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THERMAL STABILITY AND MORPHOLOGICAL CHARACTERISTICS OF THERMOPLASTIC VULCANIZATES FILLED WITH SEPIOLITE/CALCIUM CARBONATE HYBRID FILLER

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Abstract. This study investigates the thermal stability, mechanical performance, and morphological characteristics of thermoplastic vulcanizates (TPVs) derived from waste recycled polyethylene (RPE) and natural rubber (NR), incorporating calcium carbonate ($CaCO_3$) and sepiolite as a binary hybrid filler system at varying compositional ratios. The TPVs were fabricated via dynamic vulcanisation on a two-roll mill and subsequently compression-moulded. Thermogravimetric analysis (TGA) conducted in static air revealed that the incorporation of the $CaCO_3$/sepiolite hybrid filler system substantially enhanced the thermal stability of the TPVs. The onset degradation temperature ranged from 230.35 °C in the unfilled control to 472.60–579.64 °C in the filled formulations. Tensile testing showed that the formulation comprising $CaCO_3$ at 35 pphr and sepiolite at 15 pphr ($CaCO_3$35/Sep15) yielded the most favourable mechanical properties, achieving the highest tensile strength of 3.024 MPa and a percentage elongation at break of 467%, values markedly superior to those of the unfilled control (2.256 MPa and 150%, respectively). Scanning electron microscopy (SEM) confirmed that the progressive substitution of $CaCO_3$ with sepiolite resulted in progressively improved filler dispersion within the TPV matrix, attributable to the fibrous morphology and active silanol surface groups of sepiolite, which mitigated $CaCO_3$ agglomeration and enhanced filler–matrix interfacial compatibility. These findings establish $CaCO_3$/sepiolite hybrid filler systems as a technically viable and environmentally responsive strategy for enhancing the thermal and mechanical performance of waste-derived thermoplastic vulcanizates, with potential application in automotive, construction, and consumer goods sectors.

Keywords: Dynamic Vulcanization, hybrid filler system, recycled polyethylene, thermal stability, and waste valorisation.

1.0 Introduction

Elastomers in green states have better properties, but their three-dimensional network makes them difficult to recycle. (Innes *et al.*, 2022). Natural rubber is a bioresource elastomer from the terpenes family used to produce belts, shoe soles, and truck tires. (Yajima et *al*, 2019). Thermoplastics, on the other hand, lack the elasticity and flexibility of elastomers; they are not used for dynamic applications (Bhattacharya, Chatterjee, and Naskar, 2020). Polyethylene is a single-use polymer

that has caused environmental pollution (Celik et *al*, 2019). Thermoplastic vulcanizates are a class of thermoplastic elastomers made from the mechanical blending of elastomers and thermoplastics via melting techniques. Thermoplastic vulcanizates possess the exceptional properties of conventional elastomers and are adaptable to thermoplastic processes (Drobny, 2014). Natural rubber and waste polyethylene are both nonpolar polymers with poor thermal stability (Al-tarbi *et al.*, 2022). Blending polymers tends to improve tensile strength, chemical resistance, impact resistance, e.t.c. The thermal stability of polymers could be enhanced by incorporating fillers into the blends (Alghamdi, 2022; Mofokeng and Luyt, 2015). Fillers are the most important additive in rubber processing, which have a significant influence on the physico-mechanical properties of vulcanizates. Specifically, fillers have been widely used to modify various polymers such as polyethylene, polylactic acid, polypropylene, and others due to their wide availability, low cost, environmental friendliness, and other properties (Miao *et al*., 2023; Feng and Qian, 2023; Wang *et al*., 2019). One of the popular mineral fillers is calcium carbonate. Moreover, among fillers such as mica, talc, carbon black, and calcium carbonate ($CaCO_3$), $CaCO_3$-based fillers are preferred and widely used due to their higher mechanical strength, thermal properties, low cost, and ease of access (Wang *et al*., 2019; Dizaj *et al*., 2015). On the other hand, $CaCO_3$, a non-reinforcing low-cost mineral filler used in polymer processing, is obtained from sedimentary rocks (Sampath, Edirisinghe, and Egodage, 2016). It is sometimes treated to enhance its dispersion into polymer matrices and improve its properties. According to recent literature, the incorporation of $CaCO_3$ as a filler improved the properties of polymer matrices. The thermal stability of polypropylene was improved at a loading of 20 wt% $CaCO_3$, compared to pristine polypropylene. (Essabir *et al.*, 2017). Polypropylene filled with nano-$CaCO_3$ had a significant impact strength and elastic modulus, compared to neat polypropylene. The enhanced properties were attributed to thermal treatment of the composites, as $CaCO_3$ nanoparticles alone could not impart the desired properties because of poor spherulite morphology (Do Nascimento, Eiras, and Pessan, 2016). The impregnation of nano-$CaCO_3$ onto bamboo pulp fibres as reinforcement in high-density polyethylene improved the thermal stability and flame retardancy of the polymer composites (Wang *et al.*, 2019). Butadiene rubber reinforced with $CaCO_3$ nanoparticles had improved thermal stability compared to the neat butadiene. The decomposition temperature of butadiene rubber/ $CaCO_3$ composites increased by 15%. (Jin and Park, 2008). Thermal transitions of Natural rubber/low-density polyethylene blends improved after the addition of $CaCO_3$ using a coupling agent. The glass transition temperature increased by 10%. (Sampath, Edirisinghe and Egodage, 2016).

