibilizer agent and Cloisite 20A clay acting as a reinforcement.

Materials and Methods

Materials

Ground truck tire (GTR) waste separated from non-elastomeric components; vulcanization additives: rubber accelerator TBBS (N-tert-Butyl-2-benzothiazole sulfenamide) and sulfur (vulcanization agent); HDPE (trade name IA-59 from Braskem); organically modified Montmorillonite Cloisite 20A® (Bentonit União Nordeste); halloysite nanotubes of specification #685445 (Sigma-Aldrich); and maleic anhydride grafted HDPE (HDPE-MA) Polybond® 3029 (Chemtura).

The methodology is based on earlier works [5,6].

Devulcanization of GTR and Production of the Nanocomposites

The maximum power (820 W) was used to devulcanize GTR in a conventional microwave oven that had been modified with a motorized stirring system with speed control. Approximately 65 g of the GTR sample was placed in a 250 mL glass beaker and stirred at 100 rpm for 5.5 minutes.

DOI: https://doi.org/10.51573/Andes.PPS39.SS.CEP.5

After the devulcanization process, the samples were homogenized in a laboratory two roll mill, and 1 phr (parts per hundred of rubber) of TBBS and 1 phr of sulfur were added, respectively. The resulting tacky rubber sheets were manually cut into pieces of approximately 3 mm x 3 mm to produce blends in a twin-screw extruder.

The HDPE granules were pulverized using a cryogenic mill (Micron Powder Systems, model Mikro-Bantam) and then dried in an oven at 60°C for 24 hours. To create masterbatches, they were mixed with Cloisite 20A clay (resulting in the nanocomposite HDPE/Cloisite 20A) and with Halloysite clay and a compatibilizer agent (resulting in the nanocomposite HDPE/Halloysite). The resulting nanocomposites were then dried for eight hours at 60°C in a vacuum oven.

A Werner & Pfleider model ZSK 30 co-rotating twin-screw extruder was utilized to prepare the nanocomposites. The processing temperatures were as follows: 160°C (zone 1), 170°C (zone 2), 180°C (zone 3), 190°C (zone 4), 200°C (zone 5), and 210°C (zone 6). The final concentrations of clay and compatibilizer agent (when using Halloysite clay) in the matrix were both five wt%.

Production of the Blends in Twin-Screw Extruder

A Thermo Scientific twin-screw extruder, model Process 11, was equipped with two feeders to prepare the blends. The temperatures of the barrel zones were set at 180°C, except for the third zone in the second feeder, which was set at 120°C to facilitate the introduction of the rubber phase (Figure 1). The screw speed was set to 250 rpm.

The materials were taken directly from the extruder die and injected using a 12cc Explore micro injection molding machine. The temperature of the injection unit was set to 180°C while the mold temperature was maintained at 45°C. The material inside the mold was maintained at 15 bars for 10 s. The mold dimensions were in accordance with ASTM D 412 type A.

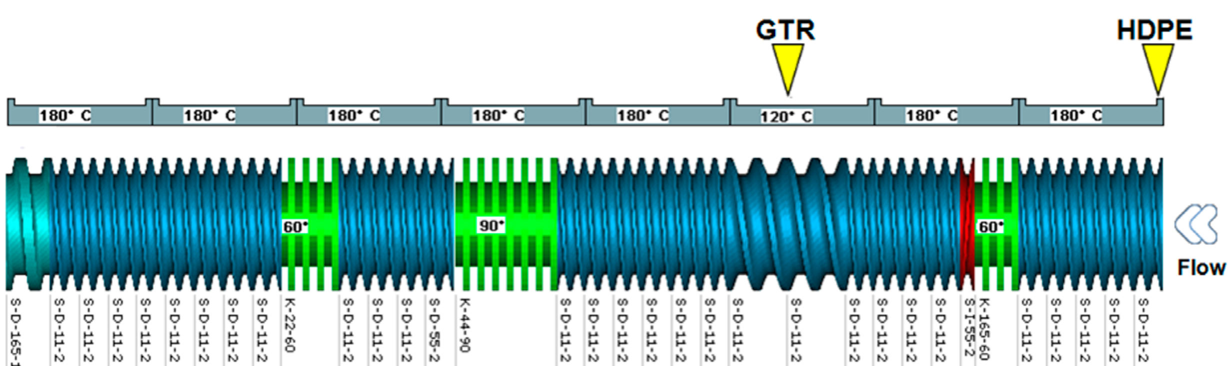

Figure 1. Screw profile employed in the processing of the polymeric blends.

