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ORIGINAL PAPER

Synergistic effects of metal stearate, calcium carbonate, and recycled polyethylene on thermo-mechanical behavior of polyvinylchloride

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ABSTRACT

Thermo-mechanical recycling process is the cheapest way to recover plastic waste such as LDPE with low ecological impact. Thus, the goal of this work is to obtain high-performance microcomposites from polyvinyl chloride (PVC), recycled low-density polyethylene (r-LDPE), calcium carbonate ($CaCO_3$), and calcium/zinc stearate ($CaSt_2$/$ZnSt_2$). The effect of the two ratios of thermal stabilizers with different concentrations on the mechanical properties and thermal stability of PVC and PVC/r-LDPE (1:1) blend was studied. The samples were characterized using infrared spectroscopy (FTIR), mechanical tests, thermal analysis, and scanning electron microscopy (SEM). The addition of 5 phr of $CaSt_2$:$ZnSt_2$ (9:1) to PVC (MC4) resulted in optimal tensile strength and elongation-at-break values. In addition, MC4 showed high thermal stability. Moreover, the incorporation of r-LDPE into PVC made the PVC matrix stronger and more stable than pure PVC, which yields high mechanical and thermal performances. Furthermore, an outstanding synergistic effect is obtained when a heat stabilizer rich in calcium is combined with $CaCO_3$ and r-LDPE. This PVC/r-LDPE blend as a composite can be used in several industrial fields.

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Keywords: Polyvinylchloride; recycled-low density polyethylene; thermal stabilizer; calcium carbonate.

INTRODUCTION

The novel industry technology positively influences the performance of composite materials in the economic sector, especially that of thermoplastic polymers, blends, and their composites [1]. For rapid economic development and significant protection of the environment, recycled plastic waste technology is a clean energy source and plays an important role in solid waste disposal [2, 3]. Agricultural plastic wastes (APW) are intrinsically difficult to recover and recycle in Algeria because of the absence of APW systems and infrastructures [4,5]. Polyvinylchloride (PVC) is one of the most important thermoplastic polymers used in industrial products, such as pipes, cables, food product containers, construction applications, and medical and electronic devices, owing to its high mechanical properties [6-8]. Lower thermal stabilization was observed for the PVC

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compared with other thermoplastic polymers such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET), owing to the dehydrochlorination reaction of PVC around 100°C [9]. The pyrolysis of PVC exhibits two interesting steps: (i) initial degradation due to the first dehydrochlorination of PVC at low temperature, and (ii) final degradation due to the strong cracking and decomposition of PVC at high temperature [10, 11]. To decrease the pure PVC degradation, it should be mixed with thermal stabilizers to produce plastic with high thermal performance, such that it can be used in several applications [12, 13]. The incorporation of a thermal stabilizer into PVC can make the zipper decomposition more difficult at both low and high temperatures, as the chlorine atom can be absorbed by the heat stabilizer [14].

The combination of commercial calcium stearate ($CaSt_2$) and zinc stearate ($ZnSt_2$) has attracted the attention of several researchers as $ZnSt_2$ can substitute labile chlorine atom of PVC chain, forming a strong Lewis acid, $ZnCl_2$, which in turn can react with HCl to undergo the dehydrochlorination reaction. On the contrary, HCl is absorbed by $CaSt_2$ to generate $CaCl_2$ and a fatty acid [15]. Moreover, calcium/zinc compounds can be considered environmentally friendly thermal stabilizers compared with organo-tin and lead compounds [16]. It is important to develop a new heat stabilizer of PVC that exhibits a synergistic effect with commercial thermal stabilizers of $CaSt_2/ZnSt_2$ [13, 17].

Li et al. found that new mixed Ca/Zn synthesized from tung oil fatty acid improved the thermal properties of PVC [18]. Moreover, Wang et al. studied the synergistic effect of tung-oil-based Ca/Zn and polyol in stabilizing polyvinylchloride [19]. The results show that the positive synergistic effect can be attributed to the hydroxyl and nitrogen groups of the heat stabilizers. In addition, Asawakosinchai et al. reported that 1,3-dimethyl-6-ami-nouracil (DAU) and eugenol are good thermal stabilizers of PVC compared with other heat stabilizers [20]. Recently, the combined effects of traditional heat stabilizers ($CaSt_2/ZnSt_2$) and tung-oil-derived imide epoxidized ester (GEABTMI) on the thermal stabilization of PVC have been successfully investigated by Wang et al. [21]. They found that the imide and epoxy functions of GEABTMI compound can scavenge free radicals and absorb the HCl generated from PVC pyrolysis. Li et al. studied the interesting mechanical properties of the PVC composite reinforced with $CaCO_3$ nanoparticles; these nanoparticles are good dispersion agents in the PVC system. This can be an effective approach to resist the migration of plasticizers from the PVC [22]. It is known that the addition of $CaCO_3$ fillers increases the thermal stability of PVC polymer [23].

