COMPACT THERMOPLASTIC POLYMER BIOCOMPOSITE BASED ON PE/PE-G-MA/EPDM/CF AND DYNAMICALLY VULCANIZED WITH DICUMYL PEROXIDE

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ABSTRACT. Polymer biocomposites are considered a way to stimulate the creation of a new type of material with much improved properties, which economically and efficiently combines the properties of at least two polymers (elastomer and plastomer) and natural reinforcing materials, which are component elements of composite materials, intended to improve their mechanical, thermal or chemical properties. This paper presents the development of dynamically vulcanized thermoplastic biocomposites, with anti-thermal and antimicrobial characteristics, using circular economy concepts for the development of "green" polymer composites, with market demand in niche areas of significant economic activity for the industry, while respecting the requirements of the economic and social environment. Dynamically vulcanized multiphase elasto-plastic polymer biocomposites are reinforced with natural calcium carbonate waste for products used in the food and pharmaceutical fields, based on elastomer (ethylene propylene terpolymer rubber – EPDM) and calcium carbonate waste dispersed in a plastomer matrix (high-density polyethylene – HDPE). The natural calcium carbonate waste was obtained from seashells, cryogenically ground to a particle size of 200-300nm and functionalized with polydimethylsiloxane (PDMS). The elastomers and calcium carbonate waste, through their micrometric dispersion in the plastomer matrix, led to the obtaining of a high-performance polymeric material with multifunctional characteristics (rubber and thermoplastic) and processing properties specific to plastics. The new material can be recycled for at least 5 cycles, without modifying its physical and mechanical properties. The experimental composites were characterized physically and mechanically by standardized methods specific to plastics.
KEYWORDS: biocomposites, dynamically vulcanized thermoplastic polymer, calcium carbonate waste, eco-design

BIOCOMPOZIT POLIMERIC TERMOPLAST COMPACT, PE BAZĂ DE PE/PE-G-MA/EPDM/CF, VULCANIZAT DINAMIC CU PEROXID DE DICUMIL

REZUMAT. Biocompozitele polimerice sunt considerate ca fiind o cale de stimulare pentru crearea unui nou tip de material cu proprietăți mult îmbunătățite, care combină în mod economic și performant proprietățile a cel puțin doi polimeri (elastomer și plastomer) și materiale de ranforsare naturale. Materialele de ranforsare naturale sunt elemente componente ale materialelor compozite, care au menirea să îmbunătățească proprietățile mecanice, termice sau chimice ale acestora. Această lucrare prezintă realizarea de biocompozite termoplaste vulcanizate dinamic, cu caracteristici antitermice și antimicrobiene, utilizând concepte ale economiei circulare pentru realizarea de compozite polimerice „verzi", cu cerere de piață în domeniile de nișă ale unor activități economice semnificative pentru industrie, cu respectarea cerințelor mediului economic și social. Biocompozitele polimerice elasto-plaste multifazice vulcanizate dinamic sunt ranforsate cu deșeu de carbonat de calciu natural pentru produse utilizate în domeniul alimentar și farmaceutic, pe baza de elastomer (cauciuc etilen-propilen-terpolimer – EPDM) și deșeu de carbonat de calciu dispersate în matrice de plastomer (polietilenă de înaltă densitate – HDPE). Deșeul de carbonat de calciu natural a fost obținut din cochilii de scoici măcinate criogenic, cu dimensiunea particulei de 200-300nm și funcționalizat cu polidimetilsiloxan. Elastomerii și deșeul de carbonat de calciu, prin dispersarea lor de ordin micrometric în matrice de plastomer, au condus la obținerea unui material polimeric performant cu caracteristici multifuncționale (de cauciuc și termoplast) și proprietăți de prelucrare specifice maselor plastice. Noul material poate fi recirculat cel puțin 5 cicluri, fără să-și modifice proprietățile fizico-mecanice. Compozitele experimentate au fost caracterizate fizico-mecanic prin metode standardizate specifice maselor plastice.
CUVINTE CHEIE: biocompozite, termoplast vulcanizat dinamic, deșeu de carbonat de calciu, eco-design

