Review Article

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A review of ternary polymer nanocomposites containing clay and calcium carbonate and their biomedical applications

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Abstract: Patchy interactions and heterogeneous charge distribution make nanoclay (NC) a promising biomaterial to interact with different biomolecules, polymers, and biological components. Many researchers have studied the polymer/clay nanocomposites in recent years. However, some deficiencies, such as poor impact strength, limit the application of polymer/clay nanocomposites in different fields. As a result, many attempts have been made to resolve this problem. Also, researchers have developed calcium carbonate ($CaCO_3$) nanoparticles as biomedical materials. The nontoxic properties and biocompatibility of both $CaCO_3$ and NC make their nanocomposites ideal for biomedical applications. In this article, a detailed review of the ternary polymer nanocomposites containing NC and $CaCO_3$ is presented. The morphological, thermal, mechanical, and rheological characteristics, in addition to the modeling of behavior and foam properties, are studied in this article. In addition, the potential challenges for ternary nanocomposites and their biomedical applications are discussed.

Keywords: polymer nanocomposites, nanoclay, $CaCO_3$, morphology, mechanical properties, biomedical application

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1 Introduction

The development of industrial and economic activities results in continuous requirements for new, low-cost, low-weight, and high-performance materials, which can meet different conditions. Polymers are good candidates for many fields, but they should be developed for special requirements [1–6]. With the advent of nanotechnology, nanocomposites with ultrafine phase dispersion of nanofiller show many unique properties along with various technological and economic opportunities [4,7–25]. The large surface area and the big aspect ratio of nanoparticles, together with the good interfacial interactions among polymer and nanoparticles, lead to exceptional behavior in polymer nanocomposites [26–39].

To progress the effectiveness of nanocomposites in industrial applications, it is vital to concurrently improve the overall properties such as modulus, strength, toughness, heat distortion temperature, *etc*., without sacrificing the processability and economical considerations. Nanoclay (NC) is a layered biomaterial with a defined structure at the nanoscale. NC commonly deteriorates the impact strength of polymer nanocomposites [40,41]. It limits the application of polymer/NC nanocomposites in various areas. Some researchers applied rubber to solve the problem, but it decreased the modulus and strength of nanocomposites [42–45].

In recent years, a strong emphasis has been carried out on the development of ternary nanocomposites due to the high potential of nanotechnology. Two dissimilar particles can handle the performances of the nanocomposites creating very exceptional features in the behavior of materials [46–50]. A great number of researchers have reported the advantages of calcium carbonate ($CaCO_3$) in nanocomposites [51–54]. Rajan *et al.* [55] investigated the in vitro cytotoxicity of high-density polyethylene composite reinforced with $CaCO_3$ nanoparticles. Their results showed that $CaCO_3$ nanoparticles provide high mechanical and tribological properties in nanocomposites. In another study, Gayer *et al.* [56] developed a composite by PLA and $CaCO_3$ for the selective laser sintering process of bone tissue engineering scaffolds and successfully demonstrated the modified additive manufacturing system.

The addition of $CaCO_3$ nanoparticles to NC nanocomposites would not deteriorate the advantages of nanocomposites, such as low-cost, low-weight, high-performance, and ease of processing, because the addition of both NC and $CaCO_3$ to the polymer matrix causes better dispersion of nanoparticles and more mechanical properties, due to the stiffening effects of both nanoparticles and increment of mixture viscosity. Moreover, the price of $CaCO_3$ is much lower than NC. Therefore, by replacing a part of clay with $CaCO_3$ in the composite, the price of the product can be reduced.

The binary nanocomposites containing NC or $CaCO_3$ have been reviewed in the previous article. In this review article, a detailed study of the ternary nanocomposites containing NC and $CaCO_3$ is presented, and also, the potential opportunities are explained for future studies. Ternary samples include the advantages of both NC and $CaCO_3$, improving the mechanical, thermal, barrier, and flame-retardant properties. So, it is important to discuss the specific properties of ternary nanocomposites. Moreover, exceptional cyto-compatibility, biocompatibility, big surface area, and charge characteristics of NC as well as high osteoconductivity and slow biodegradability of $CaCO_3$ provide the biomedical applications of ternary samples in tissue engineering, wound healing, implant, and medical devices. Here, the morphological, thermal, mechanical, and rheological properties along with the modeling of properties and their foamability properties are investigated.

2 Biomedical applications of polymer/NC/$CaCO_3$ ternary nanocomposites

NC is emerging as a biomaterial with a layered shape, nanosized, and well-defined structure [57,58]. A range of biomolecules, polymers, and biological components can physically interact with atomically thin NC due to its heterogeneous charge distribution and patchy interactions. Compared to other classes of nanomaterials, NC has excellent cyto-compatibility and biocompatibility. The high surface area and charged characteristics of NC allow it to interact with a range of small and large biomolecules and to be used for sustained and prolonged therapeutic delivery [59]. A range of synthetic and natural polymers have been combined with NC to obtain nanocomposites for biomedical applications [59]. For example, it was established that the addition of a small amount of NC to polymeric binder forms shear-thinning hydrogels [60], which are extensively used in the biomedical discipline for cells and therapeutic delivery, tissue regeneration, and adhesives [61]. In contrast, $CaCO_3$ nanoparticles have been developed as a material with interesting biomedical applications [62,63]. They are used in drug delivery (as templates for the encapsulation of bioactive compounds), the construction of biosensors, bone replacement grafts in human periodontal osseous defects, bio-mineralization, and enzyme immobilization. Due to its high osteo-conductivity, ease of production, and slow biodegradability, it has also been utilized in medicine as a bone-filling material [64]. Fadia *et al.* [65] stated that $CaCO_3$ nanoparticles are chemically inert and widely considered in the field of biosensing and drug delivery. $CaCO_3$ has unusual properties such as biocompatibility, big surface-to-volume ratio, easy synthesis, strong nature, and surface functionalization, making them a perfect candidate for biomedical requests. Actually, due to the nontoxic nature and biocompatibility of both NC and $CaCO_3$, their composites have the potential for biomedical requests such as bone tissue engineering, wound healing, implant, 3D bioprinting, medical devices, and enzyme immobilization.

3 Morphological properties

When NC interacts with polymer matrix, batch separation, intercalation, and exfoliation can occur in nanocomposites [66]. The main peaks in the X-ray diffraction (XRD) spectra of polypropylene (PP)/NC/$CaCO_3$ and poly(vinyl chloride) (PVC)/NC/$CaCO_3$ ternary nanocomposites shift to the inferior 2θ values than the peak of pristine NC [67–71]. Furthermore, the intensity of main peaks decreases, which reveals the penetration of polymer chains into the NC galleries, leading to disordered NC layers, *i.e.* mixed morphology of intercalated/exfoliated in many samples. Also, the images obtained by microscopy demonstrate the uniform dispersion of both NC and $CaCO_3$ particles in the matrix [67–71]. Some samples such as PP4/2/14 (*An*/*x*/*y* sample: *A* is the type of polymer matrix, *n* is the melt flow index [MFI] of polymer medium, *x* and *y* are the weight percentages of NC and $CaCO_3$, respectively) and PP2.5/4/5 show a completely exfoliated NC in the matrix [67,69].

The ternary nanocomposites show broader peaks in comparison to the binary specimens (Figure 1a), which indicates the higher level of exfoliated NC. TEM images also verify the observations [68]. A good dispersion of NC layers in the melt mixing process is affected by three factors, including the interaction between NC platelets and matrix, mechanical shear stress, and molecular diffusion. The high shear stress aids in removing the kinetic restrictions regarding the breakup of agglomerated NC and moving the NC platelets in the sample. The high shear stress can be obtained from the higher viscosity of melt mixing provided by the larger chains of polymer (smaller MFI). Nevertheless, the penetration of larger chains into the NC galleries is difficult. $CaCO_3$ particles can enhance the viscosity and provide a balance between diffusion and shear stress causing a high exfoliation degree [72,73]. Zare *et al.* [67,74] have also confirmed that the samples containing higher $CaCO_3$ contents show smaller peak intensities in XRD images, indicating the superior exfoliated platelets in the polymer matrix (Figure 1b).

The noble dispersion of nanoparticles has been reached using the maleic anhydride grafted PP (PPgMA) as a compatibilizer and stearic acid-treated $CaCO_3$, which produce more interfacial interactions [67–71]. The TEM images of PVC/NC/$CaCO_3$ ternary nanocomposite are illustrated in Figure 2 [71]. The darker strips and the larger spots show the NC layers and $CaCO_3$ nanoparticles, respectively. The disordered NC platelets and well-dispersed $CaCO_3$ nanoparticles are evidently observed in the PVC matrix.

