



The Effect of Calcium Carbonate-Nanoparticle on the Mechanical and Thermal Properties of Polymers Utilizing Different Types of Mixing and Surface Pre-Treatment: A Review Paper



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HIGHLIGHTS

- The nano-CaCO₃ showed appreciable mechanical and thermal properties
- The modification of CaCO₃ nanoparticles with surface pre-treatment caused enhancement of the mechanical properties twice
- Surface pre-treatment prevented the agglomeration of particles in the matrix
- The twin screw extruder method showed appreciable results

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ABSTRACT

The effect of calcium carbonate nanoparticles (CaCO₃) on the mechanical and thermal properties of various polymers was investigated in this review. The results were compared to scholarly research published between 2002-2022. Different polymers were evaluated, including Polypropylene (PP), High-density polyethylene (HDPE), Polyvinyl chloride (PVC), Low-density polyethylene (LDPE), Polyethylene (PE), and natural rubber (NR). Through this work, the effect of CaCO₃ nanoparticles that act as fillers in polymeric materials has been reviewed. It can be concluded that mechanical and thermal properties can be decreased, increased, or unchanged by increasing and decreasing the fillers to obtain optimal results. It is reasonable to conclude that most papers with nano-CaCO₃ showed improvements in appreciable mechanical and thermal properties. In general, the term "surface modification of inorganic fillers" refers to the coating of the fillers with organic materials, which can be done by physical and chemical interactions between the modifiers and the fillers. The reviewed articles revealed that modification of CaCO₃ nanoparticles with surface pre-treatment fillers caused enhancement of the mechanical properties of the polymeric matrix twice and prevented the agglomeration of particles in the matrix. Various mixing methods have been used, the most significant being a twin screw extruder, mechanical stirrer, and two-roll mill.

1. Introduction

Many laboratories have launched projects involving nanoscale particles in composites in recent years, with varying degrees of success. For example, nanosized inorganic particles have been added to polymers to enhance mechanical, thermal, toughness, and tribological performance [1]. Nanocomposites are a type of filled polymer in which nanometric fillers with property enhancements are incorporated into the polymer matrix at much lower concentrations than microfillers. Calcium carbonate is a common inorganic filler in thermoplastic polymers, such as high-density polyethylene [2] and polypropylene [3]. Because it is the cheapest commercially available and cost-reduction nanofiller in the rubber industry, nano CaCO₃ has recently attracted the interest of modern researchers as an alternative filler for carbon black. Nano CaCO₃ is also an environmentally friendly filler because it is less polluting, less toxic, and white [4]. The addition of nano CaCO₃ improves the resulting properties of rubber nanocomposites, which holds great promise for preparing commercially important rubber compounds [5]. It is a significant inorganic filler used in the plastics, rubber, and paint industries; however, its hydrophilic nature causes dispersion problems in polymer matrixes. The synthesis of nano CaCO₃ particles has been accomplished using elegant methods such as in situ deposition [6,7], conventional precipitation method [8], solution spray process [9], atomized microemulsion technique [10], microbiological precipitation [11], matrix mediated growth technique [12], solution bubbling & industrial carbonation methods [13], crystallization and sonochemical carbonization [14,15], and ultrasound cavitation technique [16]. Meanwhile, nanoparticle composite has a problem because of the high surface energy of the particles, which causes particle agglomeration. Some methods used for well-dispersed nanoparticles include ultrasonic pre-mixing [17]. In particular, nano-CaCO₃ was modified with palmitic

acid [18] and stearic acid [19,20]. Another method for improving nano-CaCO₃ dispersion is to add a small amount of a nonionic modifier during melt extrusion [21]. Calcium carbonate has been used to enhance the tensile strength of high-density polyethylene [22], fractural toughness in polypropylene [23], and mechanical properties of polyvinyl chloride [24], low-density polyethylene [25], and poly (propylene carbonate) [26]. It also improves the compressive strength, elastic modulus, and elongation of epoxy resin [27], modulus, and impact strength of acrylonitrile-butadiene-styrene [28]. The influences of calcium carbonate on natural rubber were also investigated [29], acrylonitrile-butadiene rubber [30], ethylene-propylene-diene rubber [31], styrene-butadiene rubber [32], and butadiene rubber [33].

This work aims to reveal the impact of the CaCO₃ nanoparticles on various polymers' mechanical and thermal properties using a different mixing technique and show comprehensive literature on the result.

2. Methodology

As a research methodology, a literature review based on a study of scholarly journals was conducted to construct a framework for the effect of CaCO₃ nanoparticles on the mechanical and thermal properties of the polymer. For this review, 2002 was chosen as a starting date for the search, and 2022 was chosen for the last paper research. Table 1 shows how CaCO₃ papers in scholarly journals were identified using a classification scheme. Several categories were assigned to each paper as it was reviewed: Method of mixing, Effects of CaCO₃ nanoparticles, surface pre-treatment of CaCO₃, and references.

Table 1: The classification scheme for the CaCO₃ nanoparticles literature review

Method of mixing	Surface pre-treatment of CaCO ₃	Effects of CaCO ₃ nanoparticles
Mechanical stirrer	Oleic Acid	Mechanical properties
Single screw extruder	PMMA chlorinated	Thermal properties
Twin screw extruder	poly-ethylene (CPE)
Two roll mill	Titanate
.....

In this section, the effects of CaCO₃ nanoparticles on the mechanical properties of different polymers using various methods of mixing were investigated, such as twin-screw extruder, two-roll mill, mechanical stirrer, single screw extruder, Brabender mixer, internal mixer, injection molding, and other types of mixing. Researchers aimed to determine the most effective method for mixing nanoparticles with different polymers. The results revealed that the twin-screw extruder, mechanical stirrer, and two-roll mill were the most effective among the various mixing methods. Most of the papers reviewed in this study utilized a twin-screw extruder as the mixing method.

The results, as shown in Figure 1 and Table 2, illustrate that most papers improved the mechanical properties of the composites. Figure 1(a) showed Tensile strength that 56% of the papers reported an increase, 31% reported a decrease, and 13% were not applicable due to the strong interfacial force between the polymer matrix and CaCO₃, which increased tensile strength. Figure 1(b) showed Elongation at break showed that 25% of the papers reported an increase, 19% reported a decrease, and more than half did not provide applicable data. Figure 1(c) illustrates that Young's modulus has significant results, with 88% of the papers reporting an increase, 6% reporting a decrease, and no applicability mentioned for the remaining cases. Hardness testing, as shown in Figure 1(d), was mentioned in fewer papers, and among them, 6% reported an increase, 0% reported a decrease, and 94% did not provide applicable data. Additionally, other mechanical tests, such as impact strength, as shown in Figure 1 (e), yielded appreciable results, with 44% of the papers reporting an increase, 25% reporting a decrease, and 31% either not mentioning or not providing applicable data due to interfacial adhesion in the composites. Flexural strength was mentioned in half of the papers in Figure 1(f), with 50% reporting an increase, 6% reporting a decrease, and 44% not providing applicable data, likely due to the strong bond between the CaCO₃ nanoparticles and the matrix.

The two-roll mill was the second most significant method for mixing, and fewer papers showed a decrement in mechanical properties. The results, as shown in Figure 2 and Table 2, illustrate that most publications improved the composites' mechanical properties. Figure 2 (a), Tensile strength showed that 80% of the papers reported an increase, 10% reported a decrease, and 10% were not applicable due to the strong interfacial force between the polymer matrix and CaCO₃, which increased tensile strength. Figure 2 (b), Elongation at break, showed that 70% of the papers reported an increase, 20% reported a decrease, and 10% did not provide applicable data. Figure 2 (c), Young's modulus showed positive results, with 40% of the papers reporting an increase, 0% reporting a decrease, and 60% not providing applicable data. Additional mechanical tests, such as impact strength and Shore hardness, both showed appreciable results, as shown in Figure 2 (d and e), with 30% of the papers reporting an increase, 0% reporting a decrease, but 70% not mentioning or not providing applicable data due to interfacial adhesion in the composites. Similar to hardness and impact tests, Flexural strength showed in Figure 2 (f) that 20% increased, 0% decreased, and 80% did not provide applicable data, likely due to the strong bond between the CaCO₃ nanoparticles and the matrix.