The results showed that $CaCO_3$ can absorb HCl to generate $CaCl_2$, CO_2, and H_2O [24]. Ahmad et al. investigated the synergistic effect of calcium carbonate ($CaCO_3$)/layered double hydroxides (LDHs) on the thermal degradation of PVC [25]. Many researchers reported that the incorporation of different polymers in PVC induced high thermal and mechanical performance [26-28]. Our previous experimental results revealed that the thermal stability of the PVC/LDPE blend was significantly improved by increasing the LDPE loading to values above 50 wt% [27]. To the best of our knowledge, there are no reports on the degradation behavior of PVC considering the synergistic effects of mixed metal stabilizers ($CaSt_2/ZnSt_2$) with different concentrations and different ratios of calcium/zinc stearates, with calcium carbonate ($CaCO_3$) as a micro-filler and recycled low-density polyethylene (r-LDPE). In this study, two ratios of calcium/zinc stearate metal stabilizers, $CaCO_3$ particles, and r-LDPE were added to PVC. This study investigated a new microcomposite based on PVC with high mechanical, thermal, and morphological performance, which can provide sufficient information to reveal the degradation process of PVC.

EXPERIMENTAL

Materials

The recycled LDPE films (melting point: 128°C, density: 0.9555 g cm^{-3}, and MFI: 0.92 (g/10 min, 190°C/2.16 kg)) used in the current study were collected from agricultural plastic waste (greenhouse) in Biskra, Algeria. An amorphous PVC white powder (4000M, K value = 67-72) was purchased from Enterprise National de Pétrochimie (ENIP), Skikda, Algeria. Calcium stearate ($CaSt_2$; Ca content: 6.6-

7.4%), zinc stearate ($ZnSt_2$; Zn content: 10-12%), and calcium carbonate ($CaCO_3$; 2500 mesh) were obtained from Nanjing OMYA Fine Chemical Ind. Co. Ltd. (Nanjing China). Bis (2-ethylhexyl) terephthalate (DOP, 98%) was obtained from Shanxi Sanwei Group Co., Ltd. Mixed metal stabilizers calcium/zinc stearate were prepared in the form of $CaSt_2$:$ZnSt_2$ (9:1) and $CaSt_2$:$ZnSt_2$ (1:9).

Fabrication of microcomposites

Recycled LDPE was washed with detergent and water. All materials were dried in an oven at 80°C for 12 h before blending to remove humidity. PVC and PVC/r-LDPE (1:1) microcomposites with different concentrations of mixed metal stabilizers and calcium carbonate were extruded using the twin-screw extruder, type MSH, at a processing temperature of 175°C and a screw speed of 50 rpm for 10 min from the feed zone to die zone. Details of all different samples are summarized in Table 1. The samples obtained after extrusion were cooled at room temperature, and then pressed into a square mold with dimensions of 200 mm × 200 mm × 1 mm using a heated hydraulic press at 170°C for 7 min with 200-bar pressure. After cooling to room temperature with the water system, the sample was cut off in an altered form by the computer numerical control (CNC) milling machine, before performing mechanical characterization (Figure 1).

Table 1. Compositions of the PVC and PVC/r-LDPE microcomposites.

Sample	PVC (phr)	LDPE (phr)	$CaCO_3$ (phr)	Heat stabilizer (phr) [(a)&(b)]	Plasticizer DOP (phr)
MC0	100	-	20	-	25
MC1	100	-	20	2[a]	25
MC2	100	-	20	2[b]	25
MC3	100	-	20	5[a]	25
MC4	100	-	20	5[b]	25
MC5	100	-	20	10[a]	25
MC6	100	-	20	10[b]	25
MC7	100	100	20	2[a]	25
MC8	100	100	20	2[b]	25
MC9	100	100	20	5[a]	25
MC10	100	100	20	5[b]	25
MC11	100	100	20	10[a]	25
MC12	100	100	20	10[b]	25

[(a)]Attribute to the $CaSt_2$: $ZnSt_2$= 1:9 and [(b)] attribute to the $CaSt_2$: $ZnSt_2$= 9:1 heat stabilizer.

Characterization

Fourier transform infrared spectroscopy (FTIR)

The structural analysis of the PVC and PVC/r-LDPE microcomposite samples was performed by Fourier transform infrared spectroscopy Vertex 70v (FTIR; Bruker Company, Billerica, MA, USA) coupled with an ATR Golden Gate Diamond unit. The samples were measured from 4000 to 400 cm^{-1} with a 4 cm^{-1} spectrum resolution to obtain the FTIR spectra.

Mechanical tests

Mechanical tests were conducted on samples with a standard dimension of 40.0 mm in length, 10.0 mm in width, and 1.0 mm in thickness at ambient conditions, using a mechanical testing machine (Zwick/Roell, ISO 527, Germany) at a crosshead speed of 10 mm/min following the ASTM D638 standard. Each tensile test was performed five times to report the average value.

Heat ageing test

The samples were heated in an air oven at 100 ± 1°C for 360 h (15 days), and the heat ageing of tensile strength, Young's modulus, and elongation-at-break of the samples was performed by ASTM D3045 standard to evaluate the changes in the mechanical properties after ageing.

Investigation of initial thermal stabilization for micro-composites

Congo red test

For the Congo red test, 10.0 g of each PVC sample was placed in an airtight tube and immersed in an oil bath at 180°C (refer to the GB/T 2917.1-2002 standard). Furthermore, the PVC samples were controlled by Congo red paper, and the thermal stability time was recorded when the color of the paper turned blue. The Congo red test was executed three times, and the average value was reported.