Tang *et al.* [69] developed PP/montmorillonite (MMT)/$CaCO_3$ ternary nanocomposites in a twin screw extruder by melt processing. As exposed in Figure 3, the diffraction peaks of the nanocomposite have been removed compared with the pristine MMT. The MMT nanofiller is thereby

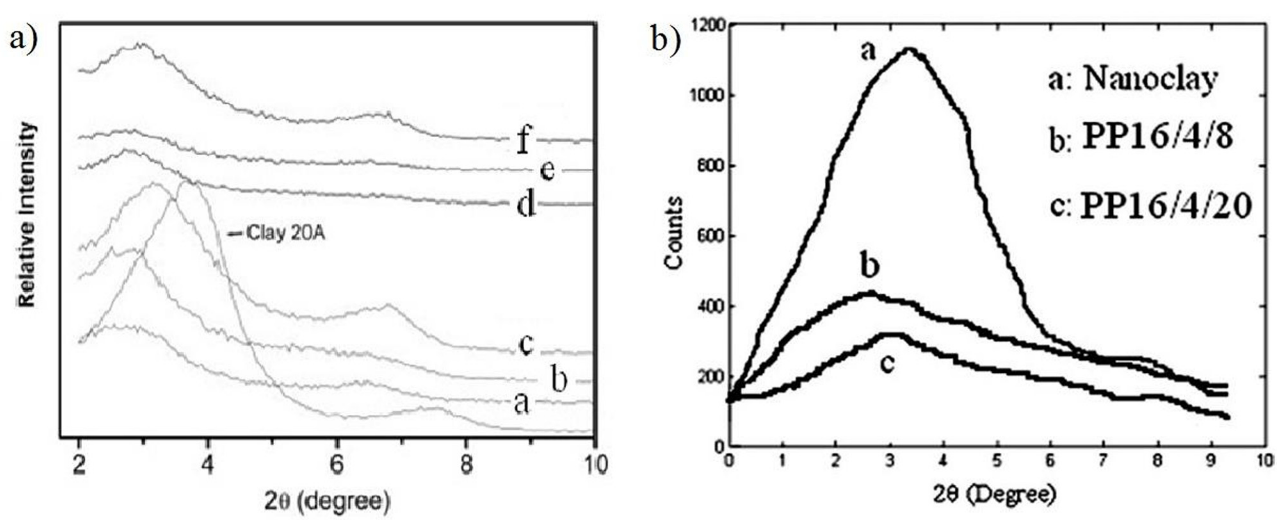

Figure 1: XRD patterns of ternary nanocomposites, (a) a: PP14.5/2/0, b: PP14.5/4/0, c: PP14.5/6/0, d: PP14.5/2/2, e: PP14.5/2/4, and f: PP14.5/4/2 and (b) NC and ternary samples (reproduced from previous studies [67,68] with permission).

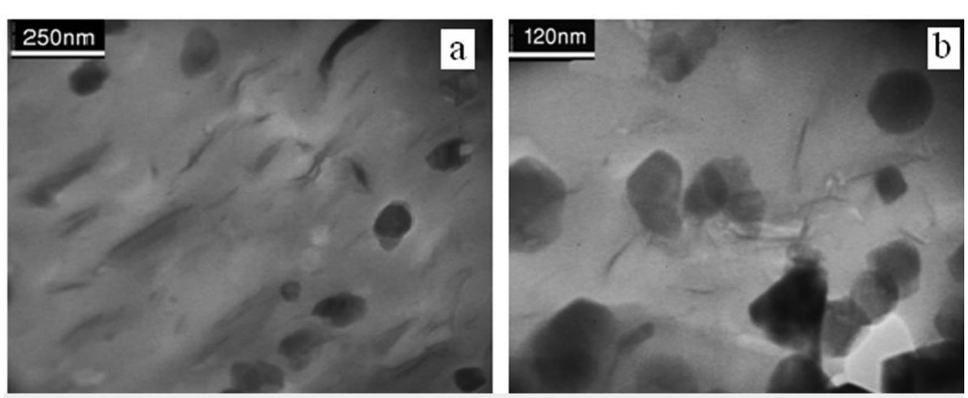

Figure 2: TEM pictures of (a) PVC/2/8 and (b) PVC/2/16 samples (reproduced from the study of Sadegh Roshanravan [71] with permission).

properly dispersed and exfoliated within the PP matrix. In another study, Dai *et al.* [70] developed a ternary nanocomposite based on high-density polyethylene (HDPE). Figure 4 illustrates a synergistic effect that MMT and $CaCO_3$ fillers could produce. Long chains of HDPE are suggested to intercalate into the MMT interlayer. The $CaCO_3$ nanofillers are simultaneously wrapped in this long chain, and a link between the HDPE chains and two different inorganic fillers is created.

Asadi *et al.* [75] have reported that the distance between NC sheets in ternary nanocomposite is higher than neat NC. The communication of hydroxyl groups of NC and carboxyl groups of PLA seems to cause the separation of NC layers and their intercalation in ternary nanocomposites. In addition, $CaCO_3$ facilitates the NC layer opening, which is thought to occur by increasing the polymer viscosity, thereby increasing the shear stress on the nanofillers. By a two-step melt mixing technique, Alavitabari *et al.* [76] proposed a nanocomposite with an HDPE matrix and two nanofillers, including NC and $CaCO_3$. XRD results demonstrated that as the PEgMA linking agent was increased in the samples, XRD peaks shifted to smaller angles, and their intensity decreased. Incorporating $CaCO_3$ also increased the distance between NC layers by causing the peaks to shift toward low angles.

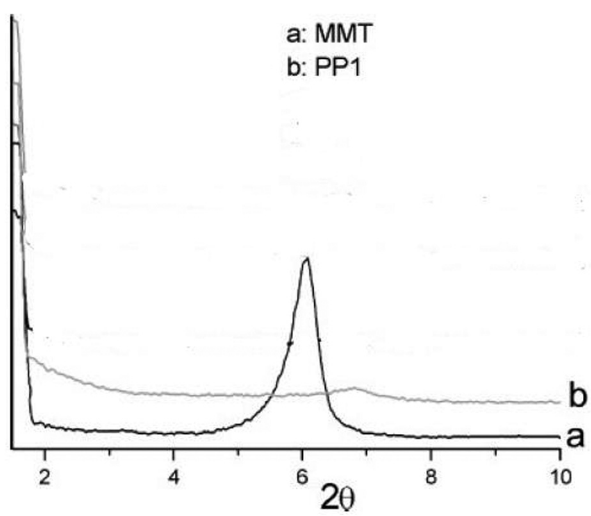

Figure 3: XRD patterns for MMT and its nanocomposite (reproduced from the study of Tang *et al.* [69] with permission).

In another work [77], it was discovered that in dual-filler samples, peak intensity is much smaller than that of binary systems based on the XRD technique. Furthermore, they investigated the effect of adding $CaCO_3$ nanofillers to the NR matrix on the dispersion of silicate nanolayers. Also, FESEM analysis revealed the excellent dispersion of both nanofillers into the polymer matrix [78]. In another study, Kapole *et al.* [79] prepared a nanocomposite containing a hybrid polymer composed of acrylic polyol–polyurethane and nanofillers of NC and $CaCO_3$ by *in situ* polymerization. They observed that adding two nanofillers to the polymeric system using *in situ* technique improved nanofiller dispersion into the polymeric matrix. The addition of both NC (platelet shape) along with $CaCO_3$ increases the viscosity of samples, which improves the dispersion of nanoparticles without aggregation. Conclusively, both intercalation and exfoliation of NC layers are observed in the ternary samples, because polymer chains are placed between the layers increasing their spacing. Increasing the distance between layers is called intercalation. However, when the order of the NC layers is disrupted along with the increase in distance, this is called exfoliation. Exfoliation is the most ideal dispersion mode for nanoparticles in the polymer matrices, because the exfoliated layers have the

