

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Mechanical Enhancement of Poly (Vinyl Chloride) Nanocomposites using CaCO₃ Nanoparticles as Impact Modifier.

AM Youssef^{1*}, IM Hegazy², AM Ramadan³, and AA Abd El-Hakim¹.

¹Packaging and Packing Materials Department, National Research Centre, 33 El Bohouth St. (former El Tahrir st.), Dokki, Giza, Egypt, P.O. 12622.

²Al Amal plastic Company for plastic pipes and fittings, Cairo, Egypt.

³Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt.

ABSTRACT

The calcium carbonate (CaCO₃) nanoparticle was successfully incorporated into poly (vinyl chloride) (PVC) matrix to prepare PVC/CaCO₃ nanocomposites. The surface of CaCO₃ nanoparticle was modified using stearic acid to modify the surface properties of CaCO₃ nanoparticle and, subsequently, to obtain compatible nanoparticles and high performance materials. For contrast, PVC-based materials, with the addition of modified CaCO₃ were examined also. The effect of CaCO₃ and surface modified on thermal and mechanical properties of PVC nanocomposites was studied. The Morphological analysis of the prepared PVC/CaCO₃ nanocomposites was evaluated using scanning electron microscope (SEM). An important enhancement in the PVC thermal stability was recorded with the addition of stearic acid modified CaCO₃ nanoparticle.

Keywords: PVC, CaCO₃, nanocomposites, SEM, mechanical properties

**Corresponding author*

INTRODUCTION

The most significant class of engineering materials is polymer composites. The combination of inorganic fillers such as clays or inorganic nonmaterial into thermoplastics polymers has been extensively experienced in industry to extend them and for developing especial properties. The first purpose of adding inorganic fillers to polymers matrix is cost reduction [1, 2]. The mechanical properties of polymer composites were enhanced by using the filler, such as hardness, toughness, dimension stability, stiffness, and mold shrinkage [3]. The influence of filler on the mechanical and other properties of the polymer nanocomposites count on filler origin, and morphology for instance particle shape and size, aggregate size, the fraction of filler, surface characteristics, and degree of dispersion[4-8].

Poly(vinyl chloride) (PVC) is recognized as the second worldwide polymer has been widely used in industrial fields for many years [9], owing to its good properties, such as respectable mechanical and electrical properties, good resistance to corrosion and decent processability. However, its low toughness and heat-softening temperature limit its application [10]. The addition of cheap fillers increasing awareness of possibilities to simultaneously improve a broad range of mechanical properties and reduce costs, still there is to stiffen the material or control the silent properties [11].

Nanocomposites based on PVC and different nanomaterials have displayed increasing attention in last few years. The influence of excellently powdered CaCO_3 on the resistance of PVC for weathering has also been investigated, but few publications concerning the effect of CaCO_3 nanoparticles on the mechanical properties of PVC or PVC blends have been reported [12, 13]. CaCO_3 nanoparticle is one of the most famous spherical nanoscale fillers used in preparation of polymer nanocomposites. Polypropylene PP/ CaCO_3 nanocomposites [14] revealed that the toughening result of CaCO_3 nanoparticles on PP matrix, but the yield strength of PP was significantly reduced, because of the nucleating effect of CaCO_3 nanoscale. Additional study indicated that the melting temperature and glass transition of polyethylene terephthalate were significantly enhanced after addition of CaCO_3 . From these two studies it was found that the organically treated CaCO_3 nanoparticles was a good nucleating agent for semicrystalline polymers[15].

Numerous efforts have been dedicated to surface-treated of CaCO_3 as nanofiller using different modifier to raise the interaction between the polymer matrix and filler. The impacts of surface modification on mechanical properties of polymer nanocomposites have been progressive [16]. The utilization of CaCO_3 nanoparticles may convey new understandings in the study of polymer-inorganic nanocomposites [17, 18]. Furthermore, the mechanical properties of CaCO_3 nanoparticles filled polymer nanocomposites, which may be very diverse from those of the micron-sized CaCO_3 incorporated into polymer composites, are infrequently studied [19].