DOI: https://doi.org/10.51573/Andes.PPS39.SS.CEP.5

The nomenclature of the samples is X GTR Y+ad/Z HDPE+W. In this notation, 'Y' represents the time of exposure of the GTR to microwaves, '+ad' the presence of vulcanization additives in the sample, and 'X' and 'Z' the amount of GTR and HDPE in the sample (in mass), respectively. 'W' represents the presence of clay, in which '20A' corresponds to the presence of the Cloisite 20A and 'Hal' corresponds to Halloysite.

Morphology and Tensile Properties

The specimens for tensile tests were cut and cryogenically fractured. They were then dried and coated with gold using a sputter coater. The morphology of the blends was analyzed using a Scanning Electron Microscope (SEM) model JMS-6701F–Jeol.

The mechanical properties of the samples were measured using a Universal Testing Machine Instron 5569 equipped with a 50 kN load cell. The test speed was 50 mm/min.

Results and Discussion

The SEM images of the samples are shown in Figure 2.

The revulcanized blends appear to have better dispersion of GTR particles in the matrix because of the addition of clays, especially Halloysite clay. This clay acts as a compatibilizer agent between phases, leading to a noticeable enhancement in particle dispersion in blends containing 80% GTR. Halloysite clay also seems to have enhanced the toughness and roughness of the HDPE phase. Li et al. [7] added an unidentified powdered rubber scrap, consisting of a polar and another apolar rubber, to a blend of ethylene-octate copolymer (POE) and HDPE, which acted as a filler. A significant enhancement in the toughness of the HDPE phase was observed. The authors proposed two potential causes for this increase: the POE particles varied in size from submicron to micron and were finely dispersed throughout the matrix; and the POE capsized the particle of the fillers on the surface, increasing the matrix's deformation ability around the fillers and its toughness. In this study, the first possibility was observed, while the second possibility may have occurred in the case of blends containing Halloysite clay.

In general, it was shown that the polymeric blends did not have satisfactory mechanical properties (Figure 3), even when the particles were more evenly dispersed in the matrix. This was particularly evident in the low elongation at break values. Upon analyzing the SEM images of blends at low amplifications, it was observed that, overall, GTR particles were well dispersed, but poorly distributed in the thermoplastic matrix. The analysis was conducted using cryogenic breakage of dumbbell-shaped tension tests, which were injection molded. Therefore, the morphology was likely influenced by the injection process.

DOI: https://doi.org/10.51573/Andes.PPS39.SS.CEP.5

The mechanical properties of the blends containing Cloisite 20A significantly decreased (as shown in Figure 3). This decrease can be attributed to voids between the GTR particles and the matrix, indicating a lack of adhesion between the phases (Figure 4). Babu et al. [8] also observed this behavior in vulcanized thermoplastic blends EOC/polypropylene (PP), where particle detachment led to poor physical properties. In regions with a lower concentration of rubber particles, white lines are visible on the fractured surfaces due to stretch-induced crystallization, suggesting that the clay has acted as a nucleation agent in the HDPE phase [9].