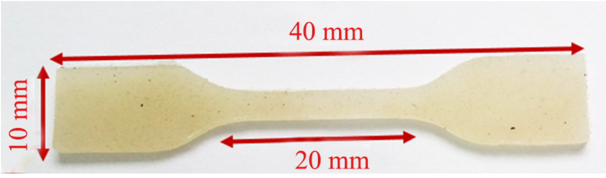


Figure 1. Geometry of the specimen.

Discoloration test

PVC and PVC/r-LDPE samples were cut into sheets with dimensions of 15.0 mm × 15.0 mm × 2.0 mm according to the GB/T9349-2002 standard. The samples were moved onto the ceramic plate in a temperature-controlled oven (V 50 e, Prolabo) at 180°C. Then, the samples were scanned every 10 min using Epson Perfection V19 to evaluate the PVC discoloration during heating.

Thermogravimetric analysis (TGA and DTG)

The TGA and DTG results of the microcomposites were obtained using SDT Q600 from TA Instruments under N_2 atmosphere with a heating rate of 10°C/min using 3-5 mg of the sample. The temperature range was from 25 to 600°C. According to DIN EN ISO 11357-1:2010-0, T_{onset} is defined as the extrapolated onset temperature calculated from the partial peak that results from the first decomposition of the PVC and PVC/r-LDPE components, $T_{10\%}$: the temperature corresponding to the decomposition of PVC and PVC/r-LDPE at the rate of 10%, and T_{max}: the temperature corresponding to the overall maximum of the PVC and PVC/r-LDPE decomposition rate.

Scanning electron microscopy (SEM)

The morphology of the microcomposites was examined using a scanning electron microscope (SEM) (JEOL JSM 6460LV) with an accelerating voltage of 20 kV. The samples were soaked in liquid nitrogen before fracturing, and then the surface and the cross-sections were coated with a thin gold layer by sputtering using EDWARDS scan-coat.

RESULTS AND DISCUSSION

Structure characterization of the PVC and PVC/r-LDPE microcomposites

FTIR tests were conducted to investigate and clarify the modifications in the functional groups of the microcomposites with different heat stabilizer ratios after heat ageing at 100°C for 360 h. The FTIR spectra in Figure 2 and Figure 3 show the characteristic bands of PVC and PVC/r-LDPE microcomposites, and the assignments of these bands are in agreement with those reported in previous studies on composites based on PVC [29-31].

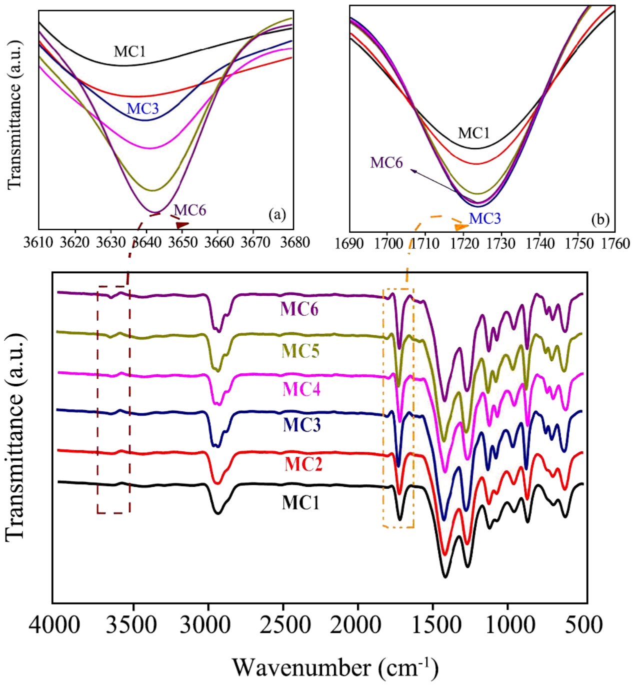


Figure 2. FTIR spectra of PVC microcomposites exposed to thermal ageing for t = 360 h at a temperature of T = 100°C: (a) OH water group superposed region, (b) CO carbonyl group superposed region.

The peaks in the region of 2940-2960 cm^{-1} correspond to the symmetric stretching of C-H in the adjacent

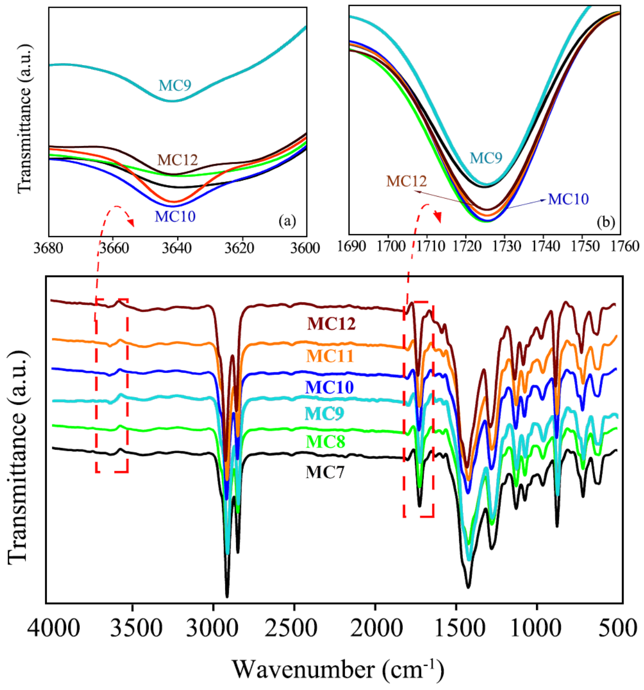


Figure 3. FTIR spectra of PVC/r-LDPE microcomposites exposed to thermal ageing for 360 h at a temperature of T = 100°C: (a) OH water group region, (b) CO carbonyl group region.