The main goal of the present study was to replacement the commercial impact modifier by CaCO_3 nanoparticles to investigate the mechanical properties of PVC/ CaCO_3 nanocomposites and achievement an accepted products in the impact test and cost saving.

MATERIALS AND METHODS

Materials

Suspension polyvinyl chloride (PVC) of K-value 58 was product of Oxy vinyls LP Dallas Texas US. Precipitated Calcium Carbonate (FC 500) was product of Formosa plastics corporation TAIPEI TAIWAN. CaCO_3 nanoparticles (SP-200, surface-modified with stearic acid), was produced by Shanghai Perfection Nanometre New Material Co., Ltd., China. Titanium dioxide (KORONOS 2220) was product of KORONOS Montreal, Canada. Poly ethylene wax (PED 521) was product of Clariant International Ltd. Calcium stearate (CA-30)) was product of Zirve Polymer Istanbul, Turkey. Processing aid (PA910) LG chem. USA. Tin stabilizer(Mark 1984E) Galata chemicals, Germany. Soya bean was obtained from (INBRFLEX A-6) FRP services New York USA.

Methods

PVC 100 phr, organic tin stabilizer 5 phr and stearic acid 0.3 phr were premixed together in a high-speed mixer for 8 min to give compounded PVC. CaCO_3 nanoparticles were dried at 70°C for 48 h in a vacuum

oven. The PVC matrix and CaCO₃ nanoparticles were melt mixed with a two-roll mixer at 140°C for 15 min to provide binary nanocomposites. The pure PVC, CaCO₃ nanoparticles, and Blendex 20 phr were mixed in the similar way to offer ternary nanocomposites. The prepared nanocomposites were molded into sheets of 1 and 3 mm in thickness by compression molding at 150°C and 20 MPa for 8 min, followed by cooling to room temperature at 10 MPa.

Table 1: The formulation of the prepared of PVC nanocomposites

Materials	amounts
PVC Resin	100 phr
Titanium dioxide	5.8 phr
Poly ethylene wax	0.125 phr
Calcium stearate	0.625 phr
Processing aid (acrylic acid)	1.7 phr
Tin stabilizer	4.2 phr
Soya bean	2.1 phr
CaCO ₃ nanoparticles	1, 3 and 5 phr

Characterization

The impact-fractured surfaces of composites were observed by scanning electron microscopy (SEM) with a HITACHI-S-2150 apparatus. The surfaces were covered with gold prior to observation. Tensile tests were performed at a crosshead speed of 10 mm/min using an Instron tensile tester according to ASTM D638M, and the flexure tests were performed using an Instron tensile tester according to ISO 178. The thermal stability was assessed on a thermal gravimetric analyzer (TGA), Perkin Elmer using about 20 mg of the samples at a heating rate of (10 °C/min) under nitrogen atmosphere. Differential scanning calorimeter (DSC), Perkin Elmer with a heating rate of (10 °C/min) under nitrogen atmosphere was used for the determination of the glass transition temperatures

RESULT AND DISCUSSION

The mechanical properties of the prepared PVC mix were studied and the obtained results were as follow

Mechanical properties of PVC nanocomposites containing different amounts of modified CaCO₃ nanoparticles compared with commercial acrylic impact modifiers

Effect of adding CaCO₃ nanoparticles on the impact strength of PVC nanocomposites

The modified CaCO₃ nanoparticles are add at different amounts to PVC matrix to study the mechanical properties specially impact test of the prepared PVC nanocomposites which compare with the PVC containing commercial impact modifiers.

Table 2 and Figure 1 revealed that, the results obtained when modified CaCO₃ nanoparticles were added with different amounts (1, 3 and 5 phr) to PVC matrix. From the Figure and Table it can be observed that the addition of surface modified CaCO₃ nanoparticles instead of impact modifiers it provide very similar mechanical results at high loading of modified CaCO₃ nanoparticles.