The mechanical stirrer was the third most important method of mixing, although fewer papers showed a decrease in mechanical properties. As shown in Figure 3 and Table 2, the results demonstrated that most publications improved the composites' mechanical properties. Figure 3 (a) shows that tensile strength yielded significant results, with 90% of papers reporting an increase, no papers reporting a decrease, and 10% not providing applicable data due to the strong interfacial force between the polymer matrix and CaCO₃, which was strong enough to increase tensile strength. Elongation at break showed that 10% of the papers reported an increase, 20% reported a decrease, and 70% did not provide applicable data, as shown in Figure 3 (b). Young's modulus showed that 30% of the papers reported an increase, 10% reported a decrease, and 60% did not provide applicable data, as shown in Figure 3 (c). Additional mechanical tests, such as impact strength and Shore hardness, both yielded

appreciable results, as shown in Figure 3 (d and e), with 40% of the papers reporting an increase, no papers reporting a decrease, but 60% not mentioning or not providing applicable data due to interfacial adhesion in the composites. Flexural strength also showed a 20% increase, with no papers reporting a decrease and 80% not providing applicable data, likely due to the strong bond between the CaCO₃ nanoparticles and the matrix, as shown in Figure 3 (f). This review article reviewed the single screw extruder, Brabender mixer, internal mixer, and injection molding, as shown in Table 2. The result showed that most papers improved the composites' mechanical properties.

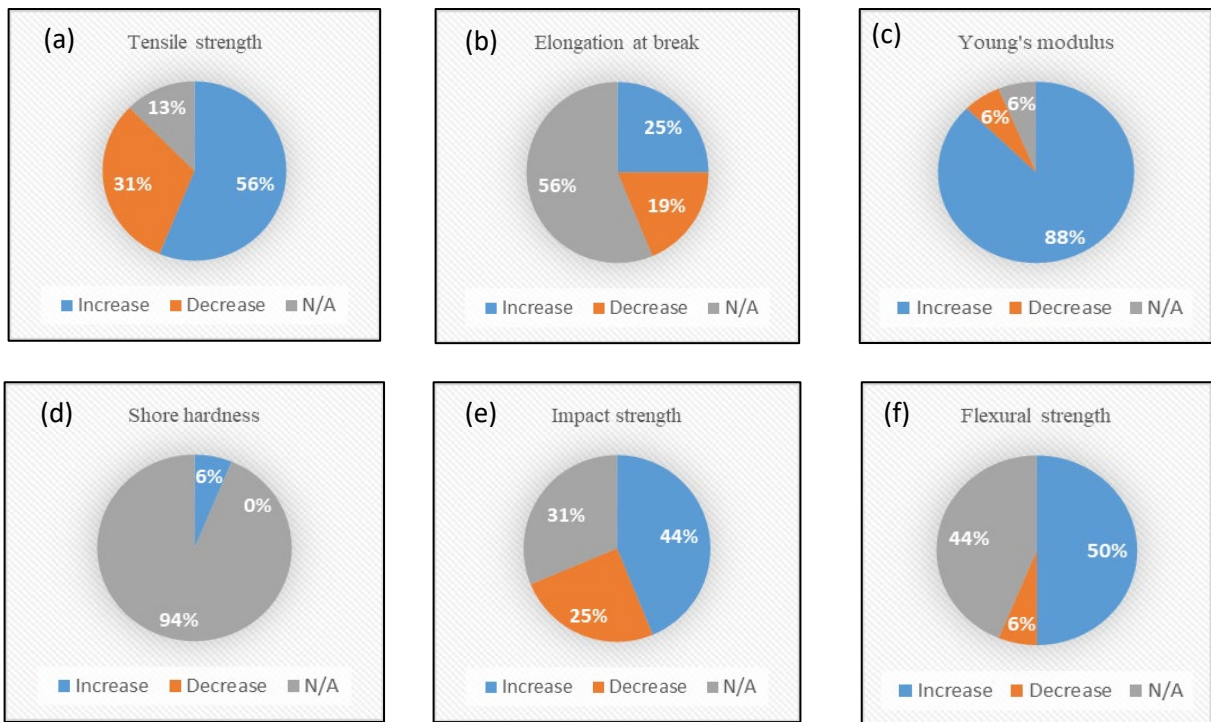


Figure 1: Influence of CaCO₃ nanoparticles on mechanical properties of different polymers using Twin-screw extruder

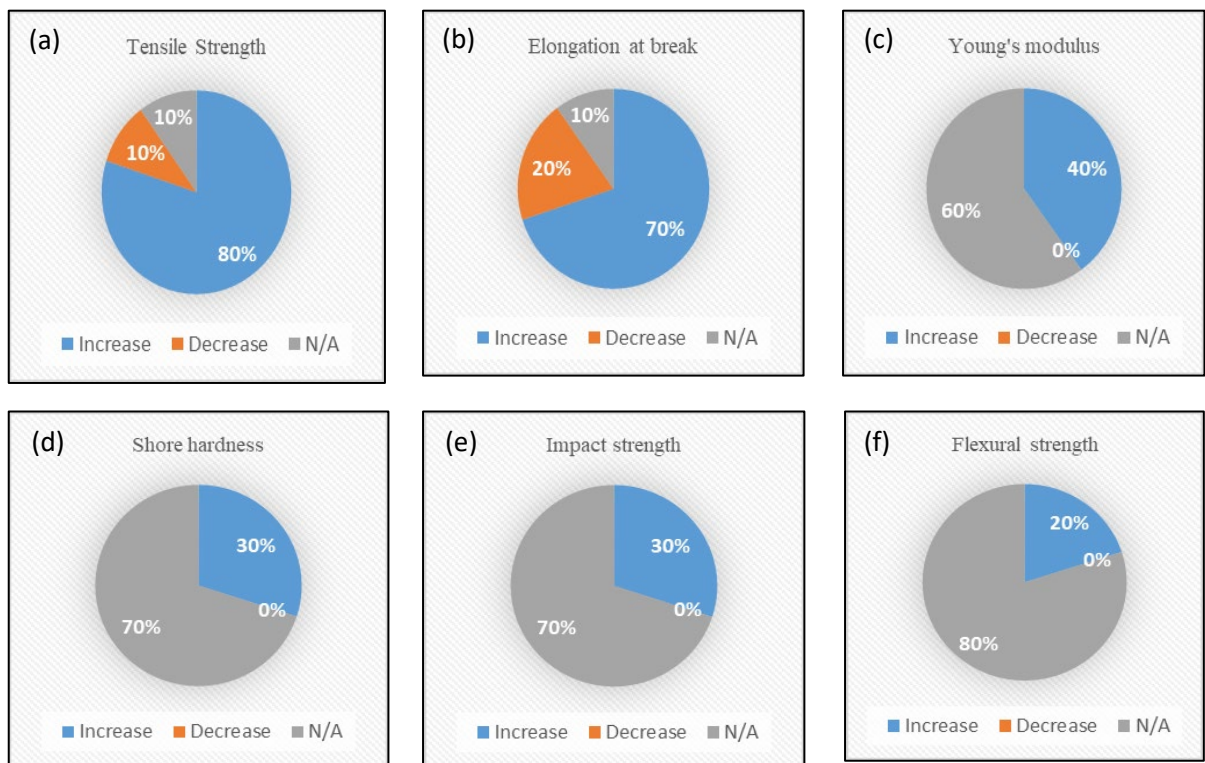


Figure 2: Influence of CaCO₃ nanoparticles on mechanical properties of different polymers using a Two-roll mill extruder