Similarly, as reported by previous studies, blends of $CaCO_3$ with other fillers in hybrid systems substantially improve the morphological and thermal properties of thermoplastics vulcanizates. A hybrid filler system with $CaCO_3$ and talc improved the mechanical properties of recycled polypropylene rubber wood composites (Srivabut, Ratanawilai, and Hiziroglu, 2018). Nanoparticles of $CaCO_3$ were used as a filler in high-density polyethylene, and the mechanical properties were evaluated. The authors reported a significant increase in the tensile strength of the composite compared to neat high-density polyethylene. The tensile strength values of the binary and ternary systems were higher than those of the neat matrix, and the ternary system exhibited better thermal stability. (Asadi *et al.*, 2020; Awan *et al.*, 2021). Sepiolite, an inorganic mineral, has been studied because of its potential as a filler in polymer matrices. It has been found to improve the thermal stability of polymers. The thermal stability of chlorinated polyethylene/Ethylene methacrylate was significantly improved by the addition of 5 wt% of sepiolite, a nanofiller, which also significantly improved the tensile properties of the blend (Farshchi and Ostad, 2020). Findings show that the use of $CaCO_3$/Sepiolite as fillers in the production of thermoplastic elastomers from waste materials is very scanty and untraceable. This

study considered improving the thermal stability of thermoplastic vulcanizates from waste polyethylene and natural rubber using $CaCO_3$/sepiolite at different proportions. This should improve the thermal stability and mechanical properties of the thermoplastic vulcanizates, thereby opening new applications.

2.1 Experimental

2.2 Materials

Polyethylene waste was obtained from the recycling outlet of the Lagos State Waste Management Authority (LAWMA) facility, Ojota, Lagos. Natural rubber and all compounding chemicals were obtained from Tony West Rubber Industries at Agboju, Lagos. $CaCO_3$ and Sepiolite were supplied by Bright Chemicals, Ojota, and China, respectively. All chemicals and materials were used as received without any purification.

2.3 Methodology

2.3.1 Compounding of the Thermoplastic Vulcanizates

The formulation in Table 1 was used to prepare the thermoplastic vulcanizate samples on a standard laboratory two-roll mill with dimensions 240mm by 475mm and a nip gap of 2cm according to ASTM D3184. The polyethylene waste was melted on the two-roll mill for about five minutes, then natural rubber (SNR 5) was added and masticated for about 10 minutes. The compounding ingredients were added in the order of activators, accelerators, and curing agents. The compound was mixed and passed through the nip of the two-roll mill several times to achieve a homogeneous mixture. The machine was operated at 70 °C, and the compounded mix was left to mature for 24 hours.

2.3.2 Curing Process

The compounded mix was placed in a hydraulic press moulding machine (model PID 28, Saumya India). This allowed curing of the composites to take place. The samples were cured at 140 °C for 4 minutes. Dumbbell-shaped samples were prepared for characterization from cured TPVs.

Table 1: Formulation for compounding Thermoplastic vulcanizates samples

Ingredients	A(pphr)	B(pphr)	C(pphr)	D(pphr)	E(pphr)	F(pphr)
NR	70	70	70	70	70	70
RPE	30	30	30	30	30	30
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
Zinc Oxide	4	4	4	4	4	4
TMTD	0.5	0,5	0.5	0.5	0.5	0.5
MBTS	1.5	1.5	1.5	1.5	1.5	1.5
$CaCO_3$	50	45	40	35	30	25
Sepiolite	0	5	10	15	20	25
Sulfur	2	2	2	2	2	2

Benzothiazole Disulfide (MBTS), Tetramethyl Thiuram Disulfide (TMTD), Natural Rubber (NR), and Recycled Polyethylene (RPE).