Table 2: Effect of adding different amounts of nanoCaCO₃ in the impact strength of PVC

Addition	Blank	3 phr commercial impact modifier	1 phr CaCO ₃ nanoparticles	3 phr CaCO ₃ nanoparticles	5 phr CaCO ₃ nanoparticles
Impact strength KJ/m ²	113.3	169.66	137.59	154.8	170.5

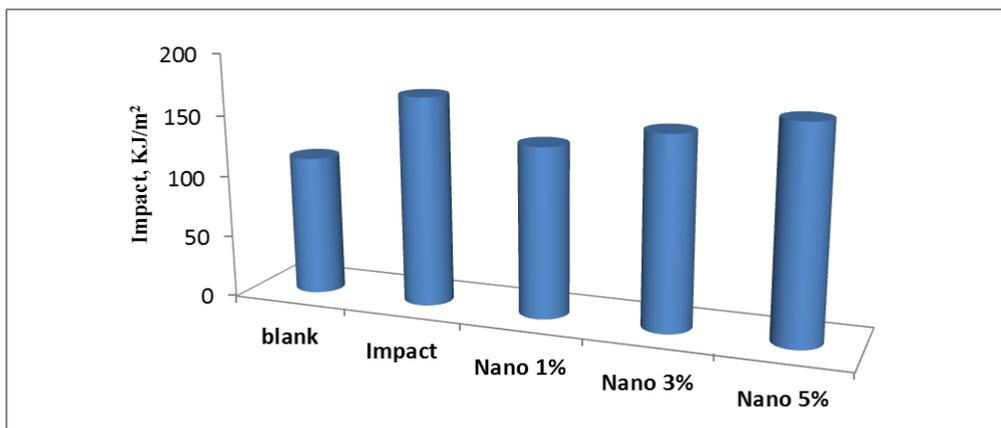


Figure 1: Effect of adding different amounts of nanoCaCO₃ in the impact strength of PVC

Correspondingly, it can be concluded that the optimum percentage for adding Surface modified CaCO₃ nanoparticle when using 5 phr as impact modifiers. This amounts of modified CaCO₃ nanoparticle gives the same results obtained when using 3 phr of acrylic modifiers.

Effect of adding modified CaCO₃ nanoparticle on the tensile strength of the prepared PVC nanocomposites

The tensile strength of the PVC nanocomposites were evaluated using different amounts of modified CaCO₃ nanoparticle in comparison with commercial impact modifiers and the obtained results were shown in Table 3 and Figure 2.

Table 3: Tensile strength of PVC/ CaCO₃ nanocomposites containing different amounts of modified CaCO₃ nanoparticles as well as commercial acrylic impact modifiers

Addition	Blank	3 phr commercial impact modifier	1 phr CaCO ₃ nanoparticle	3 phr CaCO ₃ nanoparticle	5 phr CaCO ₃ nanoparticle
Tensile Kg/Cm ²	602.15	624.28	607.34	614.01	622.62