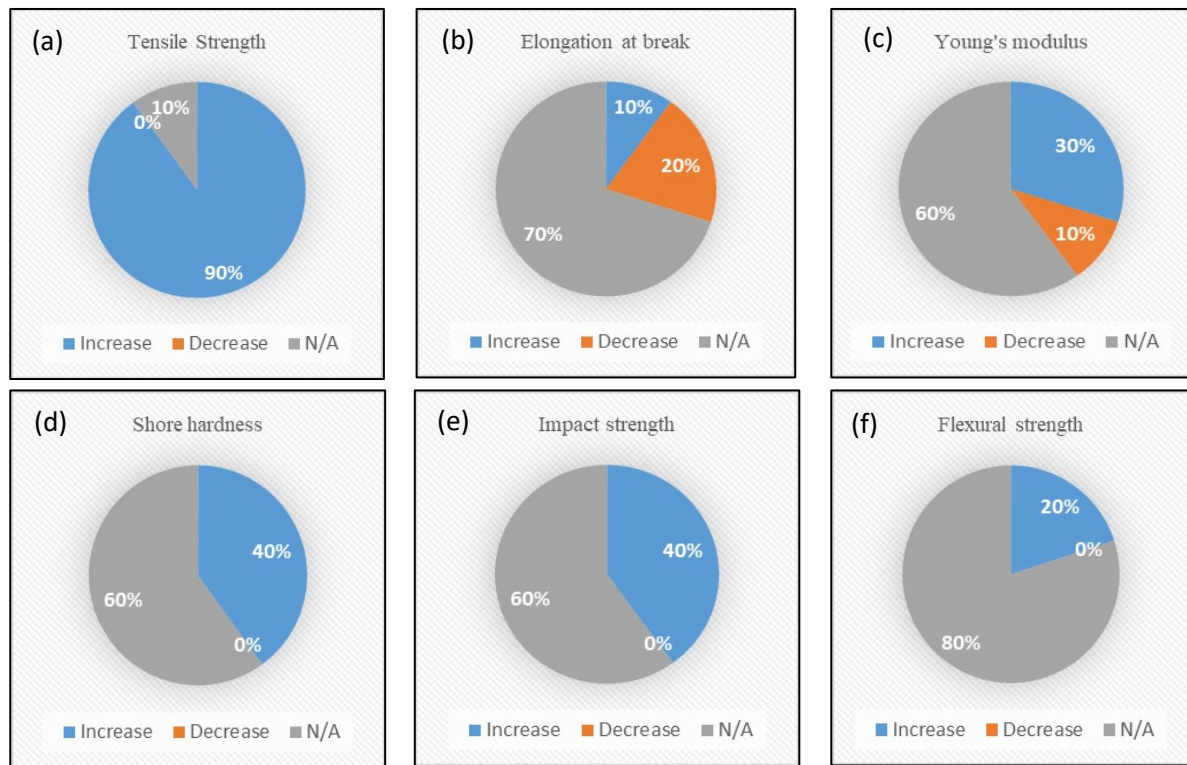


Figure 3: Influence of CaCO₃ nanoparticles on mechanical properties of different polymers using a mechanical stirrer

Table 2: Influence of CaCO₃ nanoparticles on mechanical properties of polymer using different methods of mixing

Polymeric Materials	Method Of Mixing	Shore Hardness	Tensile Strength	Elongation To break	Young's modulus	Impact strength	Flexural strength	Ref.
Twin-screw Extruder								
ABS	Twin-screw Extruder	N/A	-	N/A	+	-	N/A	[28]
ABS	Twin-screw Extruder	N/A	-	-	+	-	+	[34]
Homo (PP)	Twin-screw Extruder	N/A	+	-	+	+	+	[35]
PBT	Twin-screw Extruder	N/A	N/A	N/A	+	N/A	N/A	[36]
PEEK	Twin-screw Extruder	N/A	+	N/A	+	-	+	[37]
PLA	Twin-screw Extruder	N/A	-	+	+	N/A	-	[38]
Polyamide	Twin-screw Extruder	N/A	+	-	+	N/A	N/A	[6]
Polyamide 6	Twin-screw Extruder	N/A	+	N/A	+	-	+	[39]
POM/CB	Twin-screw Extruder	N/A	+	N/A	+	+	+	[40]
PP	Twin-screw Extruder	N/A	N/A	N/A	+	+	N/A	[23]
PPS	Twin-screw Extruder	N/A	+	N/A	N/A	+	N/A	[41]
PPS/GF	Twin-screw Extruder	N/A	+	+	+	+	+	[42]
PPS/PC/GF	Twin-screw Extruder	N/A	+	+	+	N/A	+	[43]
PS	Twin-screw Extruder	N/A	-	N/A	+	N/A	N/A	[44]
Waste PP	Twin-screw Extruder	+	+	N/A	+	+	N/A	[45]
β-polypropylene	Twin-screw Extruder	N/A	-	+	-	+	+	[46]
Two-roll mill								
BR	Two-roll mill	N/A	+	+	N/A	N/A	N/A	[33]
EPDM	Two-roll mill	N/A	+	+	N/A	N/A	N/A	[47]
NR	Two-roll mill	N/A	+	+	N/A	N/A	N/A	[29]
vulcanizate								
PBR	Two-roll mill	+	+	+	+	N/A	N/A	[48]
PP/ POE	Two-roll mill	N/A	Un-change	-	+	+	+	[49]
PPE, SBS	Two-roll mill	N/A	-	N/A	N/A	+	+	[50]
PVC	Two-roll mill	N/A	+	+	+	+	N/A	[51]
SBR	Two-roll mill	N/A	+	+	N/A	N/A	N/A	[12]
SBR	Two-roll mill	+	+	+	+	N/A	N/A	[32]
SBS	Two-roll mill	+	+	-	N/A	N/A	N/A	[52]
Mechanical stirrer								
(MMA), n-(BA)].	mechanical stirrer	+	+	N/A	N/A	+	N/A	[53]
CF/Epoxy epoxy resin	Mechanical stirrer	N/A	+	N/A	N/A	+	+	[54]
	Mechanical stirrer	+	+	N/A	+	+	N/A	[55]
NR Latex	mechanical stirrer	N/A	+	-	+	N/A	N/A	[56]
PLA	Mechanical stirrer	N/A	+	N/A	+	N/A	N/A	[57]