BIOCOMPOSITE POLYMÈRE THERMOPLASTIQUE COMPACT, À BASE DE PE/PE-G-MA/EPDM/CF, À VULCANISATION DYNAMIQUE AVEC PEROXYDE DE DICUMYLE

RÉSUMÉ. Les biocomposites polymères représentent une voie prometteuse pour la création de nouveaux matériaux aux propriétés nettement améliorées. Ils combinent de manière économique et efficace les propriétés d'au moins deux polymères (élastomère et plastomère) et de matériaux de renforcement naturels. Ces derniers, constituants des matériaux composites, visent à améliorer leurs propriétés mécaniques, thermiques ou chimiques. Cet article présente la création de biocomposites thermoplastiques à vulcanisation dynamique, dotés de propriétés antithermiques et antimicrobiennes. Cette approche s'appuie sur les principes de l'économie circulaire pour la production de composites polymères « verts », répondant à la demande du marché dans des secteurs de niche à forte activité économique pour l'industrie, tout en respectant les exigences environnementales et sociales. Des biocomposites polymères élasto-plastiques multiphasiques vulcanisés dynamiquement sont renforcés par des déchets de carbonate de calcium naturel. Ces biocomposites, destinés aux secteurs agroalimentaire et pharmaceutique, sont composés d'un élastomère (caoutchouc terpolymère éthylène-propylène – EPDM) et de déchets de carbonate de calcium dispersés dans une matrice plastomère (polyéthylène haute densité – PEHD). Les déchets de carbonate de calcium naturel, issus de coquilles de palourdes, sont broyés cryogéniquement jusqu'à une granulométrie de 200 à 300 nm, puis fonctionnalisés avec des polydiméthylsiloxanes. La dispersion micrométrique des élastomères et des déchets de carbonate de calcium dans la matrice plastomère permet d'obtenir un matériau polymère haute performance aux caractéristiques multifonctionnelles

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(caoutchouc et thermoplastique) et aux propriétés de mise en œuvre spécifiques aux plastiques. Ce nouveau matériau est recyclable au moins cinq fois sans altération de ses propriétés physiques et mécaniques. Les composites expérimentaux ont été caractérisés physico-mécaniquement par des méthodes normalisées spécifiques aux plastiques.
MOTS-CLÉS : biocomposites, thermoplastique vulcanisé dynamiquement, déchets de carbonate de calcium, écoconception

INTRODUCTION

Globally, the market for biodegradable polymeric materials has grown from $3.7 billion in 2022 to $9.5 billion in 2026, representing a compound annual growth rate (CAGR) of 20.6% for the 2022–2026 period [1]. In recent years, driven by increasing environmental concerns and the demand for sustainable materials, research has focused on replacing synthetic fibers with natural ones in various composites intended for engineering applications [2]. Furthermore, thermoplastic elastomers (TPEs) have gained attention as potential replacements for vulcanized rubber in sealing systems, owing to their recyclability and processability [3]. Currently, two types of TPE are frequently used: styrenic block copolymer TPEs (TPE-S) and vulcanized TPEs (TPE-V).