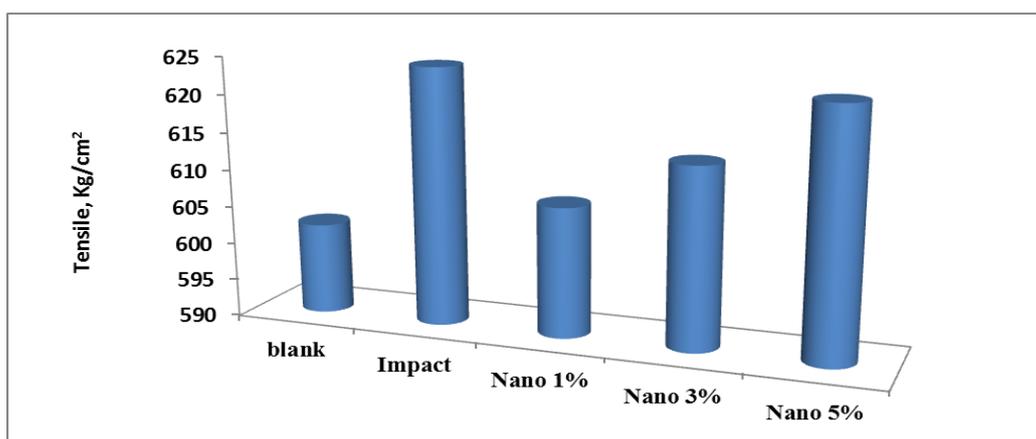


Figure 2: Tensile strength of PVC nanocomposites containing different amounts of modified CaCO₃ nanoparticles and acrylic as commercial impact modifiers

The acquired results from Table 3 and Figure 2 displayed that the effect of addition of modified CaCO₃ nanoparticles in different loadings (1, 3 and 5 phr) to PVC matrix and compared with 3 phr of acrylic impact modifiers on the tensile strength of the prepared PVC nanocomposites. It can be distinguished that the presences of 3 phr of acrylic commercial impact modifiers provide good tensile strength. The of addition of modified CaCO₃ nanoparticles by different loading (1, 3 and 5 phr) the tensile strength increased by increasing

the amounts of modified CaCO₃ nanoparticles until 5 phr when reaching the same result obtained at using 3 phr of acrylic as impact modifiers, tacking in the consideration the different in the price of materials.

Influence of addition of different loadings of modified CaCO₃ nanoparticles in the elongation percentage of the prepared PVC nanocomposites

The effect of addition of different loadings of modified CaCO₃ nanoparticles in the elongation percentage of the prepared PVC nanocomposites using different amounts comparing with 3 phr acrylic impact modifiers provide the following results which attained in Figure 3 and Table 4. The elongation % of PVC composites in presence of acrylic impact modifiers provide high elongation % compared with blank sample and the samples containing different amounts of modified CaCO₃ nanoparticles, otherwise the elongation % decreases with increasing the amounts of modified CaCO₃ nanoparticles in the prepared PVC nanocomposites as shown in Table 4.

Table 4: Elongation percentage of PVC composites containing different amounts of modified CaCO₃ nanoparticles as well as acrylic commercial impact modifiers

Added amounts	Blank	3 phr commercial impact modifier	1 phr CaCO ₃ nanoparticle	3 phr CaCO ₃ nanoparticle	5 CaCO ₃ nanoparticle
Elongation %	32.03	99	47	40	30.07

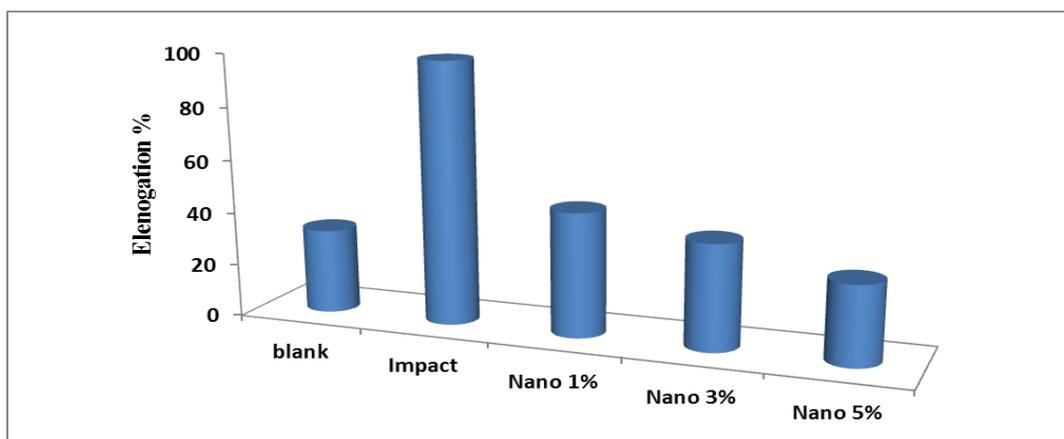


Figure 3: Effect of adding different amounts of modified CaCO₃ nanoparticles as well as acrylic impact modifiers on the prepared PVC nanocomposites.