Table 2: Continued

polyacrylonitrile (PAN)	mechanical stirrer	N/A	+	N/A	N/A	N/A	N/A	[58]
PU	mechanical stirrer	+	+	+	N/A	N/A	N/A	[59]
PU	Mechanical stirrer	+	N/A	N/A	N/A	N/A	N/A	[60]
unsaturated polyester	mechanical stirrer	N/A	+	N/A	N/A	+	+	[61]
waterborne polyurethane	mechanical stirrer,	N/A	+	-	-	N/A	N/A	[62]
Single-screw extruder								
ABS	Single-screw extruder	N/A	+	+	N/A	+	N/A	[63]
HDPE	Single-screw extruder	-	-	-	N/A	-	-	[64]
HDPE	Single-screw extruder	N/A	+	N/A	+	-	N/A	[65]
PP	Single-screw extruder	N/A	-	+	+	N/A	N/A	[66]
PPE, SBS	Single-screw extruder	N/A	-	N/A	N/A	+	+	[50]
Brabender mixer								
LDPE	Brabender mixer	N/A	+	-	+	N/A	N/A	[67]
PP/PA66	Brabender mixer	N/A	N/A	N/A	+	N/A	-	[68]
PS/HIPS	Brabender mixer	N/A	+	-	N/A	N/A	N/A	[69]
PVC	Brabender mixer	+	+	+	+	N/A	N/A	[70]
Rubber reinforced	Brabender mixer	-	+	-	+	N/A	N/A	[26]
Internal mixer								
Isotactic PP	Internal mixer	N/A	-	N/A	+	+	N/A	[71]
LLDPE/CNR	Internal mixer	N/A	N/A	N/A	N/A	+	N/A	[72]
NR	Internal mixer	N/A	+	-	+	N/A	N/A	[73]
PLA/NR	Internal mixer	N/A	-	+	+	+	N/A	[74]
Injection molding								
HDPE	Injection molding	N/A	-	-	+	-	N/A	[2]
HDPE	Injection molding	N/A	-	+	N/A	+	N/A	[75]
HDPE	Injection molding	N/A	+	-	+	N/A	N/A	[76]
i-PP/EVA	Injection molding	+	-	N/A	+	+	N/A	[77]
Other types of mixing								
(CH) / PVP-co-VAc)	solution casting method	N/A	+	N/A	+	N/A	N/A	[78]
Basalt Fiber/Epoxy	high-speed shear mixing	N/A	+	N/A	+	N/A	+	[79]
Chitosan/PVA	Electrospinning	N/A	-	-	+	N/A	N/A	[80]
Epoxy composites	Magnetic stirrer	N/A	N/A	N/A	N/A	+	+	[81]
epoxy/fly ash	ultrasonic bath stirring	N/A	+	+	N/A	+	+	[82]
Geo Polymer/fly ash	Hobart mixer	+	N/A	N/A	N/A	+	+	[83]
kenaf fiber/polyester	vacuum-assisted resin infusion (VARI)	N/A	+	N/A	+	N/A	+	[84]
Novolac Epoxy Resin	Electrical Stirrer	+	N/A	+	+	+	+	[85]
PEHA)/(PVA)	in situ polymerization	N/A	+	N/A	N/A	N/A	N/A	[86]
PF/Ep	Ultrasonication	N/A	+	N/A	+	+	+	[87]
PMMA	In-situ Polymerization	N/A	N/A	N/A	+	+	N/A	[88]
PP	Haake PolyLab	N/A	+	+	+	N/A	N/A	[89]
PP	Haake mixer	N/A	N/A	-	+	+	N/A	[90]
PPC	Twin rotary mixer	N/A	-	+	+	N/A	N/A	[91]
PS	solution blending.	N/A	N/A	+	N/A	N/A	N/A	[92]
PVAc	Emulsion methods	N/A	+	-	+	N/A	N/A	[93]
waste polypropylene (rPP)	Melt Laboplastomill	N/A	-	N/A	N/A	-	N/A	[94]

The symbol (+) represents a moderate increase in properties, and (-) describes a moderate decrease in properties. N/A: not applicable.

3. Effects of CaCO₃ Nanoparticles on Properties of Polymers

After a comprehensive examination of the effects of CaCO₃ nanoparticles to identify similarities and differences, we classify the effect of CaCO₃ into Mechanical properties and thermal properties. Additionally, we explore different surface pre-treatment methods for mixing as a pre-mixer.

3.1 Influence of CaCO₃ Nanoparticles on Mechanical Properties of Polymers

Several papers exist on the influence of nano CaCO₃ on the mechanical properties of polymers, which is thought to be the most popular topic in nanocomposite applications. Table 3 illustrates the influence of CaCO₃ nanoparticles on the mechanical

properties of different polymers. The mechanical properties include several focused areas, such as shore hardness (a and d), tensile strength (MPa), young modulus (MPa), elongation to break, flexural strength (MPa), and Impact strength (J/m). CaCO_3 was added at 9, 15, and 21nm rates in polybutadiene rubber (PBR) [48]. It can be seen that the tensile strength and Young modulus are higher for 9 nm particles in 8 wt.% of filler loading, even higher than commercial CaCO_3 . The effect of CaCO_3 nanoparticles on the mechanical of fly ash-reinforced epoxy polymer composites was studied in the literature [82]. By adding CaCO_3 nanoparticles, tensile strength, and impact strength were improved. The effect of mineral nanofiller synthesis using the solution spray method on the mechanical and thermal properties of EPDM nanocomposites, such as CaCO_3 nanoparticles 20nm, CaCO_3 microparticles (20 microns), and fly ash, sodium lauryl sulfate (SLS) as a stabilizing agent was studied. The result indicated that nano CaCO_3 showed better thermal stability and mechanical properties by adding CaCO_3 nanoparticles [47]. The influence of CaCO_3 nanoparticles on the mechanical properties of different polymers was investigated in this review.

Figure 4 and Table 3 show that most papers reported an increase in the mechanical properties of the composites. For tensile strength, as shown in Figure 4 (a), 60% of papers showed an increase, 23% showed a decrease, and 17% were not applicable because the interfacial force between the polymer matrix and the CaCO_3 was strong enough to increase tensile strength. Figure 4 (b), Elongation at break also showed good results, with 32% of the papers showing an increase, 24% a decrease, and 44% not applicable. In Figure 4 (c), Young's modulus showed a significant result, with 61% of the papers reporting an increase, 6% a decrease, and 33% not applicable. Fewer papers mentioned hardness tests, as shown in Figure 4 (d), but 17% showed an increase, 3% a decrease, and 80% were not applicable. Regarding impact strength in Figure 4 (e), appreciable results were seen, with 39% of papers showing an increase, only 11% a decrease, and 50% not being mentioned or not applicable due to interfacial adhesion in the composites. Also, in Figure 4 (f), the flexural strength mentioned in a few papers, 27% showed an increase, 4% a decrease, and 69% were not applicable due to the strong bond between the CaCO_3 nanoparticles and matrix.