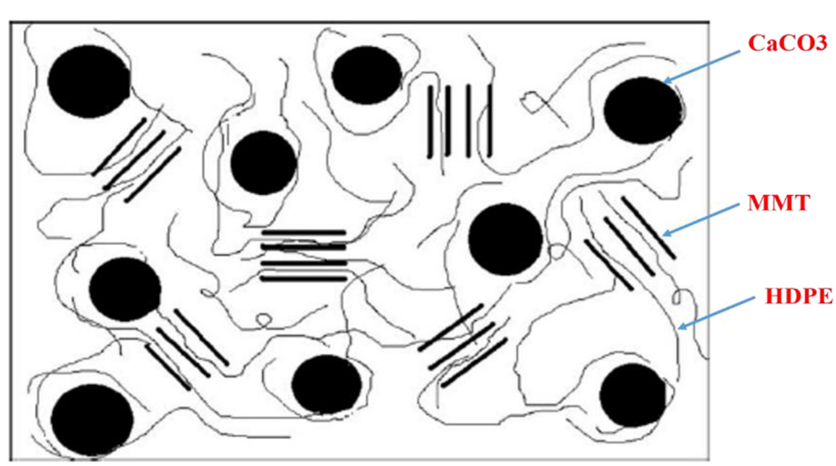

Figure 4: The synergistic effects of MMT and $CaCO_3$ in HDPE matrix (reproduced from the study of Dai *et al.* [70] with permission).

significant surface area involving the polymer chains to improve the mechanical properties of nanocomposites. The distance between NC layers is increased by the presence of $CaCO_3$ nanoparticles in ternary samples. The increase in distance can be explained by the shift of peak related to NC toward low angles in the XRD diagram, which indicates intercalation. Moreover, NC layers may be disordered in the ternary samples indicating the exfoliation. The presence of $CaCO_3$ may increase the viscosity of samples, helping for exfoliation. Nevertheless, nanoparticles such as NC and $CaCO_3$ have high surface energy, causing aggregation/agglomeration in the nanocomposites [80–82]. In other words, nanoparticles are aggregated/agglomerated in the polymer matrix, weakening their performance for stiffening. In a hydrophobic polymer matrix, the hydrophilic character of clay minerals prevents its exfoliation into discrete monolayers. This can be overcome by compatibilization, which consists of a cation exchange within the interlayer space [83]: cations of alkali metals or alkaline earth metals are substituted by voluminous organic ones, most frequently an alkylammonium. Clay mineral organophilization facilitates the penetration of polymer chains into the interlayer space, as well as the formation of an intercalated or exfoliated (delaminated) nanocomposite structure. Additionally, polymer matrix and nanoparticles should be compatible to achieve well-dispersed nanoparticles and exfoliated layers in spite of aggregation/agglomeration. In order to increase the compatibility between components, it is necessary to functionalize the surface of nanoparticles or use a compatibilizer such as PPgMA. However, filler functionalization and using compatibilizer increase the cost of nanocomposite manufacturing. Actually, both NC and $CaCO_3$ have more tendency of high aggregation/agglomeration in polyolefin polymers such as PP and LDPE, because the nanofillers are polar and polyolefin are non-polar; therefore, there is no good interaction between them, that is the reason of using compatibilizer in the system.

Table 1: Crystallization and melting characteristics of ternary nanocomposites (reproduced from [68,70,84,85] with permission)

No.	Samples	T_c (°C)	X_c	T_m (°C)	Ref.
1	PP14.5	116	53	165	[68]
2	PP14.5/2/2	121	54	164	[68]
3	PP14.5/4/2	120	48	163	[68]
4	PP14.5/2/4	120	50	164	[68]
5	HDPE0.27	121.2	39.7	135.7	[70]
6	HDPE0.27/3/12.3	115.3	50.3	130	[70]
7	PP4	116.8	43.6	163	[84]
8	PP4/4/8	127.2	45.7	164.2	[84]
9	PP16/4/8	129.4	49.1	165.5	[84]
10	PP4/2/14	129.3	47.1	164.4	[84]
11	PP4/6/14	128.1	45.1	163.8	[84]
12	PP4/4/20	130.4	45	164.2	[84]
13	PP3.2	—	46.6	—	[85]
14	PP3.2/3/15	—	51.5	—	[85]
15	PP3.2/5/15	—	52.5	—	[85]
16	PP3.2/7/15	—	51.7	—	[85]

4 Thermal properties

4.1 Melting and crystallization

The nucleation effect of nanoparticles affects the melting and crystallization performance. Since crystallization has a key impact on the features of composites, crystallization analysis is much more important to study. Table 1 shows the peak temperature of crystallization (T_c), the degree of crystallinity (X_c), and the peak temperature of melting (T_m) for different ternary nanocomposites. Obviously, the crystallization process shifts toward the higher temperature, and also, X_c increases due to the irregular nucleation impact of nanofillers. The effect of MFI of the polymer matrix (chain size of polymer) on the X_c is studied in PP4/4/8 and PP16/4/8 examples. It is known that two major factors, including the nucleation of nanoparticles and the development of spherulites, affect the crystallization. The smaller chains (higher MFI) encourage the earlier and more nucleation together with extra and easier activities. Consequently, further chains can be arranged into the crystal cells, and thus, further crystallinity is developed. X_c values of PP4/4/8 and PP16/4/8 examples validate this statement. From Table 1, although NC layers deliver numerous nucleation places, the increasing NC content reduces T_c and X_c. It can be due to the good spreading of NC layers in the matrix, which mechanically involves the polymer chains and restricts the molecular movements. In addition, higher $CaCO_3$ content increases the dispersion of NC, which limits the chain mobilities. For this reason, increasing $CaCO_3$ content slightly decreases the X_c.

The crystallization rate was also evaluated by temperature and time [84]. It was found that the slowest and the fastest crystallization processes occurred in PP4 and PP4/6/14 ternary nanocomposites, respectively [84].

The obtained n as Avrami exponent for many ternary samples are near to 2, indicating two-dimensional developments of crystals. n value for the PP4/2/14 sample is between 2 and 3 (2.12), illustrating the immediate nucleation with diffusion handling in the crystal growth [86].

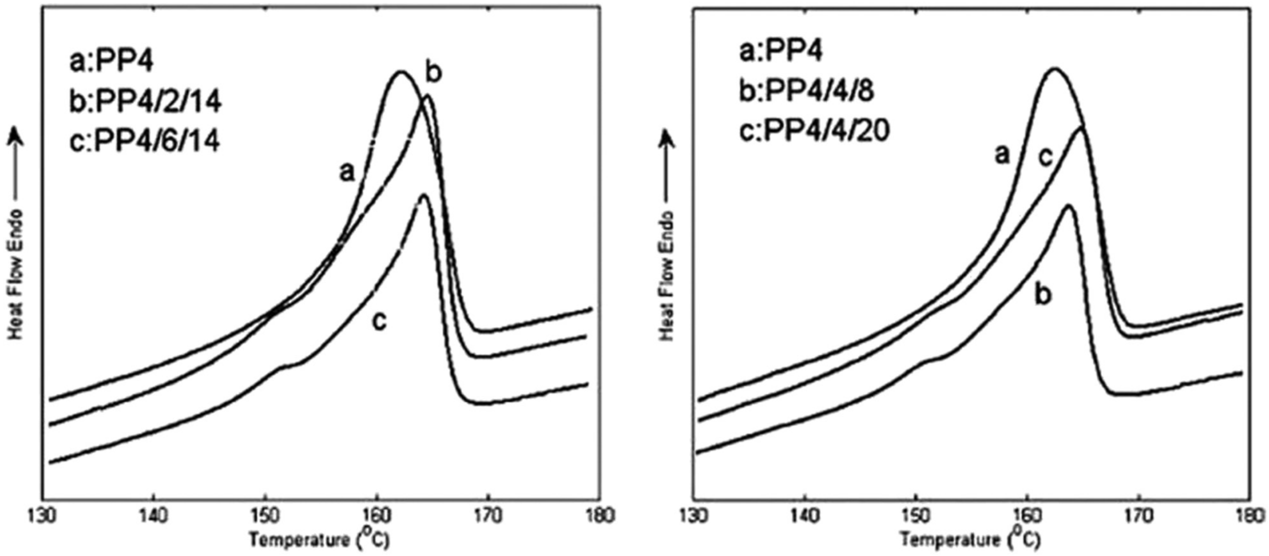

Figure 5: Melting of ternary samples (reproduced from the study of Zare and Garmabi [84] with permission).

The K values are consistent with the calculated results by the curves of the crystallization rate.

As observed in Table 1, the variation of T_m is more negligible compared to T_c. The melting curves of ternary samples show a main peak at 165°C mentioning the α-crystal and a much smaller peak at 151°C due to the β-crystal (Figure 5) [87].

The peak intensity exposes that the volume of the β-phase is too lower than the α-crystal, while NC and $CaCO_3$ can significantly encourage the nucleation of the β-phase [88–90]. As a result, β-nucleation of NC and $CaCO_3$ is disregarded as they are simultaneously used in a polymer matrix, as reported in several works [68,74,84]. Chen *et al.* [68] have reported that a PP/$CaCO_3$ sample with 4 wt% of $CaCO_3$ contains 40% of the β-phase, but the ternary nanocomposites only display the α-phase. Possibly, the dissimilarity between two nanofillers induces such behavior. The NC layers are platy with higher aspect ratio and many nucleation sites per unit surface area, while $CaCO_3$ is spherical with much fewer nucleation sites and aspect ratio [89].