From Figure 3 it can be detected that the elongation % when using acrylic impact modifiers is higher than that of blank PVC as well as PVC nanocomposites containing different amounts of modified CaCO₃ nanoparticles

Effect of presence of different amounts of modified CaCO₃ nanoparticles on the VICAT properties of PVC nanocomposites

The VICAT properties of the PVC nanocomposites deliver information of the influence of the presence of various percentages of amounts of modified CaCO₃ nanoparticles along with acrylic impact modifiers on the VICAT of the prepared PVC nanocomposites. The obtained results were shown in Figure 4 and Table 5.

Table 5: Effect of different amounts of modified CaCO₃ nanoparticles on the VICAT properties of PVC nanocomposites

Added amounts	Blank	3 phr commercial impact modifier	1 phr CaCO ₃ nanoparticle	3 phr CaCO ₃ nanoparticle	5 phr CaCO ₃ nanoparticle
VICAT	70	71.6	71.1	70.9	70.7

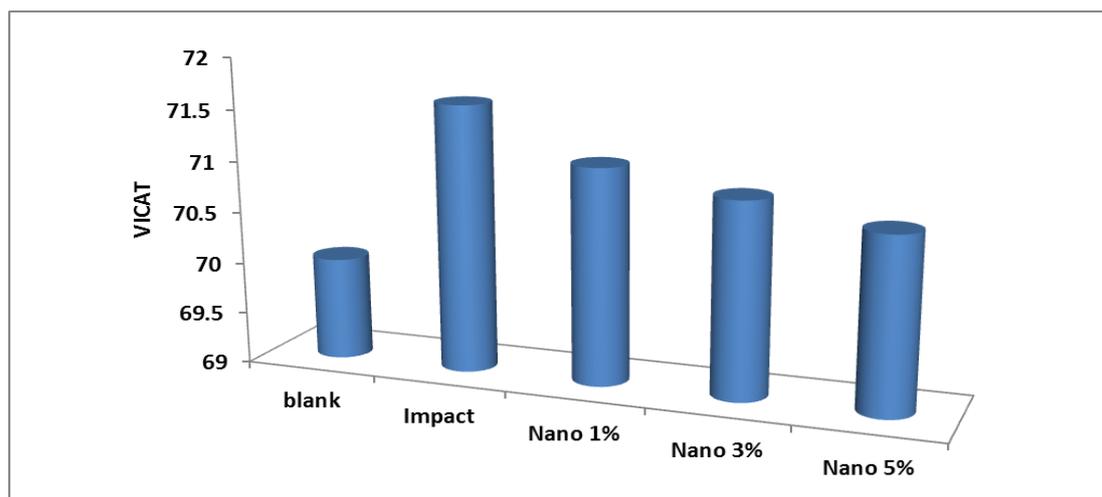


Figure 4: Effect of different amounts of modified CaCO₃ nanoparticles on the VICAT properties of PVC nanocomposites

From Figure 4 and Table 4 it can be distinguished that the presence of acrylic impact modifiers rise the VICAT temperature; nevertheless the VICAT temperature decrease from 71.6°C to 70.7°C with the occurrence of different loadings of modified CaCO₃ nanoparticles compared with blank PVC sample. Correspondingly, flattening test and heat reversion is accepted for all samples

Thermal properties of the prepared PVC nanocomposites

Due to inherent drawbacks, for instance poor thermal stability and brittleness, PVC is commonly compounded with several additives. After compounding with various nanoscale additives, such as montmorillonite, [20] silica, [22] calcium carbonate (CaCO₃), [23, 24] and aluminum oxide, [25] have been described to improve the thermal stability properties of PVC, such as heat resistance. The characteristics of PVC/CaCO₃ nanocomposites enhanced properties such as (light weight, strong strength, chemical resistance, and cheapness). Thus, the PVC nanocomposites products can be extensively applied in the fields of automobiles, houses, buildings, and packaging from food to electronic parts. Figure 5 displayed that thermal stability of pure PVC as well as PVC/CaCO₃ nanocomposites containing different ratios of modified CaCO₃ nanoparticles. It can be noticed that the PVC/CaCO₃ nanocomposites containing 5 phr of modified CaCO₃ nanoparticles is thermally stable than that of pure PVC and PVC/CaCO₃ nanocomposites containing 1 phr of modified CaCO₃ nanoparticles.