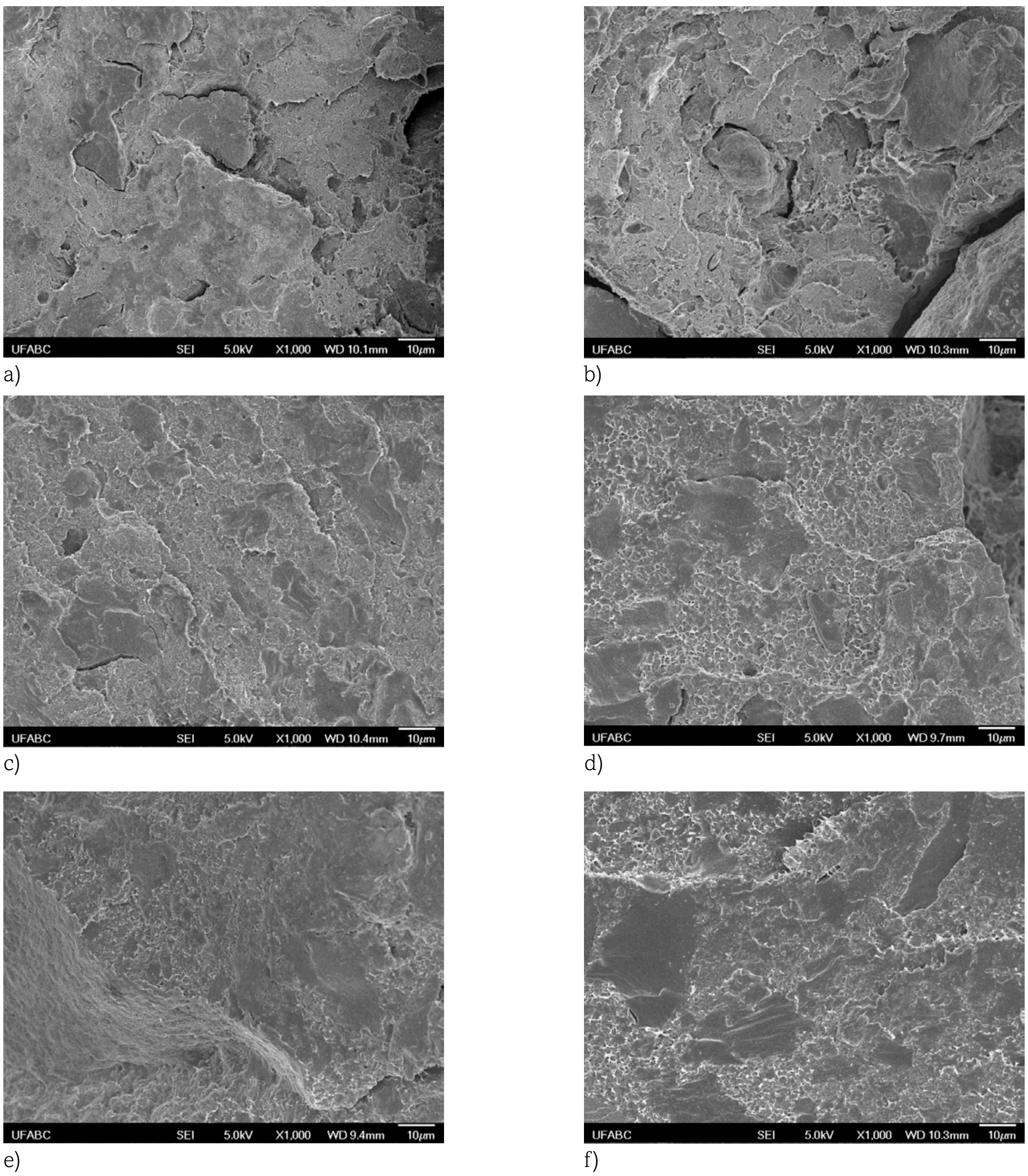

Figure 2. SEM images of the blends: (a) 60GTR5.5+ad/40HDPE, (b) 60GTR5.5+ad/40HDPE+20A, (c) 60GTR5.5+ad/40HDPE+Hal, (d) 80GTR5.5+ad/20HDPE, (e) 80GTR5.5+ad/20HDPE+20A, and (f) 80GTR5.5+ad/20HDPE+Hal.