A DSC curve for neat HDPE and nanocomposite is shown in Figure 6. Dai *et al.* [70] also showed that in the ternary nanocomposite, several small crystals are formed by two nanofillers acting as nucleating agents. This leads to a greater degree of crystallinity and a faster crystallization time than pure HDPE.

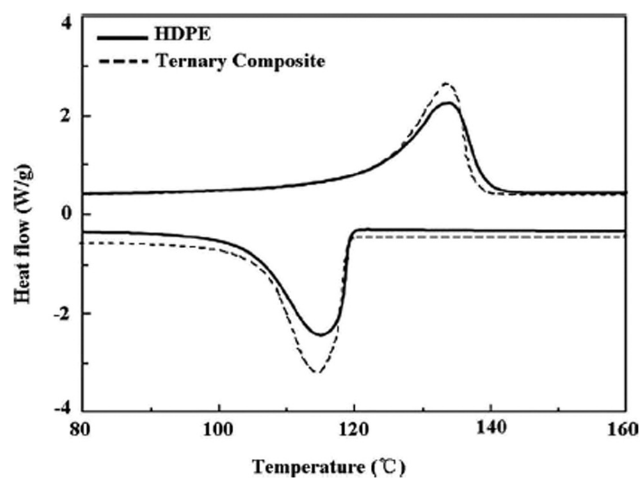

Figure 6: Differential scanning calorimetry plots for pure HDPE and ternary nanocomposite (reproduced from the study of Dai *et al.* [70] with permission).

4.2 Flammability and thermal stability

The flammability properties of the PP ternary sample were characterized in terms of the heat release rate (HRR). The peak HRR of PP/4/5 was reduced by about 53.5% in comparison with that of pure PP [69]. The main mechanism of reduction in HRR depends on the condensed phase process, and therefore, NC layers play a more significant role in the flame retardancy of ternary samples [69]. Also, it was found that the efficiency of NC for HRR drop is better than that of $CaCO_3$ owing to the layer structure of NC, which sandwiches the polymer chains. Furthermore, the high level of dispersion along with the small diameters of $CaCO_3$ nanoparticles improves the flame retardancy greater than the micron-sized particles [69].

The inorganic nanofillers with high specific surface area protect the polymer medium and thus, the thermal stability of nanocomposites improves compared to neat matrices [69–71,85]. The ternary nanocomposite of PP/4/5 showed a top weight loss temperature of 462.5°C and 5% loss temperature of 414.6°C, while a top weight loss temperature of 336.4°C and 5% loss temperature of 440.8°C were reported for neat PP [69]. It was found that the addition of NC from 2 to 6 wt% did not have a positive effect on the degradation temperature of PVC/NC/$CaCO_3$ ternary nanocomposite [71]. It may be due to the poor nanoparticle dispersion, which results in the inferior barrier properties. In addition, the enhancement of $CaCO_3$ loading increases the thermal stability. Two reasons can be suggested for this phenomenon: first, the absorption of hydrochloric acid by $CaCO_3$ nanoparticles, and second, the high dispersion of NC in the attendance of high content of $CaCO_3$, as mentioned before in Section 3. Alavitabari *et al.* [76] also verified that the nanocomposites were not ruined during mixing, and both NC and $CaCO_3$ might enhance the thermal stability of the PEgMA compatibilizer (Figure 7).

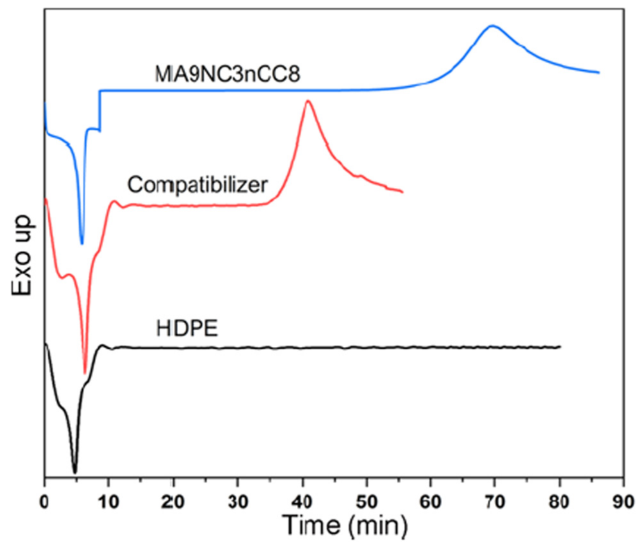

Figure 7: Results of OIT tests for various materials (reproduced from the study of Alavitabari *et al.* [76] with permission).

5 Mechanical properties

NC particles have a strong impact on the modulus and stiffness of polymers, while the $CaCO_3$ particles seem to significantly improve the toughness [91–94]. In this regard, the simultaneous addition of both nanofillers has a synergistic effect on the stiffness. It is proposed that the long chains of polymer intercalate into the NC interlayer. $CaCO_3$ nanoparticles are enwound by this long chain simultaneously. Two different inorganic fillers are linked by polymer molecules, which provide an opportunity for two fillers to have a synergistic effect on the properties of ternary composites [70].

The mechanical features of different binary and ternary nanocomposites are illustrated in Table 2. The modulus of ternary nanocomposites containing NC and $CaCO_3$ is better than that of binary nanocomposites in total cases due to the strengthening impact of nanofillers. The highest improvement of modulus is found in the HDPE 0.27/3/12.3 sample by 300% [70]. The tensile strength shows minor variation in many binary and ternary samples. The impact strength of clay-filled samples is commonly reduced, but ternary systems have higher impact strength than binary nanocomposites except for PP/NC/$CaCO_3$ samples in Chen *et al.*'s work [68]. The maximum enhancement of impact strength is obtained for the PP2.5/4/5 ternary sample by 75% [69]. The influences of various parameters on the stiffness of ternary nanocomposites are extensively discussed in the following.

Table 2: Mechanical performances of nanocomposites (reproduced from previous studies [68–70] with permission)

No.	Samples	Tensile modulus (GPa)	Tensile strength (MPa)	Impact strength	Ref.
1	PP14.5	1.75	31.8	1.8 (kJ/m^2)	[68]
2	PP14.5/2/0	2.12	35.7	1.73	[68]
3	PP14.5/4/0	2.91	35.85	1.68	[68]
4	PP14.5/0/2	1.85	32.2	2.17	[68]
5	PP14.5/0/4	1.97	31	2.78	[68]
6	PP14.5/2/2	2.43	36.9	1.77	[68]
7	PP14.5/2/4	2.53	36	1.74	[68]
8	PP14.5/4/2	2.82	36.7	1.71	[68]
9	PP2.5	—	34.6	3.4 (kJ/m^2)	[69]
10	PP2.5/4/0	—	34.8	3.8	[69]
11	PP2.5/0/5	—	35.4	4.7	[69]
12	PP2.5/4/5	—	35.2	5.9	[69]
13	HDPE0.27	0.16	15.1	437.1 (J/m)	[70]
14	HDPE0.27/3/0	0.321	31.1	309.4	[70]
15	HDPE0.27/0/12.3[a]	0.091	10.3	321	[70]
16	HDPE0.27/0/12.3[b]	0.308	17.4	564.2	[70]
17	HDPE0.27/3/12.3[b]	0.645	33.9	556.2	[70]

[a]Untreated $CaCO_3$. [b]Treated $CaCO_3$.

5.1 MFI of polymer matrix

The large improvement of tensile modulus in the PP/NC/$CaCO_3$ ternary nanocomposite was found in the smaller

MFI of PP due to the superior dispersion of nanoparticles [67]. The highest impact strength is found by the medium MFI (10 g/10 min).

5.2 NC content

The positive result of NC amount on the modulus of different ternary nanocomposites was reported [67–71]. Furthermore, the minor enhancement of tensile strength and the dropping of impact strength were shown owing to the restriction of macromolecules. The similar effects of NC amount on the modulus and impact strength of PVC/NC/$CaCO_3$ samples were also expressed [71].