CH-Cl. However, the peak at 2849 cm^{-1} in PVC/r-LDPE microcomposites is attributed to the asymmetric stretching of C-H in -CH_3 groups and -CH_2 groups. The peaks in the range of 800-870 cm^{-1} can be attributed to the calcium carbonate group $CaCO_3$. Moreover, the asymmetric stretching of C-Cl can be related to the peaks in the range of 610-730 cm^{-1}. Furthermore, the weak bands around 3620 and 3660 cm^{-1} in Figure 2a and Figure 3a, attributed to the hydroxyl group (OH) stretching of the water phase, probably resulted from the adsorption of HCl by $CaCO_3$ particles.

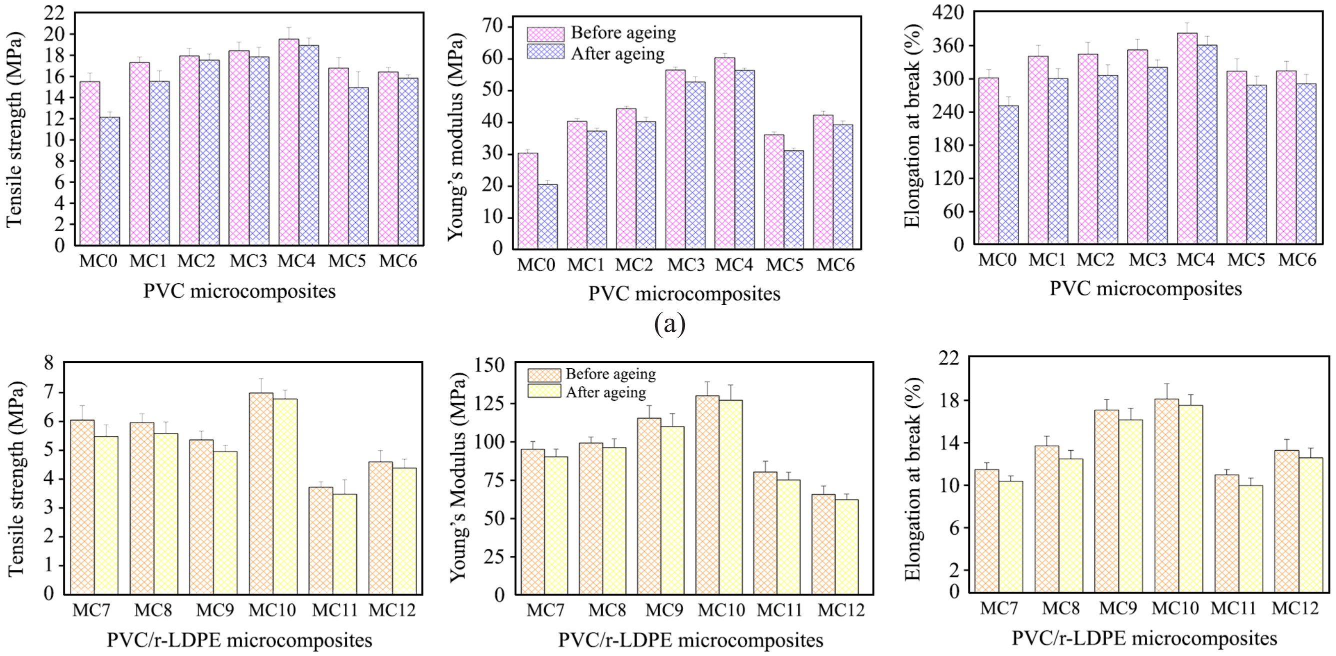
The strong peak at 1732 cm^{-1} in Figure 2b and Figure 3b is attributed to the C=O stretching in the DOP structure, and it is probably due to the oxidation process during the heat ageing test. Finally, it can be concluded that the PVC and PVC/r-LDPE microcomposites with different heat stabilizer concentrations are not significantly affected by the thermal ageing at 100°C, as shown in Figure 2 and Figure 3. The difference in the FTIR peaks between PVC and PVC/r-LDPE microcomposites is visible in the superposed intensity and shape of the characteristic bands represented above.

Mechanical properties of the PVC and PVC/r-LDPE microcomposites

The tensile strength, elongation-at-break, and Young's modulus results of the PVC and PVC/r-LDPE microcomposites before and after ageing are shown in Figures 4a and 4b and Table 2. The results show that pure PVC is more brittle compared with the PVC matrix containing heat stabilizers, $CaCO_3$, and r-LDPE polymer; these additives make the material more mechanically stable.

Figure 4a shows the variation in the tensile behavior of PVC microcomposites at different heat stabilizers ratios. The mechanical performance of the sample without the thermal stabilizer MC0 significantly deteriorates after ageing. In addition, the sample MC4 exhibits better mechanical performance than the pure PVC and other samples before and after ageing. This revealed that the optimum concentration of mixed stearate $CaSt_2$:$ZnSt_2$ (9:1) for the highest tensile strength, elongation at break, and Young's modulus is 5 phr. This concentration probably leads to good dispersion of $CaSt_2$ particles in the PVC micro-composite. From a mechanical point of view, it can be seen that 2 phr of thermal stabilizers MC1 and MC2 are slightly better than 10 phr of MC5 and MC6 with little favor of heat stabilizer with a high concentration of calcium, owing to the interaction between the polar ends of calcium stearate and the marginally polar PVC chains [32].