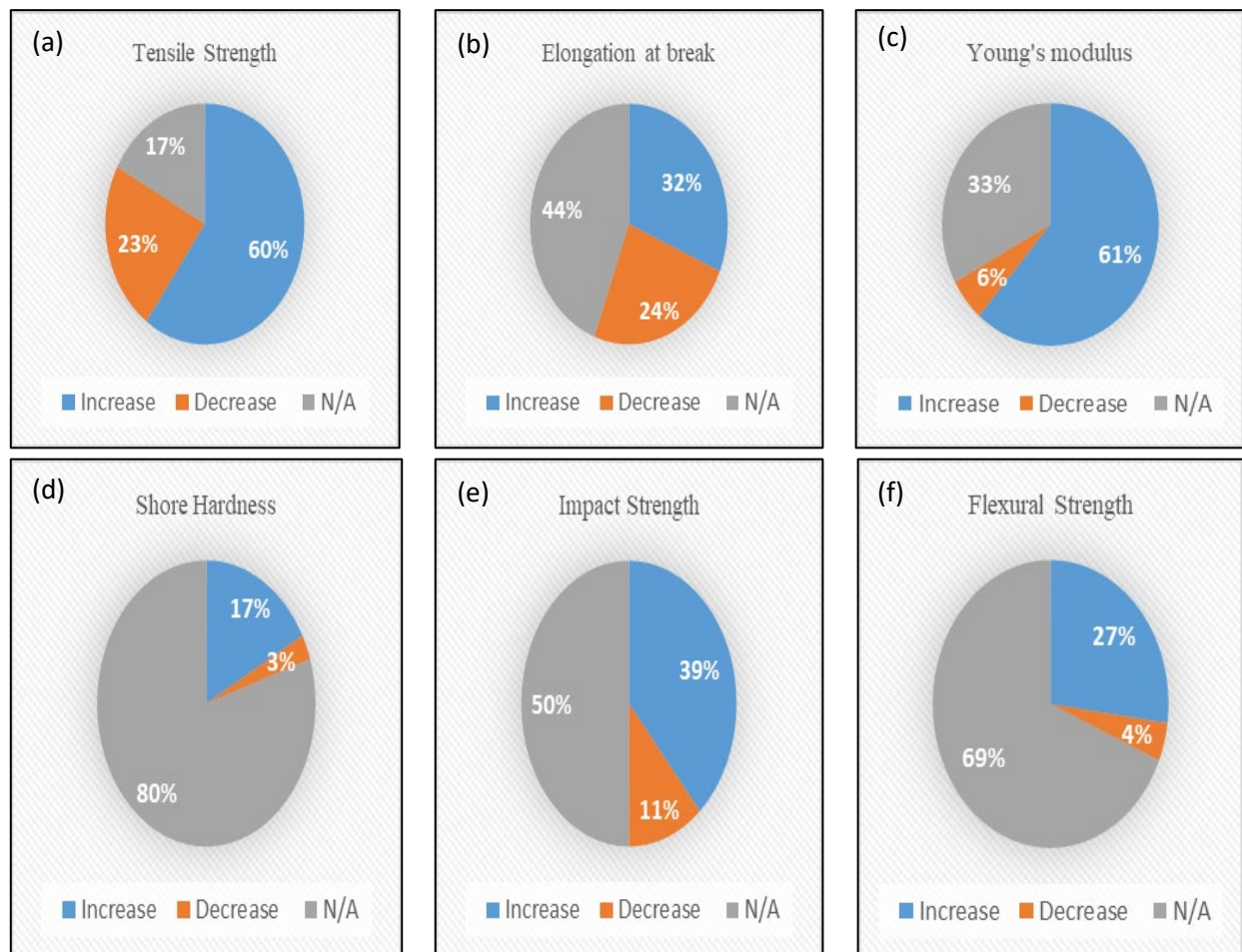


Figure 4: Influence of CaCO_3 nanoparticles on mechanical properties of various polymers

Table 3: Influence of CaCO₃ on mechanical properties of polymers

Polymeric Materials	Shore Hardness	Tensile Strength	Elongation To break	Young's modulus	Impact strength	Flexural strength	Ref.
ABS	N/A	-	N/A	+	-	N/A	[28]
ABS	N/A	+	+	N/A	+	N/A	[63]
ABS	N/A	-	-	+	-	+	[34]
Basalt Fiber/Epoxy	N/A	+	N/A	+	N/A	+	[79]
BR	N/A	+	+	N/A	N/A	N/A	[33]
CF/Epoxy	N/A	+	N/A	N/A	+	+	[54]
CH / PVP-co-VAc)	N/A	+	N/A	+	N/A	N/A	[78]
chitosan/PVA	N/A	-	-	+	N/A	N/A	[80]
EPDM	N/A	+	+	N/A	N/A	N/A	[47]
Epoxy composites	N/A	N/A	N/A	N/A	+	+	[81]
epoxy resin	+	+	N/A	+	+	N/A	[55]
epoxy/fly ash	N/A	+	+	N/A	+	+	[82]
Geo Polymer/fly ash	+	N/A	N/A	N/A	+	+	[83]
HDPE	N/A	-	-	+	-	N/A	[2]
HDPE	-	+	-	N/A	-	-	[64]
HDPE	N/A	+	N/A	+	-	N/A	[65]
HDPE	N/A	-	+	N/A	+	N/A	[75]
HDPE	N/A	+	-	+	N/A	N/A	[76]
Homo (PP)	N/A	+	-	+	+	+	[35]
i-PP/EVA	+	-	N/A	+	+	N/A	[77]
Isotactic PP	N/A	-	N/A	+	+	N/A	[71]
kenaf fiber/polyester	N/A	+	N/A	+	N/A	+	[84]
LDPE	N/A	+	-	+	N/A	N/A	[67]
LLDPE/CNR	N/A	N/A	N/A	N/A	+	N/A	[72]
MMA n-butyl acrylate.	+	+	N/A	N/A	+	N/A	[53]
Novolac Epoxy Resin	+	N/A	+	+	+	+	[85]
NR	N/A	+	-	+	N/A	N/A	[73]
NR Latex	N/A	+	-	+	N/A	N/A	[56]
NR vulcanizate	N/A	+	+	N/A	N/A	N/A	[29]
PBR	+	+	+	+	N/A	N/A	[48]
PBT	N/A	N/A	N/A	+	N/A	N/A	[36]
PEEK	N/A	+	N/A	+	+	+	[37]
PEHA)/ (PVA)	N/A	+	N/A	N/A	N/A	N/A	[86]
PF/Ep	N/A	+	N/A	+	+	+	[87]
PLA	N/A	-	+	+	N/A	-	[38]
PLA	N/A	+	N/A	+	N/A	N/A	[57]
PLA/NR	N/A	-	+	+	+	N/A	[74]
PMMA	N/A	N/A	N/A	+	+	N/A	[88]
polyacrylonitrile (PAN)	N/A	+	N/A	N/A	N/A	N/A	[58]
Polyamide	N/A	+	-	+	N/A	N/A	[6]
Polyamide 6	N/A	+	N/A	+	-	+	[39]
POM/CB	N/A	+	N/A	+	+	+	[40]
PP	N/A	N/A	N/A	+	+	N/A	[23]
PP	N/A	N/A	-	+	+	N/A	[90]
PP	N/A	-	+	+	N/A	N/A	[66]
PP	N/A	+	+	+	N/A	N/A	[89]
PP/ POE	N/A	Un-change	-	+	+	+	[49]
PP/PA66	N/A	N/A	N/A	+	N/A	-	[68]
PPC	N/A	-	+	+	N/A	N/A	[91]
PPE, SBS	N/A	-	N/A	N/A	+	+	[50]
PPS	N/A	+	N/A	N/A	+	N/A	[41]
PPS/GF	N/A	+	+	+	+	+	[42]
PPS/PC/GF	N/A	+	+	+	N/A	+	[43]
PS	N/A	-	N/A	+	N/A	N/A	[44]
PS	N/A	N/A	+	N/A	N/A	N/A	[92]

Table 3: Continued

PS/HIPS	N/A	+	-	N/A	N/A	N/A	[69]
PU	+	+	+	N/A	N/A	N/A	[59]
PU	+	N/A	N/A	N/A	N/A	N/A	[60]
PVAc	N/A	+	-	+	N/A	N/A	[93]
PVC	N/A	+	+	+	+	N/A	[51]
PVC	+	+	+	+	N/A	N/A	[70]
Rubber reinforced	-	+	-	+	N/A	N/A	[26]
SBR	N/A	+	+	N/A	N/A	N/A	[12]
SBR	+	+	+	+	N/A	N/A	[32]
SBS	+	+	-	N/A	N/A	N/A	[52]
unsaturated polyester	N/A	+	N/A	N/A	+	+	[61]
waste polypropylene (rPP)	N/A	-	N/A	N/A	-	N/A	[94]
Waste PP waterborne polyurethane	+	+	N/A	+	+	N/A	[45]
β-polypropylene	N/A	+	-	-	N/A	N/A	[62]
	N/A		+		+	+	[46]

The symbol (+) represents a moderate increase in properties, and (-) describes a moderate decrease in properties.
N/A: Not Applicable.

3.2 Influence of CaCO₃ Nanoparticles on Thermal Properties of Polymers

The effect of CaCO₃ nanoparticles on the thermal properties of polymers is another important topic. Therefore, more research is needed to fill gaps in this area, as understanding the degradation behavior of polymers and their nanocomposites is required for outdoor insulation applications. Calcium carbonate nanoparticles improved the thermal Properties of a polycaprolactone (PCL)/chitosan blend, which was studied by [95]. It can be seen that 1 wt% of nanosized CaCO₃ showed an appreciable result. The differential scanning calorimetry and thermogravimetric analysis were used to assess the thermal stability of the Chlorinated poly (vinyl chloride) CPVC/CaCO₃ nanocomposites in the literature [96]. Adding 3.75% of CaCO₃ to the matrix revealed the best result, which can improve thermal stability. The influence of CaCO₃ nanoparticles on the thermal properties of different polymers was investigated in this review. Figure 5 and Table 4 illustrate that the majority of papers showed increased thermal properties of the composites.