5.3 NC type

Sorrentino *et al.* [85] have evaluated the NC types in the ternary samples containing 15 wt% of PPgMA and 15 wt% of micro-$CaCO_3$. The higher content of Dellite 72T NC showed an increase in the ultimate strain together with a minor variation in the tensile strength. But, Nanofil 5 exhibited a reduction of ultimate strain and a growth in the tensile strength. Also, over the 5 wt% of NC, Nanofil 5 improved the modulus, while the Dellite 72T had an inverse role. Only for nanocomposites prepared with Nanofil, a further increase of Young's modulus was obtained by raising the NC concentration to 7 wt%. The main reason can be explained by the higher ability of Nanofil clay to be intercalated compared to Dellite 72T. Actually, there are strong interfacial interactions between PP and Nanofil 5, resulting in the intercalation and exfoliation of NC, while the poor interfacial interaction between PP and Dellite 72T cannot cause the intercalated/exfoliated layers weakening the properties.

5.4 $CaCO_3$ content

$CaCO_3$ content improved the tensile modulus of ternary specimens based on the PP [67,68] and PVC [71]. Although $CaCO_3$ nanoparticles promote various toughening mechanisms in the binary nanocomposites [95,96], the decline of impact strength with the growing $CaCO_3$ content is unexpectedly found in the ternary systems. When the $CaCO_3$ amount increases, the acquired dispersion of NC induces the reduction of molecular chain mobilities and, thus, the impact strength. The same behavior was wonderfully illustrated in the PVC/NC/$CaCO_3$ ternary nanocomposite [71].

Figure 8 shows 2D schemes of impact strength for PP/NC/$CaCO_3$ nanocomposite [67]. It displays that to attain the greatest impact results, MFI of 8–10 g/10 min, the NC content of 2 wt%, and the $CaCO_3$ loading of 8 wt% are required. The tensile strength shows a minor enhancement below the $CaCO_3$ concentration of 15 wt%. By increasing the level of $CaCO_3$ to 20 wt%, a slight reduction of tensile strength is observed. It is suggested that the high content of nanofillers limits the chain movement and also decreases the adhesion at the interface, reducing the tensile strength. In addition to the stiffening effect of $CaCO_3$ nanoparticles, they increase the melt viscosity of the mixture, causing more shear stress to the NC layers. The higher shear stress promotes more individual NC layers, improving the dispersion of NC [67]. In addition, the contour plots for impact strength of PVC/NC/$CaCO_3$ nanocomposite demonstrated that the top results are attained at smaller contents of NC and $CaCO_3$ [71].

5.5 Feeding rate

The feeding rate is a more effective parameter in the extrusion process [97]. More feeding rate decreases the residence time in the extruder causing imperfection breakup and dispersion of nanoparticles. On the other hand, the lower feeding rate induces further empty space in the mixing zones along with the application of low shear stress on the melt mixing, which lastly results in weak-quality mixing. Also, the degradation of materials may occur to more residence time in the extruder. Therefore, obtaining an optimized level of feeding rate is a main subject in the extrusion process. PP10/4/14 samples were prepared at different feeding rates [74]. The mechanical properties of the samples are presented in Table 3. The tensile properties slightly change at different feeding rates, but the impact strength becomes much superior at the higher feeding rate of 3 kg/h.

Tang *et al.* [69] found that the combination of nanoscale $CaCO_3$ with PP/MMT samples improved the mechanical features of the samples such as tensile properties and notch impact tests. In other words, a close contact between PP chain and the nanofiller forms a stronger interphase and, consequently, better mechanical properties for the ternary nanocomposite. Generally, an interphase is created between polymer chains and nanoparticles due to the big surface area of nanoparticles and strong interfacial interaction between polymer and filler [4,98–103]. Since

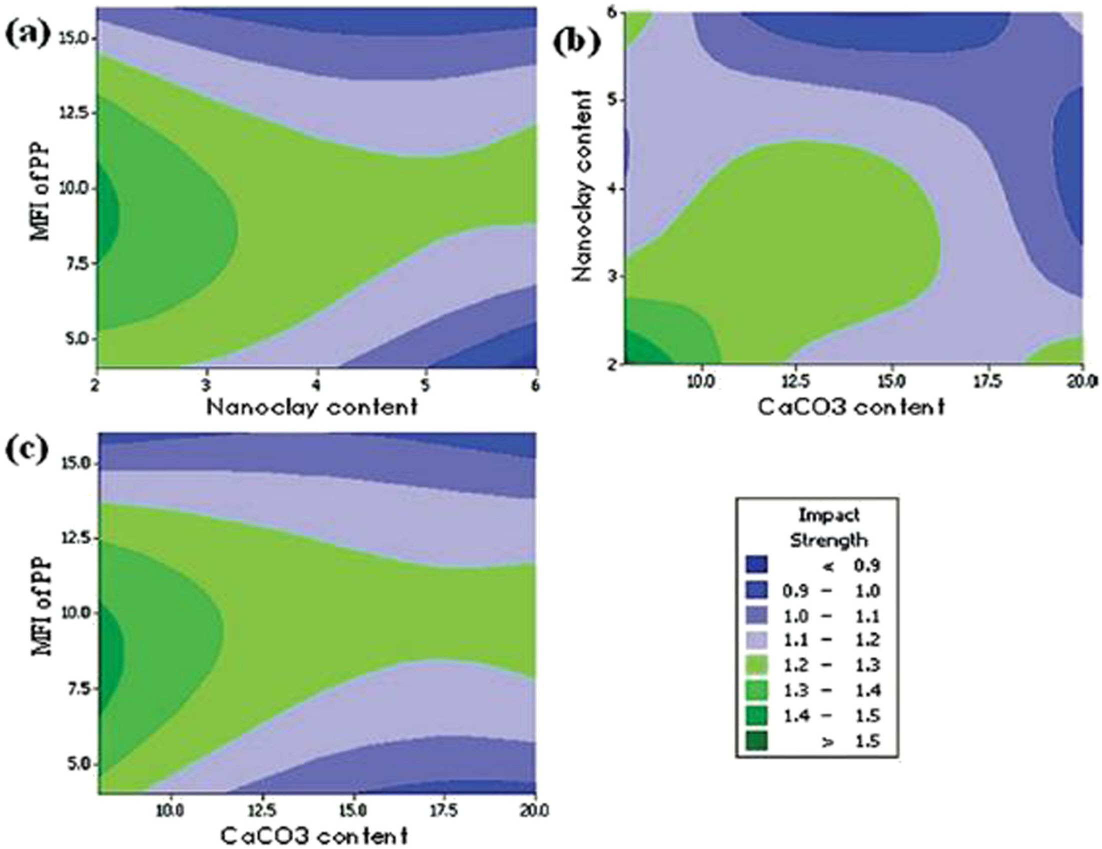

Figure 8: The impact strength for PP/NC/$CaCO_3$ samples at different levels of (a) nanoclay content and MFI of PP, (b) $CaCO_3$ content and nanoclay content and (c) $CaCO_3$ content and MFI of PP.

Table 3: Mechanical performance of nanocomposite prepared in different feeding rates of twin screw extruder [74]

No.	Feeding rate (kg/h)	Tensile modulus (GPa)	Tensile strength (MPa)	Impact strength (kJ/m^2)
1	1	2.52	38	2.83
2	2	2.54	38.2	2.54
3	3	2.48	38.1	3.2

the interphase is stronger than the polymer matrix, it plays a stiffening role in the nanocomposite. Actually, a thicker and tougher interphase causes a stronger nanocomposite and the mechanical properties of nanocomposites directly link to the interphase characteristics. The mechanical properties of ternary samples mainly depend on the interphase characteristics, and literature reports have studied this topic well. Jahan *et al.* [104] reported a ternary nanocomposite consisting of PVDF polymer matrix, $CaCO_3$, and MMT applicable as a piezoelectric material. Figure 9 shows the stress–strain diagrams of the prepared samples. They found that hybrid fillers ($CaCO_3$ and MMT) had negative effects on tensile strength due to weaker affinity between untreated $CaCO_3$ and PVDF because of the lower surface energy of PVDF. In addition, PVDF nanocomposites had a lower Young's modulus than neat

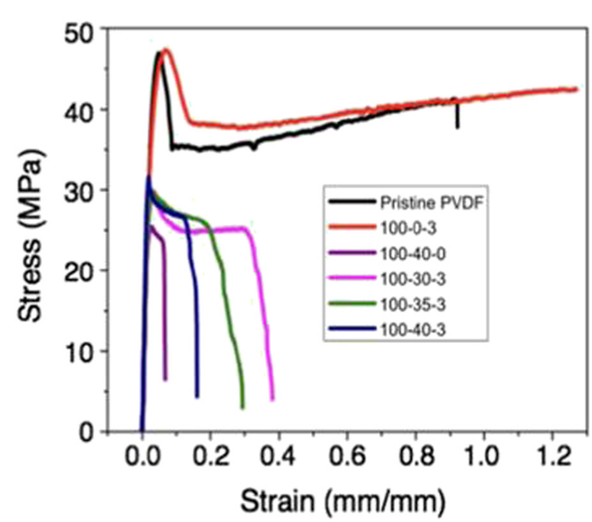

Figure 9: Tensile curves of neat PVDF and its composites (reproduced from the study of Jahan *et al.* [104] with permission).