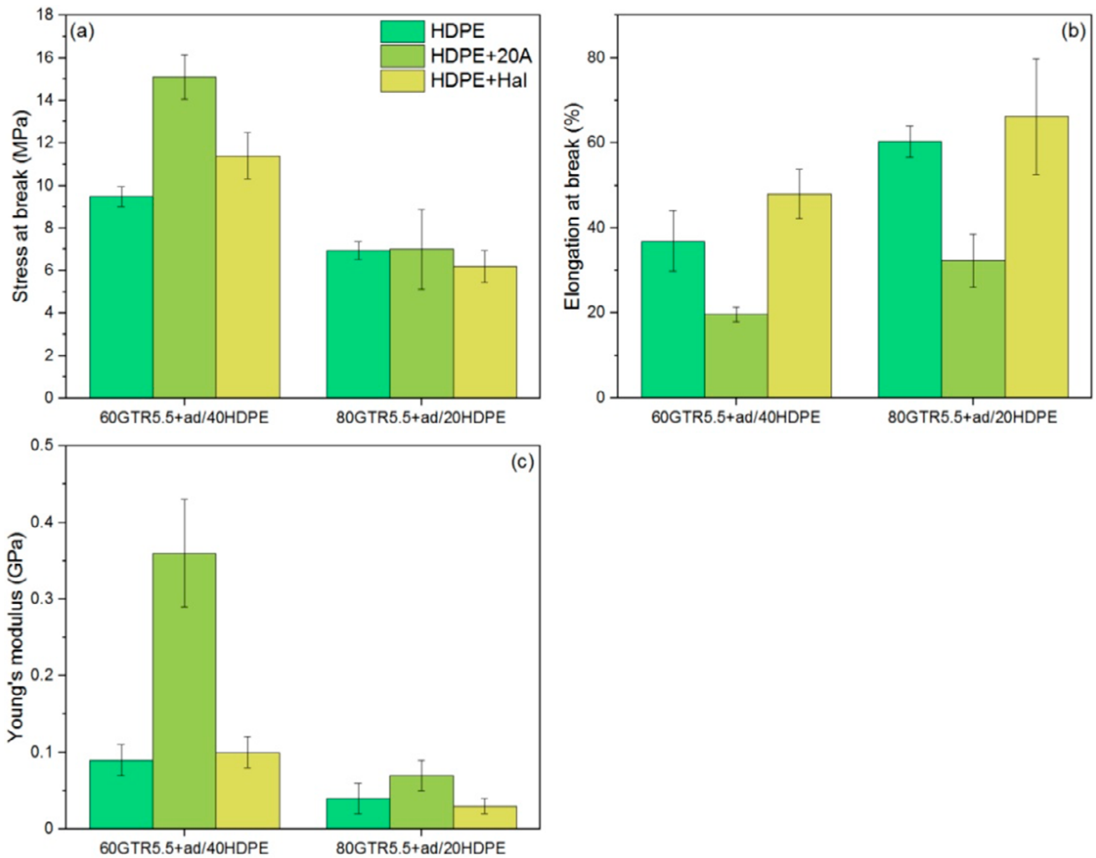

Figure 3. Mechanical properties of the polymeric blends: (a) Stress at break, (b) Elongation at break, and (c) Young's modulus.

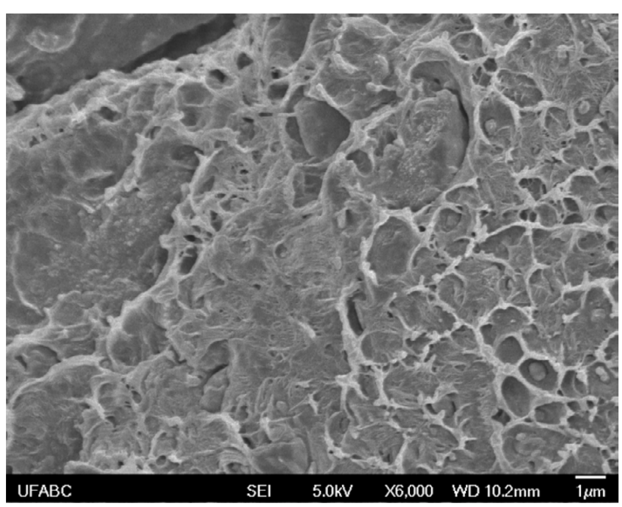

Figure 4. SEM image of the blend 60GTR5.5+ad/40HDPE+20A. The circle shows the presence of a GTR particle, and the valley between it and the matrix indicates the lack of adhesion between the phases.

Additionally, the poor mechanical properties obtained are also a result of the degradative processes that occurred during all stages of recycling GTR [10-12]. Some authors have analyzed the properties of revulcanized GTR (GTR devulcanized by microwaves and then revulcanized in a hydraulic press at 180°C) [10,11]. The results showed that the revulcanized material was oxidized and contained more carbon black. GTR, which is composed of natural rubber (NR) and styrene butadiene rubber (SBR), was degraded during all the stages of the recycling, being that NR was preferably degraded during the devulcanization by microwaves stage [12]. SBR was primarily degraded during the revulcanization stage [10,11].