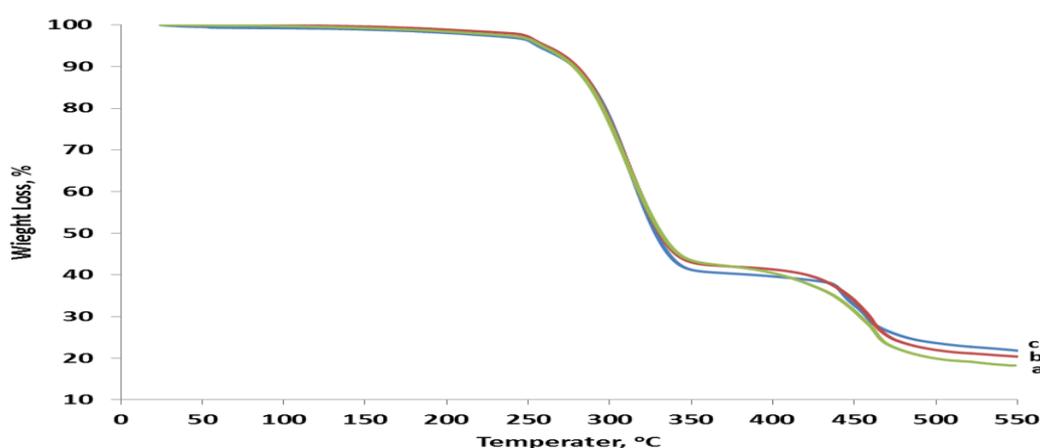


Figure 5: the TGA curves of a) PVC blank, as well as PVC/CaCO₃ nanocomposites containing different amounts of modified CaCO₃ nanoparticles, b) 1 phr, c) 5 phr

TGA curve of the PVC compound without CaCO₃ addition. Two weight-loss stages with respect to the two thermal degradation stages can be perceived in the TGA curve. The first weight-loss stage, arising within

the range of 290–320 °C, is mostly because of the HCl elimination reaction of PVC molecules and the formation of a polyene structure. The second weight-loss stage, seeming within the range of 440–480 °C, is owing to the thermal degradation of the carbon chain of PVC, which yields flammable volatiles. It can be concluded that PVC/CaCO₃ nanocomposite does not differ significantly with the addition of CaCO₃, as shown in Figure 5.

A differential scanning calorimeter was used to examine the thermal properties of pure PVC and the prepared PVC/CaCO₃ nanocomposites. The DSC thermograms of pure PVC and PVC/CaCO₃ nanocomposites containing diverse loadings of modified CaCO₃ nanoparticles (1 phr and 5 phr) were shown in Figure 6 and revealed that the glass transition temperature (*T_g*) of pure PVC is around 73 °C while the *T_g* of PVC/CaCO₃ nanocomposites having 1 phr of modified CaCO₃ nanoparticles decrease to around 72 °C while the *T_g* of PVC/CaCO₃ nanocomposites containing 5 phr of modified CaCO₃ nanoparticles decline to touch 59 °C which indicated that the modified CaCO₃ nanoparticles works as good plastizer for PVC polymers.