Figure 4b represents the influence of r-LDPE on the mechanical properties of the PVC microcomposites with 2, 5, and 10 phr of mixed metal stabilizers. The



(a)

(b)

Figure 4. Evolution of the mechanical properties of PVC and PVC/r-LDPE microcomposites before and after heat ageing.

Table 2. Mechanical testing results before and after heat ageing of PVC and PVC/r-LDPE microcomposites.

Sample	Before ageing			After ageing		
	Tensile strength σ (MPa)	Young's modulus E (MPa)	Elongation-at-break Ɛ (%)	Tensile strength σ (MPa)	Young's modulus E (MPa)	Elongation-at-break Ɛ (%)
MC0	15,55±0,8	30,33±1,1	301,02±15,2	12,2±0,5	20,4±1,3	250,5±16,2
MC1	17,38±0,5	40,24±0,9	340,3±20	15,6±1	37,23±0,9	300,09±17,9
MC2	18±0,7	44,23±0,8	344,14±21	17,6±0,6	40,2±1,4	305,76±18,9
MC3	18,5±0,8	56,41±1	351,5±19,6	17,9±0,9	52,7±1,6	320±14
MC4	19,6±1	60,32±1,3	381,62±19	19±0,7	56,4±0,6	360,34±16,5
MC5	16,84±1	36,03±0,9	313,05±22,5	15±1,5	31,1±0,7	287,91±16,5
MC6	16,5±0,4	42,27±1,2	314,11±17	15,9±0,3	39,2±1,2	290,7±16,5
MC7	6,06±0,5	95.14±5,1	11,52±0,6	5,50±0,4	90,26±4,9	10,4±0,5
MC8	5,98±0,3	99.20±4	13,72±0,9	5,60±0,4	96,22±5,7	12,5±0,8
MC9	5,38±0,3	115.33±8,3	17,06±12	4,98±0,2	110±8,6	16,12±1,1
MC10	7.00±0,5	130.19±9	18,11±1,4	6,80±0,3	127,21±10	17,5±1
MC11	3,73±0,2	80.20±7,2	11±0,5	3,63±0,5	75,03±5	10±0,7
MC12	4,61±0,4	65.44±5,5	13,3±11	4,58±0,3	62±3,9	12,6±0,9

incorporation of r-LDPE into PVC decreases the tensile strength and elongation-at-break as compared with those of PVC microcomposites. This deterioration is attributed to the crystalline structure part of the macromolecular chain of r-LDPE polymer, which makes the PVC polymer partially lose its flexibility [33]. On the contrary, Young's modulus values increase two-fold after the addition of r-LDPE into PVC microcomposites. In addition, MC10 exhibits better mechanical properties than other samples before and after ageing. In addition, the incorporation of r-LDPE enhances the mechanical stability of the PVC polymer after heat ageing. Hence, during the thermal treatment, the PVC and short-chain r-LDPE radicals react to produce r-LDPE-g-PVC copolymers [26]. The mechanical properties of the microcomposites based on PVC improve with increasing content of $CaSt_2$.

Effects of thermal stabilizers and r-LDPE on stabilizing PVC microcomposites

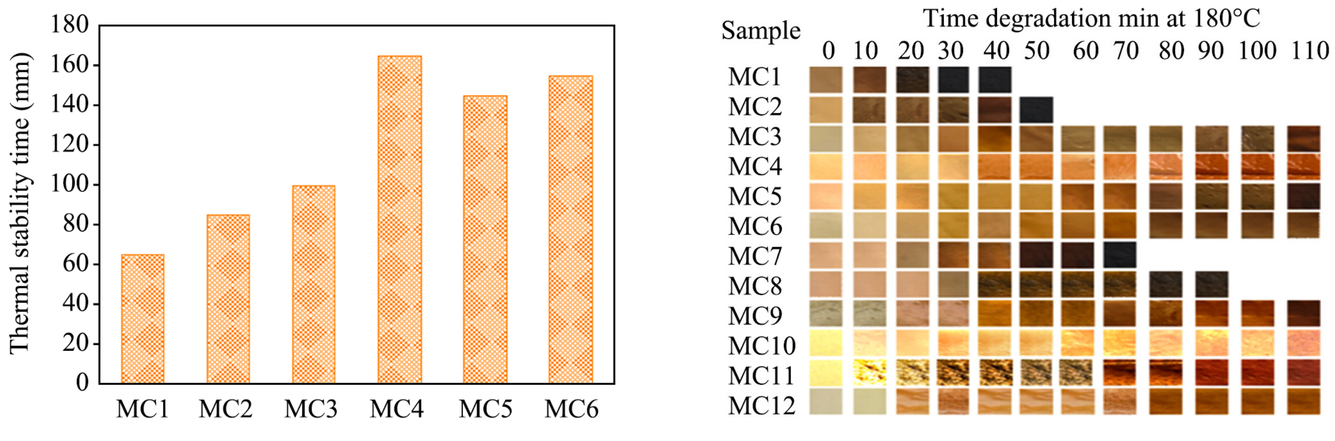
Figures 5a and 5b show the thermal stability time (Congo red test) results of PVC microcomposites at 180°C and the discoloration photos of PVC and PVC/r-LDPE microcomposites at 180°C for 110 min for three different concentrations of thermal stabilizers with $CaSt_2$: $ZnSt_2$ (9:1) and $CaSt_2$: $ZnSt_2$ (1:9), respectively. As shown in Figure 5a, the PVC microcomposites MC4 and MC6, where the thermal stabilizer is rich in calcium, have relatively high thermal stability time (t = 160 min) [34]. As shown in Figure 5b, the thermal stability increased with increasing heat stabilizer concentrations and delayed the discoloration of the PVC samples with significant resistance to discoloration of PVC/r-LDPE samples MC10 and MC12. On the contrary, the incorporation of r-LDPE into PVC resulted in much better antidiscoloration compared with PVC microcomposites. In addition, the samples rich in zinc stearate (MC1, MC3, MC5, MC7, MC9, and MC11) quickly turned to a dark color. The reason for this is that $ZnSt_2$ can remove the initial coloration by substituting labile chlorine atoms from the PVC chain. However, the heat stabilizer rich in calcium stearate increases the PVC stabilization time owing to the inhibition of $ZnCl_2$, which is responsible for the dehydrochlorination process. As is known, $CaSt_2$ could react with $ZnCl_2$ to regenerate $ZnSt_2$ and $CaCl_2$ via an ester exchange reaction (Reaction 1)