Dynamically vulcanized thermoplastics (TPE-Vs) constitute a special class of engineering materials consisting of a cross-linked rubber phase dispersed within a thermoplastic matrix [4]. Finished products processed from TPE-Vs exhibit physical-mechanical properties similar to those of vulcanized rubber. Moreover, TPE-Vs can be melted and reshaped using conventional processes specific to thermoplastic materials [5]. It has been established that the process of dynamic vulcanization of thermoplastic and rubber blends yields polymer composites with superior mechanical properties, as well as greater impact and thermal resistance, compared to samples prepared by simple blending without crosslinking agents. It has been demonstrated that TPE-Vs are utilized in the automotive industry. Among the types of rubber and thermoplastic materials used to produce TPE-Vs, natural rubber (NR) and polypropylene (PP) are frequently employed [6]. Historically, Ethylene Propylene Diene Monomer (EPDM) has remained the most widely used material for the production of sealing systems (weatherstripping/gaskets). The TPE-Vs typically selected for the manufacture of such seals consist of a blend of polypropylene and small particles of EPDM rubber. Polypropylene is a popular thermoplastic material used in a wide range of applications; it is characterized by unique properties, such as a high melting point and resistance to both high temperatures and chemical substances. Furthermore, it exhibits good processability, a hallmark of thermoplastic materials [7-8]. Previous studies indicate that the properties of TPE-Vs depend on their phase morphology [9-11]. Polymer composites are considered a promising avenue for creating new types of materials with significantly enhanced properties, combining the advantages of polymers with the characteristics of reinforcing materials [12]. Reinforcing materials are, therefore, components of composite materials designed to improve their mechanical properties. They appear in various forms and orientations, depending on the required properties: 1. enhancement of mechanical characteristics; 2. improvement of thermal resistance; 3. compatibility with the composite matrix; 4. good adaptability to processing methods; 5. low weight; 6. low cost, etc. [13].

In this study, natural calcium carbonate was selected as a reinforcing agent. Seashells are marine organic remains that possess good mechanical properties; their structure consists of approximately 95% calcium carbonate and less than 5% organic and inorganic compounds [14]. Shells contain various polymorphic forms of $CaCO_3$—prismatic, lamellar, lenticular, foliated, crossed-lamellar (including complex crossed-lamellar), and homogeneous—which result in a diverse range of structural configurations [15]. The antimicrobial effect is achieved by functionalizing the reinforcing agent (based on calcium carbonate) through silanization or the adsorption of long-chain alkyl compounds, to which an ammonium-type group can be

grafted [16]. While research exists demonstrating the feasibility of functionalizing carbonates (including calcium carbonate) [17], there are no known publications describing such functionalization—particularly in the context of composite materials. This paper presents the development of a hybrid polymeric biocomposite—based on PE, PE-g-MA, EPDM, and functionalized natural calcium carbonate—that is compact, possesses antimicrobial properties, is resistant to high temperatures, and exhibits a biodegradation effect, due to the use of calcium carbonate waste.

EXPERIMENTAL

Materials and Methods

Materials

All composites contain the same two polymers: the EPDM elastomer (Nordell IP 3745P-DuPont) and the low-density polyethylene (LDPE-SIDPEC, Egyptene), in 50:50 and 25:75 ratios. EPDM is plasticized with paraffinic oil in 100% percentage.

In addition to the polymers, other additives were used, as follows: compatibilizer: polyethylene graft maleic anhydride (PE-g-MA, Sigma Aldrich); crosslinking agent: dicumyl peroxide, powder – Perkadox F40, AkzoNobel, Germany; activators: zinc oxide and stearic acid – Bayer, Germany; antioxidants: Dilauryl Thiodipropionate (Irganox 1010) and 2,2,4-Trimethyl-1,2-Dihydroquinoline polymer (Flectol TMQ), R.E.Carroll Inc. New Jersey, USA; seashell waste.

Functionalization of Seashell Waste

Functionalization of seashell waste was achieved by mixing with a stirrer with helical paddles, for 2h at a temperature of 80°C with slow dripping of polydimethylsiloxane (PDMS) and a speed of 40 rpm. Different percentages of functionalizing agent relative to the amount of waste were experimented, but the percentage of 7% was selected, being considered optimal due to the degree of absorption, the elimination of particles agglomeration, work method and the favorable influence on the physical-mechanical characteristics of the composite.

Table 1: Formulations for peroxide-crosslinked polymer biocomposites, filled with functionalized $CaCO_3$ waste (20% and 40%) and plasticized (100 parts by weight of paraffinic oil per 100 parts by weight of elastomer – EPDM). EPDM/HDPE ratios: 50/50 and 25/75.