Conclusion

The research results indicated that the inclusion of clays impacted the morphology and mechanical properties of the dynamically revulcanized blends composed of HDPE/GTR devulcanized via microwaves. Halloysite clay appeared to enhance the compatibility between the phases of the blends, while Cloisite 20A seemed to enhance the crystallinity of the matrix and/or reinforce the revulcanized blends.

Acknowledgments

The author thanks Prometeon Pneus, Braskem, Bentonit União Nordeste, Chemtura, and Prof. Dr. Rosario Bretas for the donation of the material. CAPES, FAPESP (process number 2010/15799-6) and CNPq (process number 201891/2011-5) for the financial support.

References

1. C. Rosales, N. A. Hocine, C. Bernal, and V. Pettarin, "Toughness improvement of LLDPE/PP blend by incorporation of GTR waste," *Polymer Bulletin*, vol. 81, no. 8, pp. 6743-6760, Jun. 2024.
2. V. Y. Levin, S. H. Kim, A. I. Isayev, J. Massey, and E. VonMeerwall, "Ultrasound devulcanization of sulfur vulcanized SBR: Crosslink density and molecular mobility," *Rubber Chemistry and Technology*, vol. 69, no. 1, pp. 104-114, 1996.
3. F. D. B. de Sousa, "Dynamic-mechanical properties of dynamically revulcanized blends composed of ground tire rubber/high-density polyethylene reinforced with different clays," *AIP Conference Proceedings*, vol. 2884, no. 1, p. 190002, Oct. 2023.
4. F. D. B. de Sousa, "Influence of the addition of clays in the rheological properties of dynamically revulcanized blends composed of high-density polyethylene/ground tire rubber devulcanized by microwaves," *AIP Conference Proceedings*, vol. 2607, no. 1, May 2023.

5. F. D. B. de Sousa, G.-H. Hu, S. Hoppe, and C. H. Scuracchio, "Influence of devulcanization and revulcanization of ground tire rubber in dynamic mechanical properties of blends ground tire rubber/high density polyethylene," *AIP Conference Proceedings*, vol. 2139, no. 090002, pp. 090002-1-090002-4, Aug. 2019.

6. F. D. B. de Sousa and C. H. Scuracchio, "Influence of dynamic revulcanization of ground tire rubber in blends composed of high-density polyethylene/ground tire rubber devulcanized by microwaves ," *AIP Conference Proceedings*, vol. 2289, pp. 020051-1-020051-5, 2020.

7. Y. Li, Y. Zhang, and Y. X. Zhang, "Morphology and mechanical properties of HDPE/SRP/elastomer composites: effect of elastomer polarity," *Polymer Testing*, vol. 23, no. 1, pp. 83-90, 2004.

8. R. R. Babu, N. K. Singha, and K. Naskar, "Effects of mixing sequence on peroxide cured polypropylene (PP)/ethylene octene copolymer (EOC) thermoplastic vulcanizates (TPVs). Part. I. Morphological, mechanical and thermal properties," *Journal of Polymer Research*, vol. 17, no. 5, pp. 657-671, 2010.

9. Y. Tsai, J. H. Wu, Y. T. Wu, C. H. Li, and M. T. Leu, "Reinforcement of dynamically vulcanized EPDM/PP elastomers using organoclay fillers," *Science and Technology of Advanced Materials*, vol. 9, no. 4, 2008.

10. F. D. B. de Sousa, A. Zanchet, and C. H. Scuracchio, "From devulcanization to revulcanization: Challenges in getting recycled tire rubber for technical applications," *ACS Sustainable Chemistry & Engineering Journal*, vol. 7, no. 9, pp. 8755-8765, May 2019.

11. F. D. B. de Sousa, A. Zanchet, H. L. Ornaghi Júnior, and F. G. Ornaghi, "Revulcanization kinetics of waste tire rubber devulcanized by microwaves: Challenges in getting recycled tire rubber for technical application," *ACS Sustainable Chemistry & Engineering Journal*, vol. 7, no. 18, p. 15413-15426, Aug. 2019.

12. F. D. B. de Sousa, C. H. Scuracchio, G. H. Hu, and S. Hoppe, "Devulcanization of waste tire rubber by microwaves," *Polymer Degradation and Stability*, vol. 138, pp. 169-181, 2017.