$$ZnCl_2 + CaSt_2 \longrightarrow ZnSt_2 + CaCl_2 \qquad (1)$$

Reaction 1. Reaction of zinc chloride with calcium stearate to calcium chloride and a "regenerated" zinc stearate.

Thermal properties of the PVC and PVC/r-LDPE microcomposites

The thermo-gravimetric curves of PVC and PVC/r-LDPE microcomposites with different metal mixed heat stabilizers ratios are plotted in Figures 6a-d. The important temperatures and different thermal degradation levels of PVC and PVC/r-LDPE microcomposites are summarized in Table 3. As shown in the TGA graphs, the thermal degradation of PVC and PVC/r-LDPE occurred in two main steps. Figures 6a and 6b show

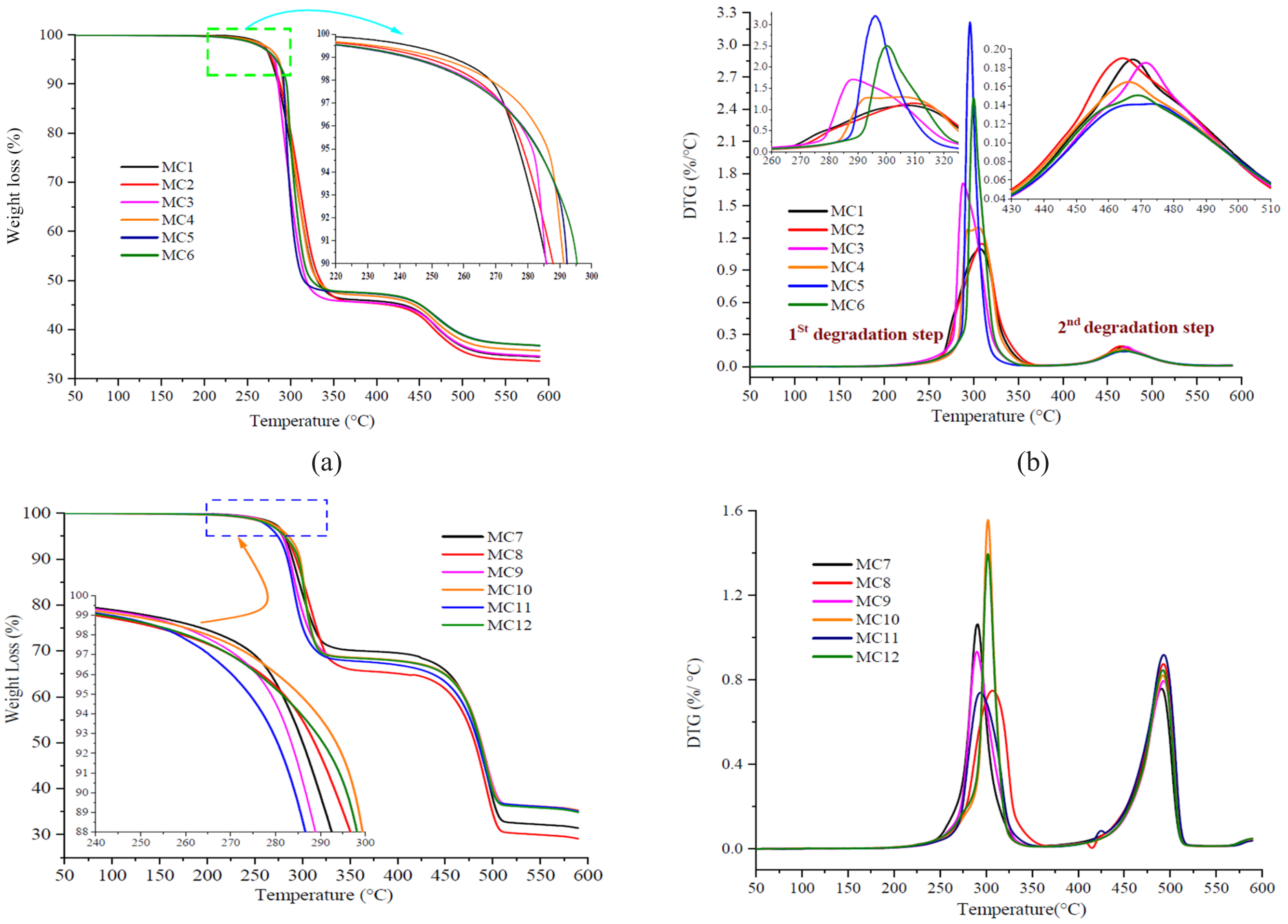


(a) (b)