Biocomposites	S0-Control	PP2A20	PP2A40	VP2A20	VP2A40
EPDM-Nordel IP 3745P	50	50	50	25	25
Paraffinic oil, premix (EPDM with paraffinic oil, 50:50)	-	50	50	25	25
LDPE	50	50	50	75	75
PE-g-MA	-	7	7	7	7
Zinc oxide	5	5	5	5	5
Stearic acid	0.4	0.4	0.4	0.4	0.4
Flectol TMQ	1	1	1	1	1
Irganox 1010	1	1	1	1	1
$CaCO_3$ waste from seashells, functionalized	-	20	40	20	40
Perkadox F40	3	4	4	3.5	3.5

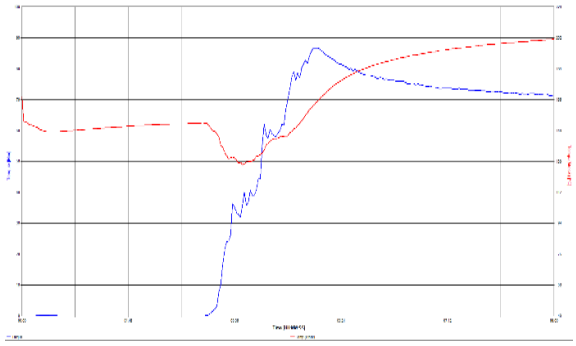
The formulations presented in Table 1 were prepared using a Plasti-Corder Brabender Mixer 350 E (Figure 1), which features the following specifications: 3 heating/cooling zones (using compressed air), a heating temperature range of 0–300°C, a capacity of 350 cm^3, a maximum rotational speed of 300 RPM, and a pressure of 600 bar.



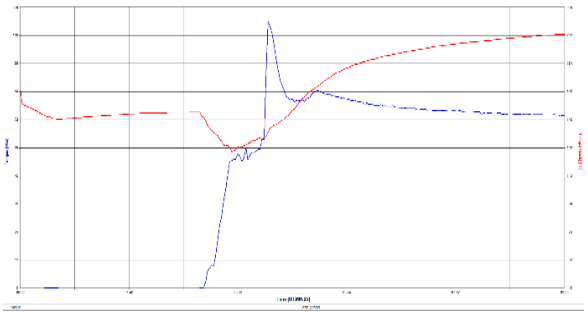
Figure 1. Plasti-Corder Brabender Mixer 350 E

The operating procedure and parameters for the Brabender Plasticorder mixer are as follows:

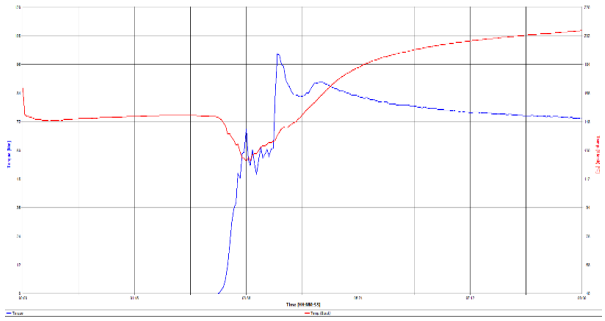
- At a temperature of 150–175°C, the polyethylene is added; once it has softened and plasticized, the EPDM is introduced, and the mixture is blended for 2 minutes at a mixing speed of 350–370 rpm. Following homogenization, the calcium carbonate waste—derived from processed and functionalized seashell fragments—is added, along with antioxidants, compatibilizing agents, zinc oxide, and stearic acid. Mixing continues at a speed of 250–280 rpm until all ingredients are incorporated and the mixture is uniform;
- The temperature is lowered to approximately 80°C, and the vulcanizing agent—dicumyl peroxide—is introduced;
- The mixture is removed from the mixer and processed using molds—specifically those designed for the test specimens required for physico-mechanical and chemical characterization—or it is granulated for subsequent extrusion or injection molding. Finally, the material undergoes physico-mechanical and morpho-structural characterization.