Table 4: Influence of CaCO₃ nanoparticles on thermal properties of polymers

Polymeric Materials	Method of Mixing	Glass transition temperature (°C)	Thermal Stability	Ref.
BR	Two-roll mill	+	+	[33]
Chlorinated poly (vinyl chloride) CPVC	Two-roll mixer	+	+	[96]
EPDM	Two roll mill	+	+	[47]
Epoxy composites	Magnetic stirrer	+	+	[81]
HDPE	twin screw mixer	N/A	-	[97]
HDPE	injection molding	N/A	+	[75]
i-PP	Brabender Plastograph	+	+	[98]
i-PP/EVA	injection molding	N/A	+	[77]
LDPE	Brabender Plasti-Corder	Un-change	Un-change	[67]
methyl methacrylate (MMA), n-butyl acrylate (BA)]	mechanical stirrer	+	+	[53]
NBR	Two-roll mill	N/A	+	[99]
NR	Internal mixer	+	+	[100]
oil palm trunk/PVC	Mechanical stirrer	N/A	+	[101]
PAN	mechanical stirrer	N/A	+	[58]
PBR	Two-Roll mill	+	+	[48]
PBT	twin-screw extruder	+	N/A	[36]
PCL/Chitosan	Melt blending technique	+	+	[95]
PE	Mechanical mixer	+	+	[102]
PEEK	Twin-screw extruder	+	+	[37]
PEHA)/ (PVA)	in situ polymerization	+	+	[86]
PET	Mechanical stirrer	+	+	[103]
PET	In situ preparation	N/A	+	[104]

Table 4: Continued

PET	in situ polymerization	+	+	[105]
PET	mechanical stirring	+	+	[106]
PET	Batch mixer	+	+	[107]
PF/Ep	Ultrasonication	N/A	+	[87]
PLA	solution casting	+	+	[108]
PLA	twin screw extruder	N/A	-	[109]
PLA	Mechanical stirrer	-	-	[57]
PLA/	Twin screw extruder	+	+	[38]
EPR-g-MAH				
PLA/NR	Internal mixer	Unchanged	N/A	[74]
PMMA	Ultrasound mixing	+	+	[110]
PMMA	mechanical stirring	+	+	[111]
PMMA/PS	solution mixing technique	+	+	[112]
Polyamide	Twin screw extruder	+	+	[6]
POM/CB	twin-screwextruder	+	+	[40]
PP	twin screw extruder	-	-	[23]
PP	Haake Polylab	N/A	+	[89]
PP	twin-screw extruder	-	-	[113]
PP/PA66	Brabender Plastograph	N/A	+	[68]
PPC	Twin rotary mixer	+	+	[91]
PS/HIPS	Brabender Plastograph	+	+	[69]
PU	mechanical stirrer	N/A	+	[114]
PU	hand stirring	N/A	+	[115]
PU	mechanical stirrer	N/A	+	[59]
PU	Mechanical stirrer	N/A	+	[60]
PVAc	Emulsion methods	-	N/A	[93]
PVC	two-roll mill	+	+	[51]
PVC	solution blending	N/A	+	[116]
PVC	Brabender Plasticorder	+	+	[70]
SBR	two-roll mill	+	+	[12]
Soybean Based Hybrid	Noncontact THINKY	+	+	[117]
Unsaturated Polyester	hybrid mixer			
waterborne	mechanical	N/A	+	[62]
polyurethane	stirrer			

The symbol (+) represents a moderate increase in properties, and (-) describes a moderate decrease in properties. N/A: not applicable.

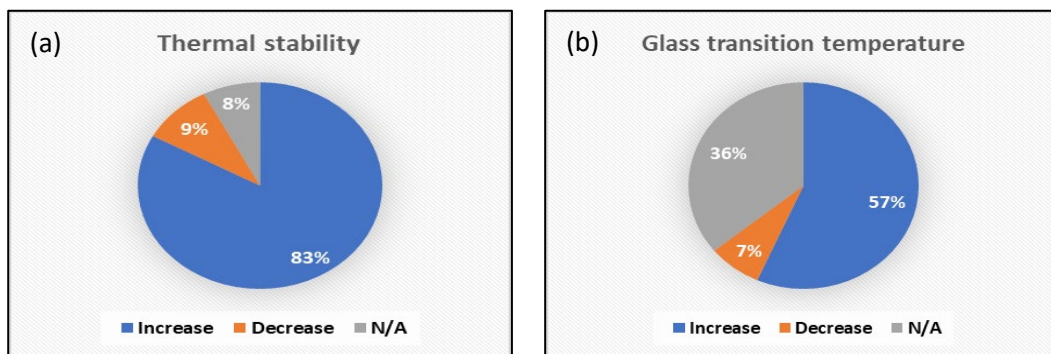


Figure 5: Influence of CaCO₃ nanoparticles on thermal properties of various polymers

Thermal stability is shown in Figure 5 (a), which showed a significant result, with 83% of papers reporting increased thermal stability, only 9% of papers showing decreased thermal stability, and 8% not being applicable because of the high cross-linking structure and uniform dispersion of the modified CaCO₃ increasing thermal stability. Also, the glass transition temperature of the polymeric materials increased in 57% of papers, decreased in only 7%, and was not mentioned or not applicable in 36% of papers, as illustrated in Figure 5 (b). Those increments happened due to strong interactions between the nanoparticles. It can be seen that adding CaCO₃ nanoparticles to a polymeric material showed a significant result.

3.3 Influence of Surface Pre-Treatment of CaCO₃ Nanoparticles on Mechanical Properties of Polymers

In general, surface modification of inorganic fillers refers to applying organic coatings to the fillers, which can be accomplished through physical and chemical interactions between the modifiers and the fillers. The effect of different surface pre-treatments as a modifier for CaCO₃ nanoparticles has been reviewed. Figure 6 (a and b) showed a significant result of PTT/CaCO₃: 1% CaCO₃ and PTT/CaCO₃: 2% CaCO₃, respectively, using titanate as a modifier. It can be seen that using these

pre-treatment techniques improved mechanical performance twice, as shown in Table 5 and Figure 7 (a and b). It prevented particle agglomeration as shown below in Figure 8 (a and b), in which oleic acid was used as a modifier. It showed appreciable results and prevented the agglomeration of the nanoparticles. It is difficult to control without these pre-treatments.

When preparing a CPE/nano-CaCO₃ of 40nm by masterbatch, chlorinated polyethylene (CPE) was used as an interfacial modifier in the literature [118]. Morphology analysis revealed that the nano-CaCO₃ particles in the PVC matrix were encapsulated with a CPE layer. The impact strength of the nanocomposites was significantly improved twice by incorporating CPE, giving a high value of 745 J/m. The effect of nano-CaCO₃ on the mechanical properties of PVC and PVC/Blendex blends using a two-roll mill was investigated by [119] to create ternary composites.