2.4 Physico-mechanical properties

2.4.1 Tensile Strength and Elongation at Break

The mechanical analysis of the thermoplastic vulcanizates was carried out using a computerized universal mechanical testing machine (Instron series 3369). The load cell was 50 KN. The tensile strength and Young modulus of the Vulcanizates were evaluated according to ASTM D 412.

2.4.2 Abrasion Loss

The weight of the samples was measured before they were placed in the DIN abrasion tester (model ROCKY-DR, Qualitet, India). The samples were placed in the sample holder, and the machine was turned on. The roller rotated for approximately 4.2 minutes. The samples were removed, and the final weight was recorded. The abrasion resistance was determined by subtracting the final weight from the initial weight. The machine operated at 40 revolutions/min, and the diameter of each specimen was 15mm. Equation (1) was used to determine the abrasion loss percentage

$$\%\, Abrasion\ loss\ = \frac{W1 - W2}{W1}\ \times 100 \quad (1)$$

W_1: weight before abrasion test in grams

W_2: weight after abrasion test in grams

2.4.3 Hardness Test

Hardness was measured according to the ASTM D2240 standard using a Rex Durometer with Shore A. The test was carried out using three points of each sample, and the average value was determined. A load of 12.5N was applied, and the sample was left for 15 seconds after indentation; its value was recorded. This was carried out on three points on the specimens, and the average readings were evaluated.

2.5 Swelling Test

Rectangular-shaped specimens, 15mm by 10 mm, were cut out of the dumbbell-shaped vulcanizates. The vulcanizates were immersed in different solvents in a bottle for 24hours. The initial weight was recorded before immersing in the solvents, and the final weight after 24 hours was recorded. The samples were carefully removed from the solvents and blotted to remove excess solvents before being weighed. The swelling percentage in each solvent was evaluated. The solvents used were Ethanol, Petrol, Diesel, and Kerosene. The percentage swelling index of the vulcanizates was determined with the equation below

$$\%\, Swelling\ \ Index = \frac{W2 - W1}{W1}\ \times 100 \quad (2)$$

2.6 Thermal Analysis

The thermal stability of the vulcanizates was analyzed with thermogravimetric analysis. Thermogravimetric analysis was carried out using the Thermogravimetric Analyzer Q50 series. An empty crucible is placed on the sample groove, and the instrument is allowed to load, after which the instrument is zeroed. The holding sample pan was then removed and loaded with 10g of the sample. The sample was placed in a temperature-controlled furnace and then subjected to a temperature gradient between 25 °C and 600 °C. The test was carried out in static air. The onset of degradation, the temperature at degradation, and the residual weight were noted.

2.7 Morphological Analysis

Scanning Electron Microscope (SEM) was used to examine the morphology of the vulcanizates. (JOEL JSM 7600F field emission SEM. Japan). The specimens were coated with a thin layer of platinum to eliminate electrical charges generated during the test.

3.0 Results and Discussion

3.1 Physico-Mechanical Properties of Vulcanizates

Table 2 shows the tensile strength, % elongation, young modulus, abrasion resistance, and hardness.

Samples	Samples Composition		Tensile strength (MPa)	% Elongation	Young Modulus (MPa)	Abrasion %	Hardness Shore A
	$CaCO_3$	Sepiolite					
A	50	0	1.631	298	2.22	7	32.5
B	45	5	2.426	208	2.67	7	44.77
C	40	10	2.952	433	1.98	7	34.13
D	35	15	3.024	467	1.64	7	32.35
E	30	20	2.27	254	3.00	7	42
F	0	0	2.256	150	3.09	8	48