Figure 5. (a) Thermal stability time (Congo red test) of PVC microcomposites at 180°C. (b) Discoloration photos of PVC and PVC/r-LDPE microcomposites at 180°C for 110 min.

that the first degradation of PVC begins around 277°C with significant loss of weight, which is attributed to the dehydrochlorination of PVC, and the second degradation is related to the scission of polyene sequences [10].

The onset degradation temperature of PVC microcomposites is in the range of 276-290°C. The samples MC1 and MC2 have lower decomposition temperatures



(a) (b)

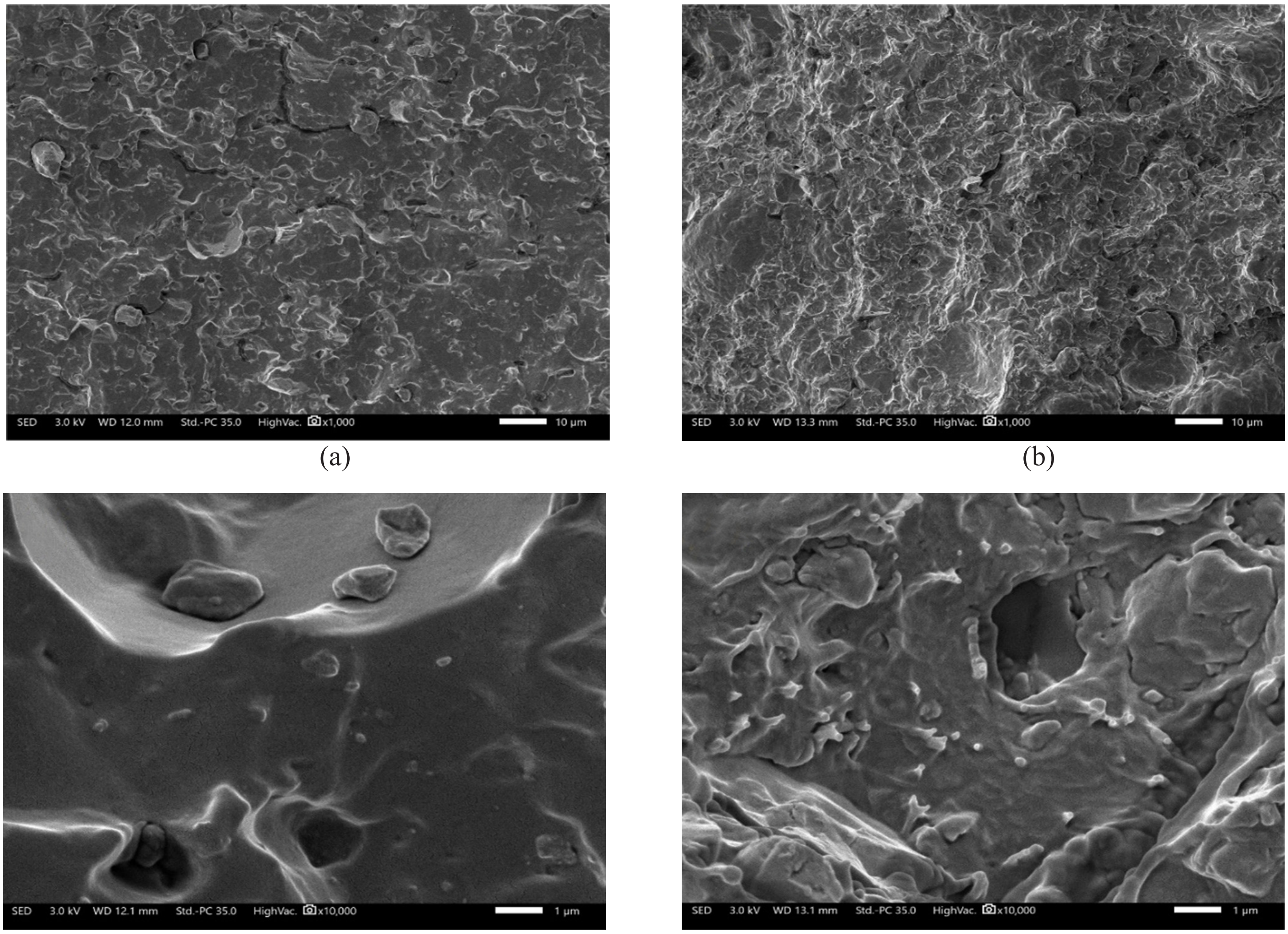
(c) (d)

Figure 6. (a, b) TGA and DTG curves of PVC and (c, d) TGA and DTG curves of PVC/r-LDPE microcomposites.