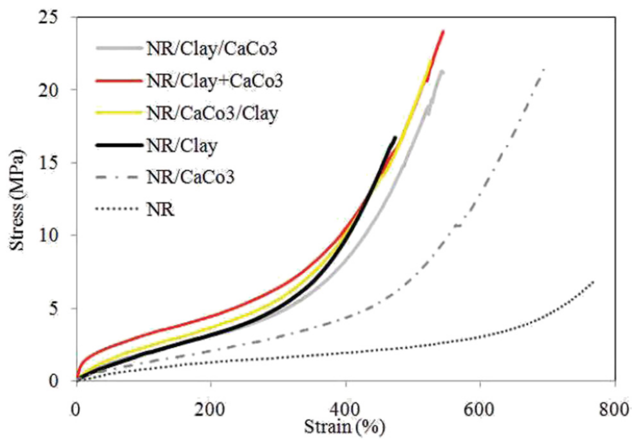

Figure 10: Stress–strain curves of NR/NC/$CaCO_3$ nanocomposites (reproduced from the study of Ghari *et al.* [78] with permission).

PVDF. PVDF nanocomposite was thus made more flexible and deformable under load, thus improving its piezoelectric properties.

Compared to pure PLA, ternary nanocomposites had higher modulus and better tensile strength [75]. By using two kinds of nanofillers in the PLA matrix, the ternary nanocomposite can achieve remarkable improvements in mechanical properties.

In a study by Alavitabari *et al.* [76], they found that by increasing the NC loading, the tensile modulus of nanocomposites increases. In addition, shear stresses during melt compounding may be increased due to the presence of $CaCO_3$. Consequently, NC platelets can be intercalated and exfoliated into the HDPE matrix.

In addition, in another study [77], it was concluded that NR-based hybrid nanocomposites containing MMT and $CaCO_3$ had a 445% growth in tensile strength, a 144% enhancement in stress at 100% strain, and only a 3% growth in elongation at break compared to neat NR. The excellent mechanical properties could be due to the appropriate distribution of MMT and $CaCO_3$ in the medium. Accordingly, they concluded that it was necessary to use a second filler, and especially to use MMT to improve filler dispersion.

In a recent study, Ayaz [105] investigated the impact and flexural power of a nanocomposite composed of PP, NC, and $CaCO_3$ with PPgMA. The incorporation of NC into the nanocomposite reduced the impact strength but enriched the flexural strength. As confirmed by SEM images, they found that incorporating PPgMA into the nanocomposite significantly enhanced the dispersion of NC and $CaCO_3$ and thus enhanced the impact and flexural powers. Ghari *et al.* [78] also analyzed the nanocomposites containing NR, NC (Cloisite 15A), and $CaCO_3$. Figure 10 shows that hybrid nanocomposites have a higher modulus at all elongations than single-phase nanocomposites. Moreover, strain-induced crystallization occurs in hybrid nanocomposites. Actually, Young's modulus and tensile strength increase when two fillers are added to NR.

Kapole *et al.* [79] observed that $CaCO_3$ plays a key character in the improved characteristics of the acrylic polyol–polyurethane/NC/$CaCO_3$ nanocomposite such as abrasion resistance and hardness. Furthermore, NC incorporation enhances abrasion resistance, moisture resistance, and scratch hardness. Ahmed *et al.* [106] prepared a nanocomposite composed of HDPE and a combination of two nanofillers ($CaCO_3$ and bentonite). It was found that all of the stress-softened samples contained excessive amounts of NC and $CaCO_3$. When rigid nanofillers are present in sufficient quantities, they entirely contribute to the toughness jump. In another study, Awan *et al.* [107] developed a ternary nanocomposite based on HDPE, $CaCO_3$, and NC by melt blending. The hardness value of ternary nanocomposites increased compared to neat HDPE. By incorporating spherical $CaCO_3$ nanofillers into the nanocomposite, mechanical properties were increased, while NC nanofillers affected the chain structure and mobility.

6 Modeling of mechanical properties

Response surface methodology can present a suitable relation between variables and outputs [44,108,109]. The links between the responses comprising tensile modulus and impact strength and the polymer MFI, NC, and $CaCO_3$ amounts were obtained for PP/NC/$CaCO_3$ system [67]. The tensile modulus was also examined using simple models [110]. It has been shown that some models such as Hirsch, Inverse rule of mixtures, Kerner-Nielsen, and Halpin-Tsai can successfully predict the tensile modulus. Halpin-Tsai predictions are matched to the experimented data at smaller aspect ratios. Probably, $CaCO_3$ raises the shear stress during mixing and thus, reduce the aspect ratio of NC layers.

It was also found that some parameters such as the Poisson ratio of polymer and maximum packing filler fraction have not a strong effect on the Kerner–Nielsen predictions [110]. Therefore, the modified equation of the Kerner–Nielsen model was modified and the calculated modulus by this model is well matched to the experimented results (Figure 11) [110]. Besides, the predictions of tensile modulus by the Takayanagi model are much more than the experimental data [110]. As a result, the Takayanagi model was modified for the ternary system. The agreement among theoretical and tentative data is very outstanding using the modified Takayanagi model.

Based on Ji model, Zare and Garmabi [111] planned a model to predict the modulus and interphase features of ternary systems comprising two nanoparticles (NC and $CaCO_3$). They compared the results by the proposed model with the experimented data. The experimental tensile moduli match well to the developed model, whereas the original Ji model shows considerable disagreement. Thus, the planned model suitably reflects the impressions of interphase and filler dispersion on the modulus.

Zare *et al.* [112] recommended a model for determining the interphase properties of ternary nanocomposites. They revealed that the interphase depth differently links to filler dimensions and concentrations of filler and interphase. Also, it was stated that the interphase strength straightly links to filler–polymer interface bonding. Furthermore, this group developed the Hashin–Shtrikman model for approximating Young's modulus of ternary nanocomposites