The physico-mechanical properties of the thermoplastic vulcanizates are presented in Table 2. Table 2 shows that the samples filled with 50pphr of $CaCO_3$ had the least tensile strength of 1.631MPa. This could be attributed to poor dispersion of $CaCO_3$ in the polymer matrix and thereby reducing its reinforcement. A similar trend was observed by a previous study (Egodage, Edirisinghe and Lanka, 2019). Thermoplastic vulcanizates filled with $CaCO_3$ 35/Sep 15pphr had the highest tensile strength of 3.024MPa. The high tensile strength of Thermoplastic vulcanizate of sample D($CaCO_3$ 35/Sep 15pphr) is ascribed to the fibrous nature of the sepiolite and the interaction of the $CaCO_3$ within the polymer blend which allows a good dispersion within thereby balancing the stress transfer of the blends (Zaini *et al.*, 2018). The thermoplastic vulcanizates with no filler had the highest value of young modulus, 3.089MPa while the sample D ($CaCO_3$ 35/ Sep 15) had the lowest value of young modulus. The young modulus of a material describes its stiffness, the generation of internal resistance within the material increases its stiffness and hence, such a material is less susceptible to elastic deformations.

The percentage elongation of the thermoplastic vulcanizates in Table 2 shows that the thermoplastic vulcanizates with $CaCO_3$35/Sep15 pphr compositions had the highest (467%), and the unfilled sample had the lowest (150%). The percentage elongation describes ductility, tenacity, toughness, and the brittle nature of a polymer. The unfilled sample is brittle compared to the filled thermoplastic vulcanizates, while the thermoplastic vulcanizates filled at $CaCO_3$35/Sep15 are ductile and can withstand significant deformation before failure. Hardness is the property of a material that allows it to resist permanent distortion, penetration, and scratching. Thermoplastic

vulcanizates without filler had the highest value of 48, while sample D with filler loading of $CaCO_3$35/Sep15 pphr had the least value of 32. Shore A. The abrasion loss of thermoplastic vulcanizates was the same except for unfilled thermoplastic vulcanizates, with an abrasion loss of 8%. The abrasion loss of the thermoplastic vulcanizates revealed that the composites had low resistance to surface wear.

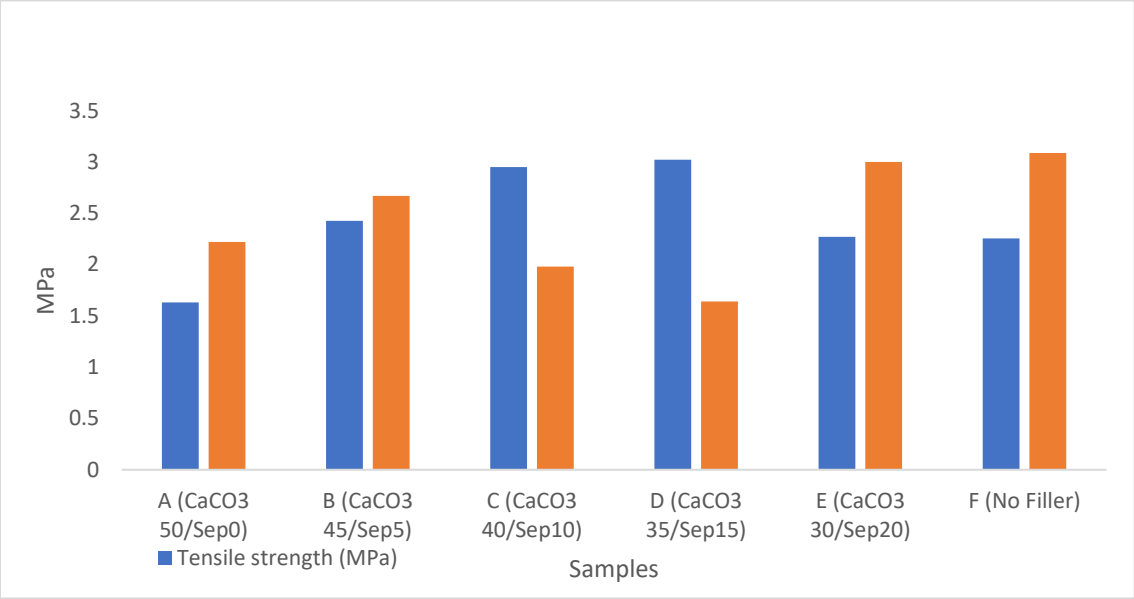

Figure 1: Tensile strength and Young modulus of Thermoplastic Vulcanizates

3.2 Swelling Percentages of TPNR Vulcanizates

Table 3: Swelling percentage of thermoplastic vulcanizates in common solvents

SAMPLES	FILLER COMPOSITION		ETHANOL (%)	PMS (%)	DIESEL (%)	KEROSENE (%)
	$CaCO_3$	Sep				
A	50	0	0	459	113	314
B	45	5	6	242	86	300
C	40	10	76	235	152	124
D	35	15	15	289	114	196
E	30	20	60	296	145	236
F	0	0	8	362	214	333