Table 3. Interested decomposition temperatures and weight loss levels of PVC and PVC/r-LDPE microcomposites.

Sample	Decomposition temperature							
	T_{Onset} (°C)	$T_{10\%}$ (°C)	First stage			Second stage		
			T_{max} (°C)	Mass loss (%)	T_{range} /(°C)	T_{max} (°C)	Mass loss (%)	T_{range} /(°C)
MC1	277.28	285.36	399.54	54.07	277-343	468.30	66.50	442-490
MC2	278.72	286.43	301.22	3.10 5	278-350	464.63	67.50	440-493
MC3	281.13	284.10	288.00	54.00	281-335	474.49	66.30	441-494
MC4	285.55	291.29	302.91	51.09	286-355	473.75	64.21	444-498
MC5	283.30	292.24	296.23	52.51	283-330	470.27	63.00	445-502
MC6	284.61	295.56	300.32	52.23	284-339	470.02	62.10	446-501
MC7	283.52	289.83	290.20	31.00	283-315	490.6	67.40	468-505
MC8	284.48	293.53	305.80	34.00	285-317	491.01	70.50	463-508
MC9	281.00	286.72	290.03	31.45	281-323	490.55	64.60	470-509
MC10	290.20	297.72	304.82	31.35	290-325	492.51	63.50	474-511
MC11	277.22	285.44	292.65	31.90	276-322	490.06	68.55	471-508
MC12	286.42	296.06	300.19	31.50	286-324	492.23	64.85	472-510

as compared to any other PVC microcomposites owing to the small amount of heat stabilizer incorporated in the PVC matrix. Moreover, if the heat stabilizer is increased, the PVC degradation gets delayed significantly in the MC4, MC5, and MC6 samples, in which MC4 sample shifts to higher values. As expected, the thermal stability of the samples containing high calcium concentration is much better than that of the samples



(a) (b)

(c) (d)

Figure 7. SEM images of the fracture surfaces of (a,c) MC4 and (b,d) MC10 microcomposites.

with high zinc concentration in mixed metal stabilizer. This is because of the ability of $CaSt_2$ to absorb more HCl, which leads to much lesser dehydrochlorination and higher stability of PVC microcomposites.

Figures 6c and 6d represent the influence of r-LDPE on the thermal degradation of PVC, which play the same role as a heat stabilizer. Similarly, to PVC degradation, the optimum concentration of mixed stearate $CaSt_2$:$ZnSt_2$ (9:1) for the degradation of PVC/r-LDPE microcomposite is 5 phr. Moreover, it can be concluded that the incorporation of r-LDPE into PVC enhances the values of onset degradation temperatures to a maximum of 290°C and retards the degradation process [35,36]. According to the mechanism proposed by Thongpin et al. [37] and Sombatsompop et al. [26], the beginning of the co-cross-linking process results in macro-radical recombination reactions, which leads to the formation of short PVC chains grafted with r-LDPE at high temperatures.

Fracture surface morphology of the PVC and PVC/r-LDPE microcomposites

Figure 7 shows the SEM micrographs for the fracture surfaces of PVC and PVC/r-LDPE with $CaCO_3$ particles and $CaSt_2$:$ZnSt_2$ (9:1). Figures 7a and 7d show that the hydrophilic $CaCO_3$ micro-particles were highly aggregated in the PVC matrix, with several voids, leading to a decrease in the interfacial adhesion between the $CaCO_3$ particles and the PVC matrix [38]. Figures 7b and 7d reveal good compatibility between the $CaCO_3$ microparticles and the PVC/r-LDPE mixtures compared with the PVC matrix, owing to the good distribution of $CaCO_3$ in the blend. As the PVC was blended with r-LDPE, the $CaCO_3$ particles were well dispersed in the PVC/r-LDPE blend, which led to a strong interfacial interaction between PVC/r-LDPE and the $CaCO_3$ microparticles [39]. These findings are in agreement with the mechanical behavior of microcomposites.

CONCLUSIONS

This work highlights the importance of different additives, such as mixed metal calcium/zinc stearate, $CaCO_3$ particles, and r-LDPE, and their positive effects on enhancing the properties of polyvinylchloride (PVC). $CaSt_2$/$ZnSt_2$ stearate alone as heat stabilizer does not influence the degradation and mechanical properties of PVC; however, the addition of r-LDPE to PVC enhances the performance of the latter to be used in several fields. The optimum ratio of $CaSt_2$:$ZnSt_2$ (9:1) was 5phr, which results in good thermal stability and high mechanical performance of the PVC microcomposites before and after the heat ageing test. r-LDPE with a ratio of 50 phr, as a thermoplastic polymer, exhibited the highest Young's modulus before and after heat ageing; this confirmed its ability to be a highly effective compound for retaining the thermal stability of PVC. Thermal analysis revealed the excellent synergistic effects of $CaCO_3$, a heat stabilizer rich in calcium, and r-LDPE for enhancing the thermal stability of PVC. SEM micrographs showed that the $CaCO_3$ microparticles are well dispersed in the PVC/r-LDPE blend, which leads to a strong interfacial interaction between PVC and r-LDPE.

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CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Samira Maou: Writing - original draft, Methodology. Yazid Meftah: Writing-original draft, formal analysis. Ahmed Maghezzi: Conceptualization, Supervision.

CONFLICTS OF INTEREST STATEMENT

The authors declare that they have no conflicts of interest.

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