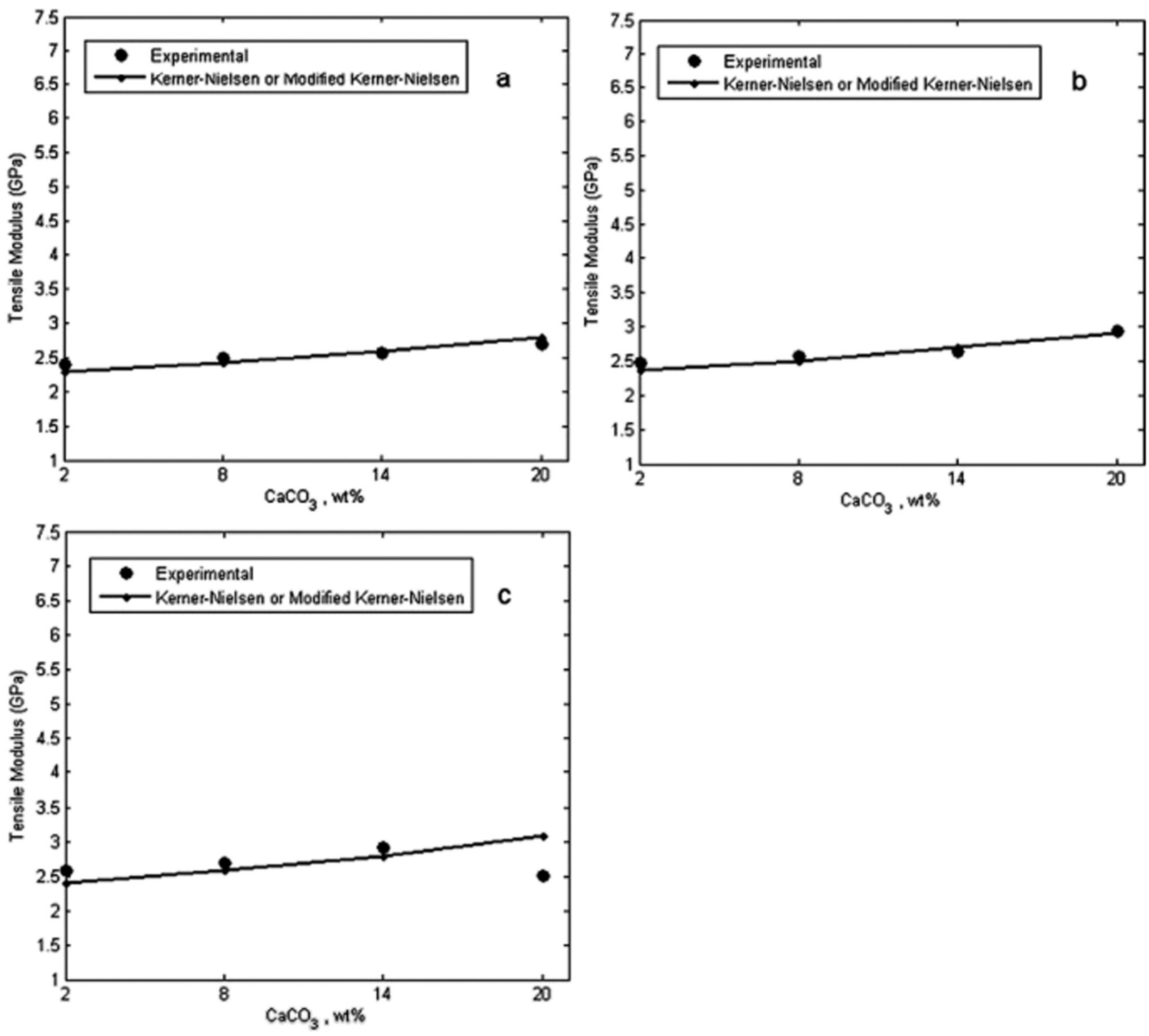

Figure 11: Experimental data and predicted tensile modulus by modified Kerner-Nielsen model at NC contents of (a) 2 wt%, (b) 4 wt%, and (c) 6 wt% (reproduced from the study of Zare and Garmabi [110] with permission).

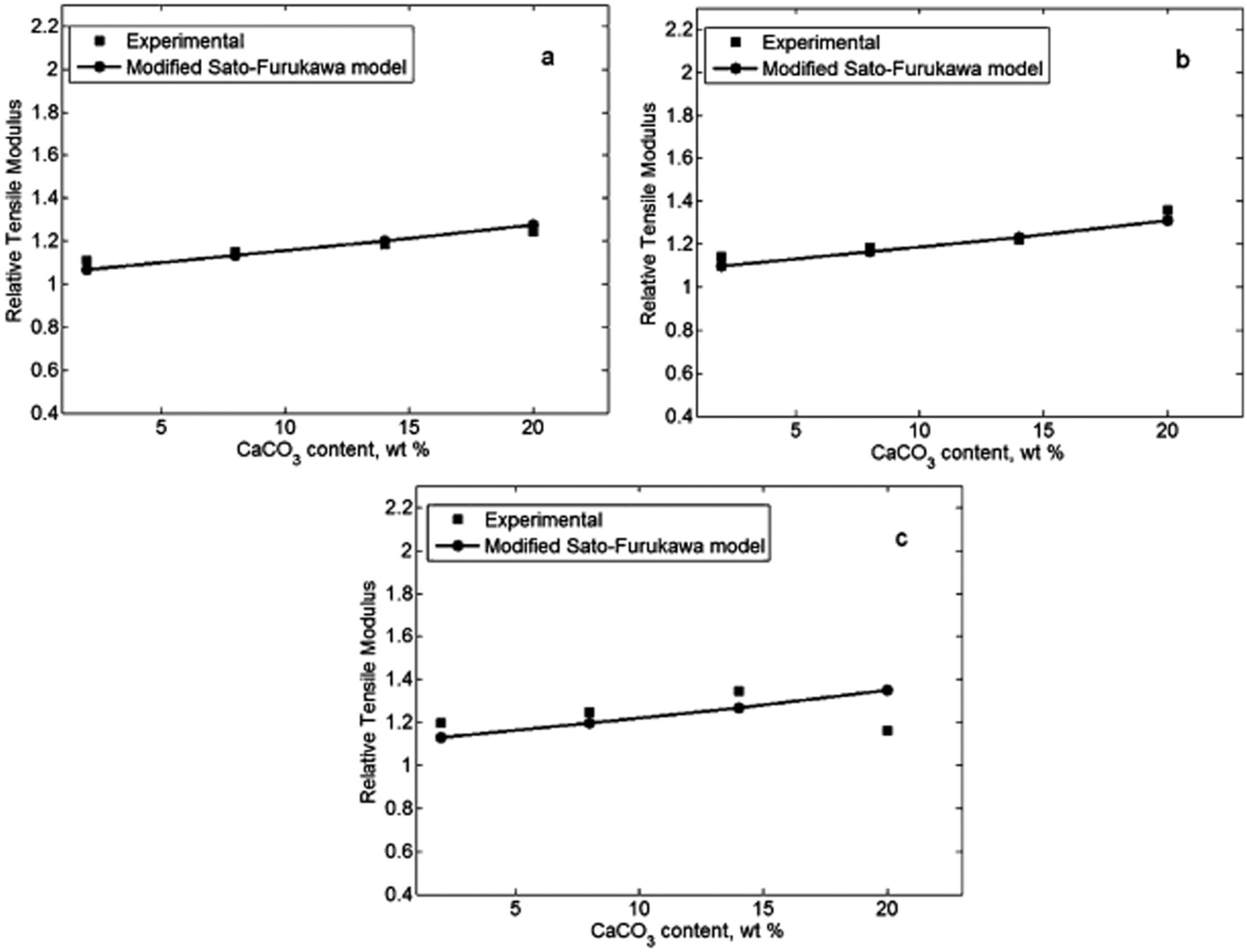

Figure 12: The calculations of relative modulus by modified Sato–Furukawa model in NC concentrations of (a) 2 wt%, (b) 4 wt%, and (c) 6 wt% (reproduced from the study of Zare and Garmabi [114] with permission).

made of PP, NC, and $CaCO_3$ [113]. By ignoring interphase, the Hashin–Shtrikman model underestimates the bulk, shear, and Young's moduli of samples. However, the proposed model is capable of predicting Young's moduli of ternary nanocomposite by considering the deepness and power of interphases.

Zare and Garmabi [114] studied the interface adhesion between MMT and $CaCO_3$ and PP matrix using a mechanical property model. Based on the faultless adhesion among nanofillers and PP, the Sato–Furukawa model was advanced for the tensile moduli of ternary nanocomposites. There is a fine arrangement among experimented grades and the proposed model that suggests the filler–filler and polymer–nanofiller contacts in the samples (Figure 12). Additionally, it was reported that the highest interface bonding is formed in the composites encompassing 4 wt% of NC, and various $CaCO_3$ amounts up to 20 wt%.

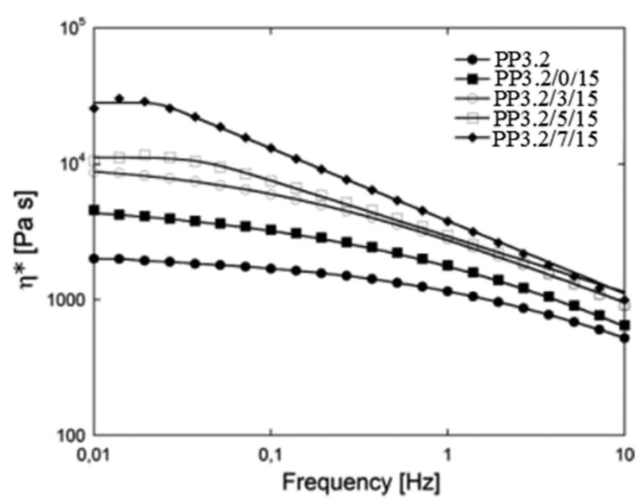

Figure 13: The complex viscosity of binary and ternary nanocomposites at different shear rates (reproduced from the study of Sorrentino *et al.* [85] with permission).

7 Rheological characterizations

The rheological behavior of PP/NC/$CaCO_3$ system was described in the study of Sorrentino *et al.* [85]. The agreement between measured data and fitted complex viscosity was outstanding. The viscosity of samples increases much more with the addition of NC layers associated with the platelet content or aggregates hindering the polymer chain rotations and movements (Figure 13). Also, the complex viscosity of the ternary system is higher than that of the micro-composite [115]. A distinct shear thinning behavior of ternary nanocomposite is demonstrated in the low frequency. The neat polymers have a same viscosity at a big range of shear rates. However, the samples with filler amount higher than a specified range display shear thinning at whole shear rates (Figure 13) [116,117].