The swelling test results of the composites are given in Table 2, while the diagram is presented in Figure 2. The magnitude of penetration of each solvent into the thermoplastic vulcanizates has been measured and used as a measure of swelling. The swelling mechanism involves the diffusion of solvent molecules into the polymer matrix, which causes a sharp change in the polymer's volume. As diffusion progresses, the dimension of the vulcanizates increases until an equilibrium point is reached between the solvent and the vulcanizate. Ethanol, with the lowest swelling index, had a lower swelling percentage than the other common solvents. The swelling percentage is in the ascending order of Ethanol<Diesel <Kerosene< PMS. Similar trend was reported by Marković *et al* (2020).

3.3 Thermal Properties of TPNR Vulcanizates

Table 4: Thermal properties of Thermoplastic Vulcanizates

Sample	Initial Weight (%)	T onset (℃)	T peak (℃)	T end set (℃)	Degradation (℃)	Residual mass (%)
A	100	472.60	322.64	477.30	4.70	2.68
B	100	579.64	352.64	584.40	4.71	2.70
C	100	484.40	448.26	489.69	5.79	2.80
D	100	489.69	438.26	534.40	44.71	2.80
E	100	574.40	428.26	789.49	215.09	2.80
F	100	230.35	320.50	400.25	170.00	2.00

From Table 4, Sample F, a neat NR/RPE blend, exhibits the lowest onset temperature of 230.35 °C, highlighting its thermal vulnerability without mineral fillers. This finding aligns with Uğraşkan, *et al.* (2019), who identified low thermal stability in unfilled natural rubber due to oxidative degradation of the polyisoprene chains. In contrast, Sample A, with only $CaCO_3$ as a filler, increased the onset temperature to 472.60 °C, due to its barrier effect against heat and oxygen, delaying thermal degradation. Hayeemasae *et al*. (2024) found similar results, confirming that $CaCO_3$ enhances thermal stability. Binary-filled formulations (Samples B–E) with $CaCO_3$ and sepiolite show improved stability, particularly Samples B and E, at 579.64 °C and 574.40 °C, respectively. This improvement may be due to the synergistic effect of sepiolite's properties, which created a tortuous path for oxygen diffusion, offering greater thermal protection. This is consistent with Wongwa *et al*. (2022). Sample A ($CaCO_3$ only) reached a T peak of 322.64 °C, having a delayed degradation onset, but this does not affect the decomposition mechanism significantly. This suggests that $CaCO_3$ acts primarily as a physical barrier in early thermal degradation. In contrast, binary filled formulations exhibited higher T peak values: Sample C at 448.26 °C, Sample D at 438.26 °C, and Sample E at 428.26 °C. These increases are attributed to sepiolite fibres creating a physical network that limits polymer chain mobility, thus slowing thermal degradation post-onset, supported by Shahamatifard, Rodrigue, and Mighri,(2023). This highlights sepiolite's role in enhancing thermal resistance in elastomeric composites.