S0



PP2A40



VP2A40

Figure 2. Torque and temperature variations over time, recorded using the Brabender Plasticorder, for the samples S0, PP2A40 and VP2A40

From the Brabender plastograms specific to each mixture—partially shown in Figure 2—the vulcanization parameters (induction time, vulcanization time, and maximum torque) were determined. Based on the rheological data presented in Table 2, the following observations can be made:

- The reference sample (S0)—which contains no calcium carbonate waste or plasticizer—exhibits the shortest induction times (T_i) and vulcanization times (T_v) compared to the filled and plasticized samples;
- Peroxide-based vulcanization results in the lowest values for the vulcanization parameters across all polymer structures (reference, filled, and plasticized);
- The presence of the waste material, regardless of the amount of plasticizer used, influences T_i and T_v by increasing the vulcanization parameters in proportion to the quantity of waste present.

Table 2: Rheological characteristics of thermoplastic polymer biocomposites dynamically vulcanized with dicumyl peroxide, consisting of plasticized polymeric materials filled with functionalized calcium carbonate waste

Rheological indices	S0 - Control	PP2A20	PP2A40	VP2A20	VP2A40
Induction time*, min.	0.2	3.5	3.6	2.5	3.0
Optimal vulcanization time**, min.	0.8	4	5.5	3.5	4.0
Maximum shear torque, N/m	960	940	940	180	340

*Induction time = T_i = time required for crosslinking initiation

**Optimal vulcanization time = T_v = T_i + time taken to reach the maximum shear

The optimal technological parameters for a functional process tailored to the microstructure are as follows:

- For the mixer:

- The chamber fill level is as follows:
  - 1 for an EPDM/HDPE ratio of 50/50;
  - 1.1 for an EPDM/HDPE ratio of 25/75;
- Temperature: 180 ± 20°C;
- Rotor speed: 80 ± 1 rpm;
- Processing time: 8 minutes;

- For the electric press:

a) Preheating: 4 min × 190 ± 20°C × 1 atm;
b) Pressing: 5 min × 190 ± 20°C × 190 atm;
c) Cooling: approx. 10 min × 23 ± 20°C × 190 atm.

Testing Methods

Tensile tests of the samples were carried out according to SR ISO 37:2020 using a Schopper Tensile Testing machine 1445, at a constant crosshead speed of 500 ± 5 mm/min.

Hardness of the samples was measured by Shore “A” Durometer according to SR ISO 48-4:2022.

Abrasion resistance was carried out according to ISO 4649/2024, the cylinder method, using a pressure of 10 N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper. A wearing tester with abrasive cloth having granulation of 212–80 mm (PE 80). The samples used were obtained from rolled blends and pressed into sheets, then cutting with a rotating die and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm.

RESULTS AND DISCUSSIONS

Table 3: Physical-mechanical properties of reference polymer structures, filled and plasticized with 100 parts by weight of oil. EPDM/HDPE ratio: 50/50. Peroxide crosslinking system.

Properties	S0 Control	PP2A20	PP2A40	VP2A20	VP2A40
Normal state					
Hardness, °Sh A	96	95	97	95	96
Elasticity, %	28	22	26	22	23
300% modulus, N/mm^2	-	-	-	-	-
500% modulus, N/mm^2	-	-	-	-	-
Tensile strength, N/mm^2	6.8	13	9.3	8.4	10
Elongation at break, %	280	190	173	280	180
Residual elongation, %	25	93	65	93	63
Tear strength, N/mm	63	87	81	99	78
Density, g/cm^3	0.95	1.10	1.13	1.09	1.14
Wear, mm^3	107	202	204	210	212
Accelerated ageing – 168h /100°C					
Hardness, °Sh A		96	98	95	96
Elasticity, %		26	24	24	26
300% modulus, N/mm^2		-	-	-	-
Tensile strength, N/mm^2		16.1	11.3	10.2	13.1
Elongation at break, %		80	153	160	120
Residual elongation, %		23	36	73	64
Tear strength, N/mm		98	88.2	88	105
Accelerated ageing – 336h /100°C					
Hardness, °Sh A		97	96	96	97
Elasticity, %		22	20	24	24
300% modulus, N/mm^2		-	-	-	-
Tensile strength, N/mm^2		16.2	11	9.7	12.7
Elongation at break, %		40	160	200	120
Residual elongation, %		16	20	72	51
Tear strength, N/mm		91	92	86.5	92