The unlimited enhancement of viscosity is caused by the network as the shear rate reaches zero leading to yield stress. The trend is due to the dispersed filler, which can be connected to make a network [115]. The complex viscosity

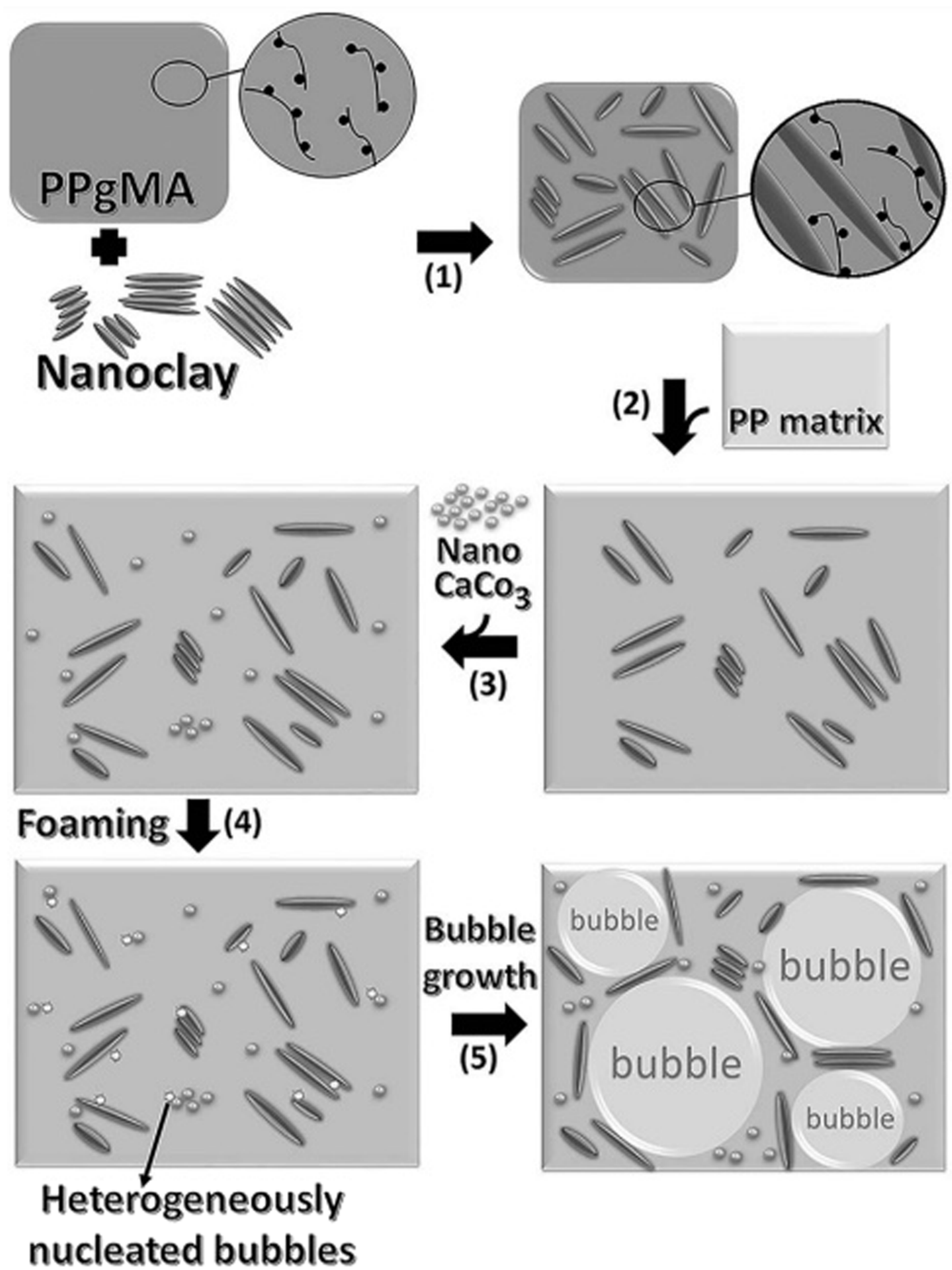

Figure 14: A schematic for manufacturing of PP/NC/$CaCO_3$ nanocomposite foam (reproduced from the study of Mohammad Mehdipour *et al.* [119] with permission).

of PLA was greatly improved when NC and $CaCO_3$ were added simultaneously [75]. In comparison with neat PLA, ternary nanocomposites have a higher complex viscosity. Based on observations of Asadi *et al.* [75], it can be concluded that concurrently using NC and $CaCO_3$ results in a significant increase in PLA viscosity.

Alavitabari *et al.* [76] discovered that at smaller frequencies, the viscoelasticity is further sensitive to the quantity of nanofillers in HDPE/NC/$CaCO_3$ samples. By increasing the NC percentage, storage modulus became less dependent on frequency, and thus viscoelasticity altered from liquid-like to solid-like. However, as $CaCO_3$ content increased, complex viscosity and storage modulus also increased. $CaCO_3$ has a higher percolation threshold than NC due to its lower aspect ratio and smaller surface area than NC, and therefore, has a slighter influence on the viscoelastic behavior. Nanofillers form three-dimensional structures, which reduce the polymer chain mobility and increase energy storage. Evaluation of linear viscoelastic features indicates that the presence of secondary nanofillers contributes to the fine dispersion of layered nanofillers.

8 Foam properties

Lian *et al.* [118] prepared a nanocomposite foam based on polystyrene (PS) with various concentrations of NC and $CaCO_3$ by CO_2 as a blowing agent. They systematically examined the effects of dual nanofillers, foaming pressure, and temperature on the foams and their cellular structure. G', G'', and η^* improved by incorporating nanofillers in the entire scanning frequencies range. NC has a higher enhancement of PS rheological properties than $CaCO_3$ at the same concentration of the nanofillers. All PS/NC/$CaCO_3$ nanocomposites exhibit pseudo-plastic fluid characteristics. In addition, the higher modulus of ternary nanocomposites resulted from the improved melt strength, which increases the stability of cellular structure during the foaming process. Hence, $CaCO_3$ and NC reveal a substantial synergistic influence on the improvement of foaming properties attributed to the diverse roles of nanofillers during cell nucleation and development.

Mohammad Mehdipour *et al.* [119] prepared a ternary nanocomposite foam based on branched PP, $CaCO_3$, and NC by a solid-state foaming process. A schematic of foam preparation is shown in Figure 14. Several variables affecting the morphology of foams were studied, including temperature and saturation pressure. By the use of NC during foaming, the density of the cells was increased, the cell size was reduced, and melt strength, and cell stability were improved.

By adding $CaCO_3$, foamability and cell density were improved. By simultaneously combining NC and $CaCO_3$, foams had a higher cell density and a smaller cell size. Moreover, DSC analysis demonstrated that foamed nanocomposites had a higher crystallinity than unfoamed samples, and DMTA analysis indicated that foamed nanocomposites had a higher tan δ than unfoamed samples. Although the biomedical applications of ternary nanocomposite foams were not studied in the literature, it was stated that low cytotoxic potential, good biocompatibility, cellular structure, and mechanical properties of nanocomposite foams are suitable for scaffolds in bone tissue engineering and wound dressing materials [120–122].

9 Conclusions and prospective challenges

This review article studied the ternary systems including polymer, NC, and $CaCO_3$. A comprehensive study was conducted on the impacts of $CaCO_3$ and NC on the structure, mechanical features, thermal behavior, foamability, and rheological characteristics of this system. According to the reports, nanofillers with a complete dispersion in a polymer matrix improved the physical and rheological properties of nanocomposites. However, a challenge is the distribution of nanofillers in the polymer mediums. Poor dispersion weakens the interfacial interphase reducing the final properties of nanocomposite. Therefore, the dispersion quality of nanofillers is one of the key parameters in the ternary samples. Much attempt is necessary to develop the nanocomposites as industrial products. However, the development of processing technologies in terms of quantity, quality, and cost for business is one of the main challenges for ternary nanocomposites. The potential applications of ternary nanocomposites include automobile, aerospace, household, construction, transportation, consumer products, and packaging in the food industry. The ternary nanocomposites can offer an extraordinary combination of stiffness, toughness, ease of processing, and cheapness that is difficult to obtain with other materials. As mentioned, NC can interact with a wide range of polymers and biological components. Also, $CaCO_3$ can be used in drug delivery, enzyme immobilization, encapsulation of bioactive compounds, biosensors, and tissue engineering. Generally, the nontoxic nature and biocompatibility of both NC and $CaCO_3$ provide the biomedical applications of polymer/NC/$CaCO_3$ samples in bone tissue engineering, wound healing, implants, 3D bioprinting, drug delivery, medical devices, and enzyme immobilization. The interest in these nanocomposites has grown recently since their configuration and structure can be changed to provide the desirable aims. It is expected that the ternary nanocomposites can be more developed for various biomedical requests.

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