3.4 Morphological Analysis

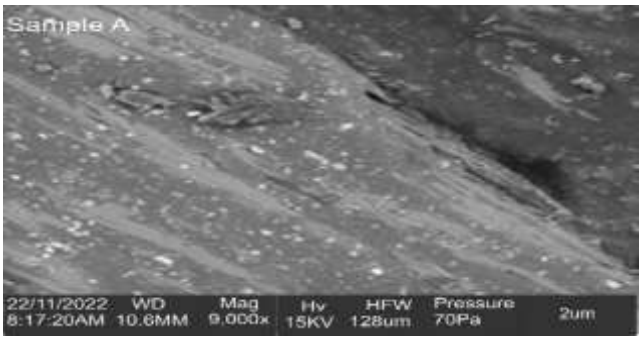

Figure 1: SEM of Sample A

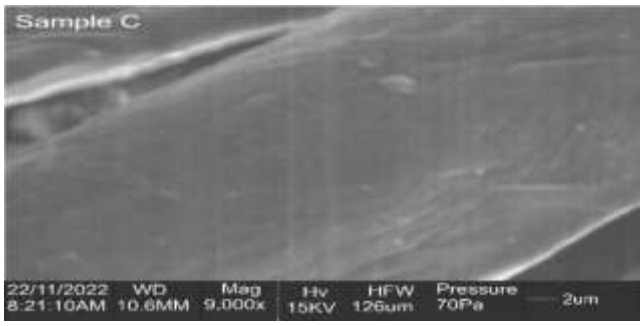

Figure 2: Morphology of Sample C

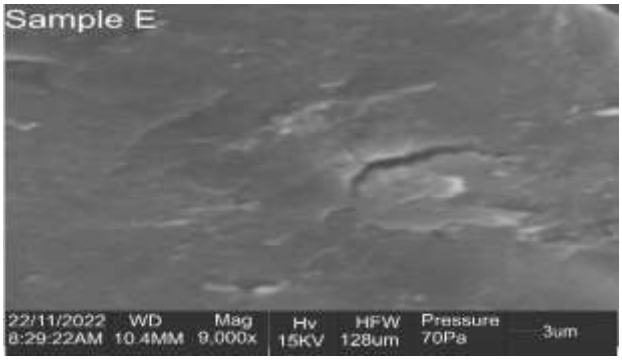

Figure 3: Morphplogy of sample E

Figures 1 – 3 show the SEM images of thermoplastic vulcanizates, samples A, C, and E. These three were selected to assess the morphology by comparing the samples filled with only $CaCO_3$ at 50pphr, $CaCO_3$ 40/Sep10, and $CaCO_3$ 30/Sep20 pphr. Figure 1 shows a poorly dispersed $CaCO_3$ in the polymer matrix compared to Figures 2 and 3, where there was relatively good dispersion of the fillers in the matrix. $CaCO_3$, a non-reinforcing filler, has been described in the literature to have poor adhesion with polymer matrices except when treated to improve its adhesion and dispersion into the polymer matrix. (Sampath, Edirisinghe and Egodage, 2019). This is because agglomeration, which occurs within the $CaCO_3$ particles, accounts for its poor reinforcement in polymer matrices. This is observed in the tensile strength of Sample A, which had the lowest tensile strength of 1.631MPa. The addition of Sepiolite improved the adhesion of the filler with the polymer matrix as can be observed in Figures 2 and 3. Sepiolite has been reported to act as a coupling silane agent and has little or no agglomeration of its particles within polymer matrices.(Samper *et al.*, 2015). This accounts for the increase in the tensile strength of the $CaCO_3$/Sepiolite-filled samples.

3.4.1 Sepiolite/ $CaCO_3$ Working Mechanism

Sepiolite, a fibrous inorganic magnesium-rich silicate material, has a special crystal structure which gives it a large specific surface area and high surface activity. The active Silanol groups impart to sepiolite its reinforcing and adsorption properties. It is proposed that the synergy between the $CaCO_3$ and sepiolite was as a result of the high reactivity of the sepiolite due to the presence of silanol groups, which possibly initiate more active sites within the polymer matrix thereby increasing the interaction between the ternary system. The fibrous and crystalline morphology of

the sepiolite reduced the agglomeration of $CaCO_3$ within the thermoplastic vulcanizates. Sepiolite has been used as a compatibilizer in thermoplastic starch/polyethylene blends and it was reported to have improved the interaction between the polymer composite (Samper *et al.*, 2015). Sepiolite has a compatibilizing effect; increasing the sepiolite composition improves thermal stability and mechanical properties, but a decline in the properties is observed at higher loading.

4.0 Conclusion

In this research, the thermal stability, mechanical properties and morphology of thermoplastic vulcanizates prepared from waste polyethylene and Natural rubber filled with $CaCO_3$/Sepiolite hybrid filler has been investigated and were compared with thermoplastic vulcanizate without filler system. TGA showed that the thermal degradation temperature of the filled system was between 500^OC and 600^OC which was higher than the onset degradation for the control sample. The DSC showed a decrease in the glass-transition temperature of the filled samples relative to the control sample. The melting temperature of the filled samples was significantly higher than that of the control sample. Tensile strength of thermoplastic vulcanizate filled with $CaCO_3$ 50pphr was the least (1.60MPa), while thermoplastic vulcanizate filled with $CaCO_3$ /Sepiolite (35/15)pphr had the highest tensile strength.

The stiffness of the control sample was higher than all filled thermoplastic vulcanizates, while the ductility of the filled vulcanizates was higher than that of the control sample. SEM analysis of the samples showed better dispersion of the hybrid filler in the thermoplastic vulcanizates compared to the sample filled with $CaCO_3$ only.

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