The PVC compound, nano-CaCO₃, and Blendex 20 phr were mixed similarly. The result revealed that impact strength increases two times than matrix, and elongation at break increased till 5 wt% of CaCO₃ nanoparticle. Impact energy and crystallization of polypropylene/CaCO₃ nanocomposites with nonionic modifiers were studied in the literature [21]; the tensile properties of the PP/CaCO₃ (85/15) nanocomposite were not significantly changed by adding 1.5 wt percent nonionic modifier, but the notched Izod impact energy of the composites was significantly increased and the distribution of particles uniformly dispersed. Triethoxy vinyl silane (TEVS) was used as a modifier for nano CaCO₃ particles ranging from 50-90 nm. The result revealed that nanoparticles' deagglomeration and uniform distribution were achieved using the Ultra-sonication technique [16]. The effect of various surface pre-treatments on CaCO₃ nanoparticles has been studied. As shown in Table 5 and Figure 9, these pre-treatment techniques improved mechanical performance twice and prevented particle agglomeration, as shown in Figure 6. The results, as shown in Figure 9 and Table 5, showed that most papers improved the mechanical properties of the composites.

In addition to the mechanical testing, tensile strength illustrated in Figure 9 (a), which showed 60% of papers had increased tensile strength, 30% had decreased tensile strength, and 10% were not applicable due to the strong interfacial force between the polymer matrix and the CaCO₃. In Figure 5 (b and c), Young's modulus and elongation at break showed the same result, with 50% of the papers showing an increase, no papers showing a decrease, and 50% not being applicable. Furthermore, flexural strength and shore hardness showed similar results, as shown in Figure 5 (d and f). In these few papers, these two tests, with 10% showing an increase, no papers showing a decrease, and 90% not being applicable. The results revealed that impact strength showed appreciable improvements, as shown in Figure 9 (e), with 80% of the papers reporting increased impact strength, no papers showing decreased impact strength, and 20% not mentioning or being not applicable due to interfacial adhesion in the composites.

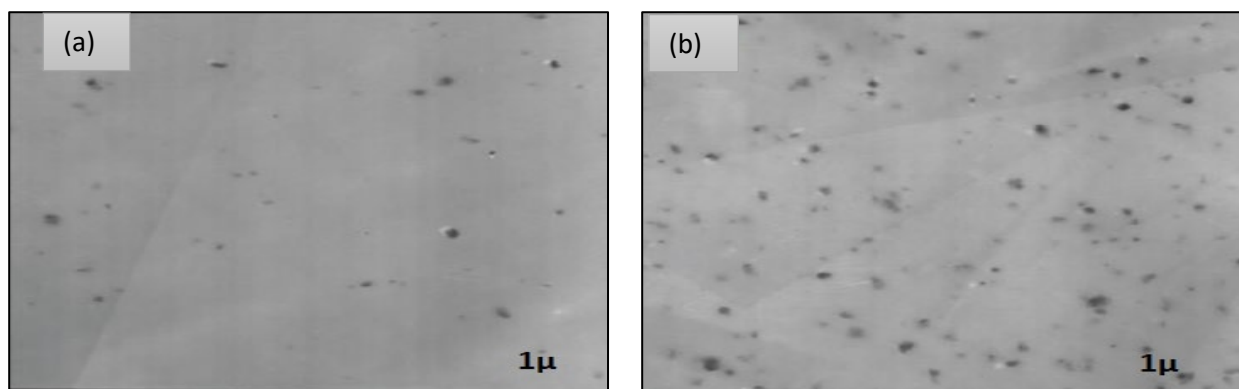


Figure 6: Transmission electron micrographs of nanocomposites (a) PTT/CaCO₃ 1% CaCO₃ and (b) PTT/CaCO₃ 2% CaCO₃ using titanate as a modifier [120]

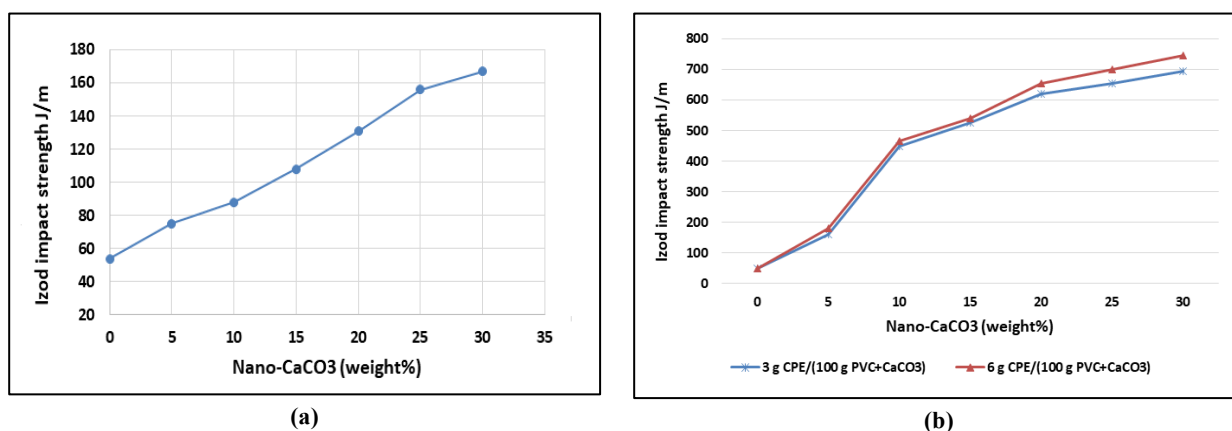


Figure 7: PVC/CPE/nano-CaCO₃ nanocomposites vs. nano-CaCO₃ content. (a) without CPE. (b) Using Chlorinated Polyethylene CPE [118]

Table 5: Influence of Surface pre-treatment fillers of CaCO₃ on mechanical properties of polymers

Polymeric Materials	Surface pre-treatment fillers	Method of Mixing	Shore hardness	Tensile Strength	Elongation at break	Young's modulus	Impact strength	Flexural strength	Ref.
PP	Stearic acid with monolayer-coated	Haake mixer	N/A	-	N/A	+	++	N/A	[20]
Isotactic PP	Polyoxyethylene nonylphenol (PN), silica	twin screw extruder	N/A	-	++	+	++	N/A	[21]
NBR	chlorinated poly-ethylene (CPE)	Sol-get	+	++	+	N/A	N/A	N/A	[99]
PVC	Stearic acid	Melt blending and masterbatch	N/A	-	++	+	++	N/A	[118]
PVC and PVC (BLEDEX 338)	Stearic acid	Two-roll mixer	N/A	+	+	N/A	++	N/A	[119]
PTT	tri(dioctylpyrophosphateoxy) titanate (CT-114)	twin-screw extruder	N/A	+	+	+	++	N/A	[120]
PP	Oleic Acid	twin-screw extruder	N/A	N/A	N/A	N/A	++	+	[121]
PP	styrene-acrylic polymer emulsion (SAPE)	twin-screw extruder	N/A	++	N/A	N/A	N/A	N/A	[122]
PVC	PMMA	two-roll mill	N/A	+	N/A	+	+	N/A	[123]
PVC	Titanate	two roll-mix	N/A	+	N/A	N/A	++	N/A	[124]

The symbol (+) represents a moderate increase in properties, (++) a significant improvement, and (-) a moderate decrease in properties. N/A: not applicable.