Based on the data presented, the following observations can be made:

Normal State:

- *Hardness* is high (95–97 °ShA), regardless of the amount of calcium carbonate waste or oil, due to the morphology of the composite;

- *Elasticity* is lower (22–26%) compared to the control sample, due to plasticization with paraffinic oil; the amount of carbonate waste has very little influence on elasticity;

- *Tensile strength* exhibits the following characteristics:

  - It is superior to that of the reference mixture, showing an increase of approximately 20%;
  - The highest value (13 N/mm²) is obtained for the structure (PP2A20) loaded with PDMS-functionalized calcium carbonate waste and plasticized with 100 parts of oil (relative to the amount of EPDM);
  - The value decreases in proportion to the amount of waste used in the mixture;

- *Elongation at break* is lower than that of the control sample, due to peroxide crosslinks that offer greater resistance to stretching. It is observed that loading and plasticization—compared to an unloaded and unplasticized mixture—result in lower values for this parameter; these values decrease as the amounts of oil and filler increase;

- *Residual elongation* is lower than that of the control sample, which will result in low compression set for the peroxide-cured structures. In general, compared to the control structure, loading and plasticization lead to higher permanent set values; furthermore, as the amounts of filler and plasticizer increase, the value of this parameter generally increases as well.

- *Tear resistance* shows significantly better values compared to the reference compound (unfilled and unplasticized)

crosslinked with peroxide. For this type of crosslinking, the addition of fillers and plasticizers results in values approximately 25–32% higher, regardless of the amount of oil and filler used.

- *Regarding wear*: although it is about 50% higher than in structures crosslinked with sulfur and accelerators, it is 100% better than that of conventional elastomeric compounds. As the amount of oil and filler increases, wear resistance improves by approximately 25–40%, with the best results achieved when using active silica.

Thermo-oxidative Aging:

Following thermo-oxidative aging (for 7 and 14 days at 100°C), the following observations are made:

- *Hardness* remains nearly constant after both 7 and 14 days, maintaining the same value.

- *Elasticity* is unaffected by the aging process.

- *Tensile strength* increases by 10–15% after 7 days, indicating that the elastomeric crosslinking process is continuing. After 14 days, this parameter stabilizes, signifying that the composite is fully crosslinked. This behavior is observed across all structures, regardless of the filler content.

- *Tear resistance*, for the same reasons, shows higher values after 7 days, while remaining nearly constant thereafter (after 14 days).

- *Elongation at break* and residual elongation tend to decrease by approximately 5% and 10%, respectively, after 7 days of aging; by 14 days, these values become very low.

Therefore, following thermo-oxidative aging (7 and 14 days at 100°C), an improvement in technical parameters is observed—attributed to continued elastomer crosslinking—which is more pronounced in peroxide-crosslinked composites. Very minor variations are noted in the physical-mechanical properties (hardness, elasticity, elongation, strength), indicating good long-term resistance at elevated temperatures.

CONCLUSIONS

The overall results can be considered important. The optimum values of the main physico-mechanical parameters, characteristic for thermoplastic vulcanizates (high values of °Shore A hardness, 300% modulus, stress at break, tear strength and low values of strain at break, elasticity), were obtained in the case of vulcanized with dicumyl peroxide. This was confirmed by the physico-mechanical tests. Furthermore, resistance to high temperatures through the use of calcium carbonate waste has been demonstrated via accelerated aging tests, with the values of the physical-mechanical characteristics after 336 hours at 100°C being similar to those in the initial (normal) state.

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