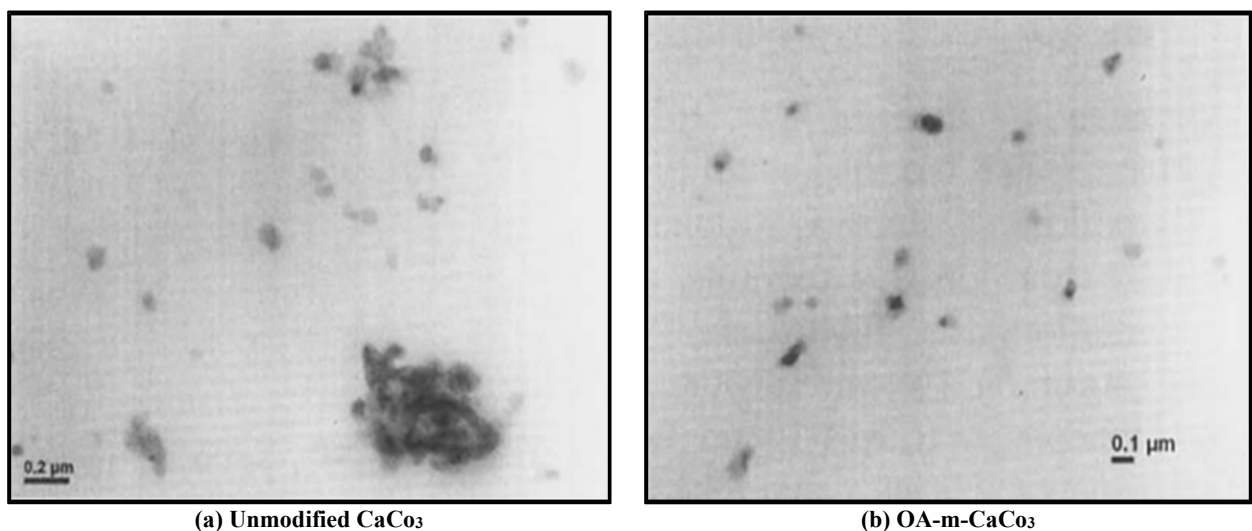


Figure 8: TEM image (a) Unmodified CaCO₃ (b) modified CaCO₃ nanoparticles in PP matrix (PP/CaCO₃=97/3) using oleic acid as a modifier [121]

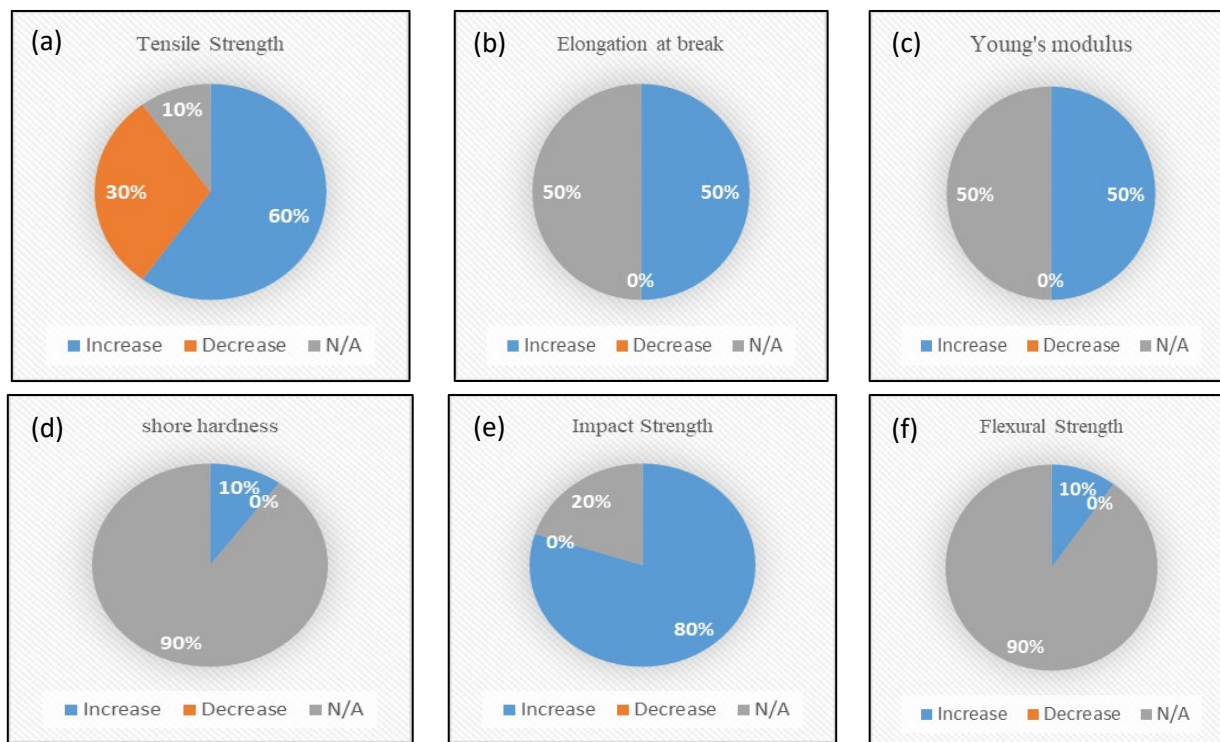


Figure 9: Influence of CaCO₃ nanoparticles on mechanical properties of different polymers using surface pre-treatment as a modifier

4. Conclusion

The influence of nano-CaCO₃ particles on various polymers' mechanical and thermal properties has been reviewed. The papers published between 2002 and 2022 were investigated in this review article. More than 61.54% (64 papers) of the total number of papers have been published since 2011. The Journal of Applied Polymer Science has published the most papers (6 papers, 5.77%) related to CaCO₃ nanoparticles topics. Using CaCO₃ nanoparticles as a filler, the following results were obtained:

- 1) The effect of surface pre-treatment as a modifier of CaCO₃ on the mechanical properties of polymers has been studied, which showed a significant effect on the mechanical properties of polymers and prevented the agglomeration of the particles.
- 2) Different mixing methods have been used, the most significant being a twin screw extruder, mechanical stirrer, and two-roll mill.
- 3) It is possible to conclude that most papers containing nano-CaCO₃ demonstrated significant mechanical and thermal properties improvements.

List of abbreviations

Abbreviation	Definition	Abbreviation	Definition
	Polyurethane	PLA	Polylactic acid
ABS	Acrylonitrile butadiene styrene	PMMA	Poly (methyl methacrylate)
BR	Butadiene rubber	POM/CB	Polyoxymethylene/carbon black
CF	Carbon-fiber	PP	Polypropylene
CNR	Cyclic Natural Rubber	PP/ POE	polypropylene/poly(ethylene-co-octene)
CPE	chlorinated polyethylene	PPC	Polypropylene carbonate
EPDM	Ethylene Propylene Diene Monomers	PPE	Polyphenylene Ether
EVA	Ethylene-vinyl acetate	PPS	Polyphenylene sulfide
HDPE	High-density polyethylene	PS/HIPS	Polystyrene /High Impact Polystyrene
LLDPE	Linear low-density polyethylene	PTT	Poly (trimethylene terephthalate)
MMA	methyl methacrylate	PU	
NBR	Butadiene Nitrile Rubber	PVA	Polyvinyl alcohol
NR	Natural rubber	PVAC	Polyvinyl acetate
PA66	Polyamide	PVC	Polyvinyl chloride
PAN	Polyacrylonitrile	S. N	Source number
PBR	Polybutadiene Rubber	SBS	Styrene-butadiene-styrene
PBT	Polybutylene terephthalate	PLA	Polylactic acid
PC/GF	Polycarbonate/ glass fiber	PMMA	Poly (methyl methacrylate)
PCL	Polycaprolactone	POM/CB	Polyoxymethylene/carbon black
PEEK	Polyether ether ketone	PP	Polypropylene

PEHA	Pentaethylenehexamine	PP/ POE	polypropylene/poly(ethylene-co-octene)
PF/Ep	Phenol formaldehyde/ Ethylene propylene	PPC	Polypropylene carbonate
PPS	Polyphenylene sulfide	PPE	Polyphenylene Ether
PS/HIPS	Polystyrene /High Impact Polystyrene		

Author contributions

Conceptualization, N. Mahmood. and M. Hikmat; methodology, M. Hikmat; formal analysis; N. Mahmood; data curation, M. Hikmat; writing—original draft preparation, N. Mahmood; writing—review and editing; M. Hikmat. All authors have read and agreed to the published version of the manuscript.

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Data availability statement

The data supporting this study's findings are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

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