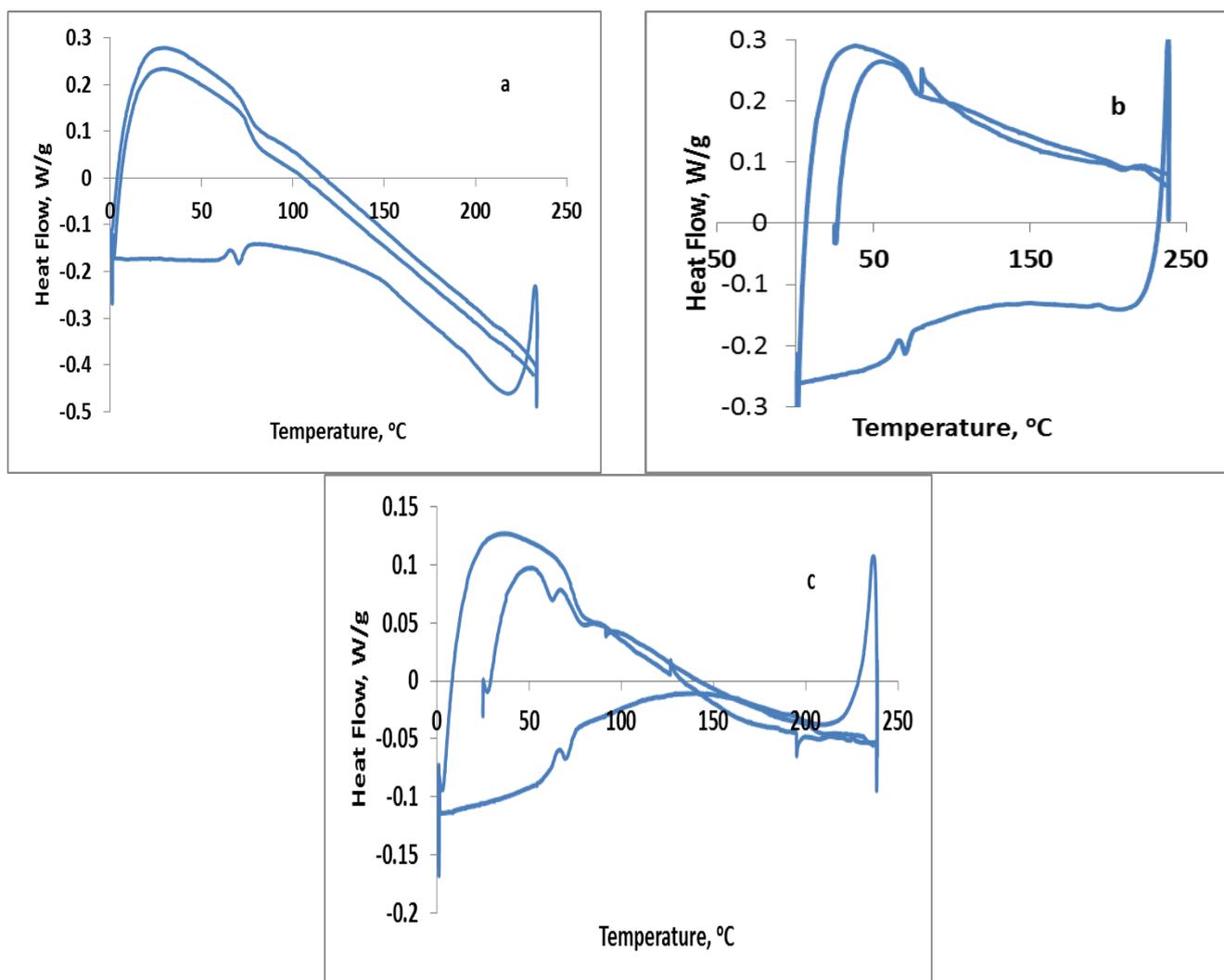


Figure 6: The DSC thermograms of a) PVC blank, as well as PVC/CaCO₃ nanocomposites containing various amounts of modified CaCO₃ nanoparticles, b) 1 phr, c) 5 phr

SEM Examination

In Figure 7, SEM micrographs of the fractured surface of pure PVC as well as PVC/CaCO₃ nanocomposite containing the different amounts of modified CaCO₃ nanoparticles

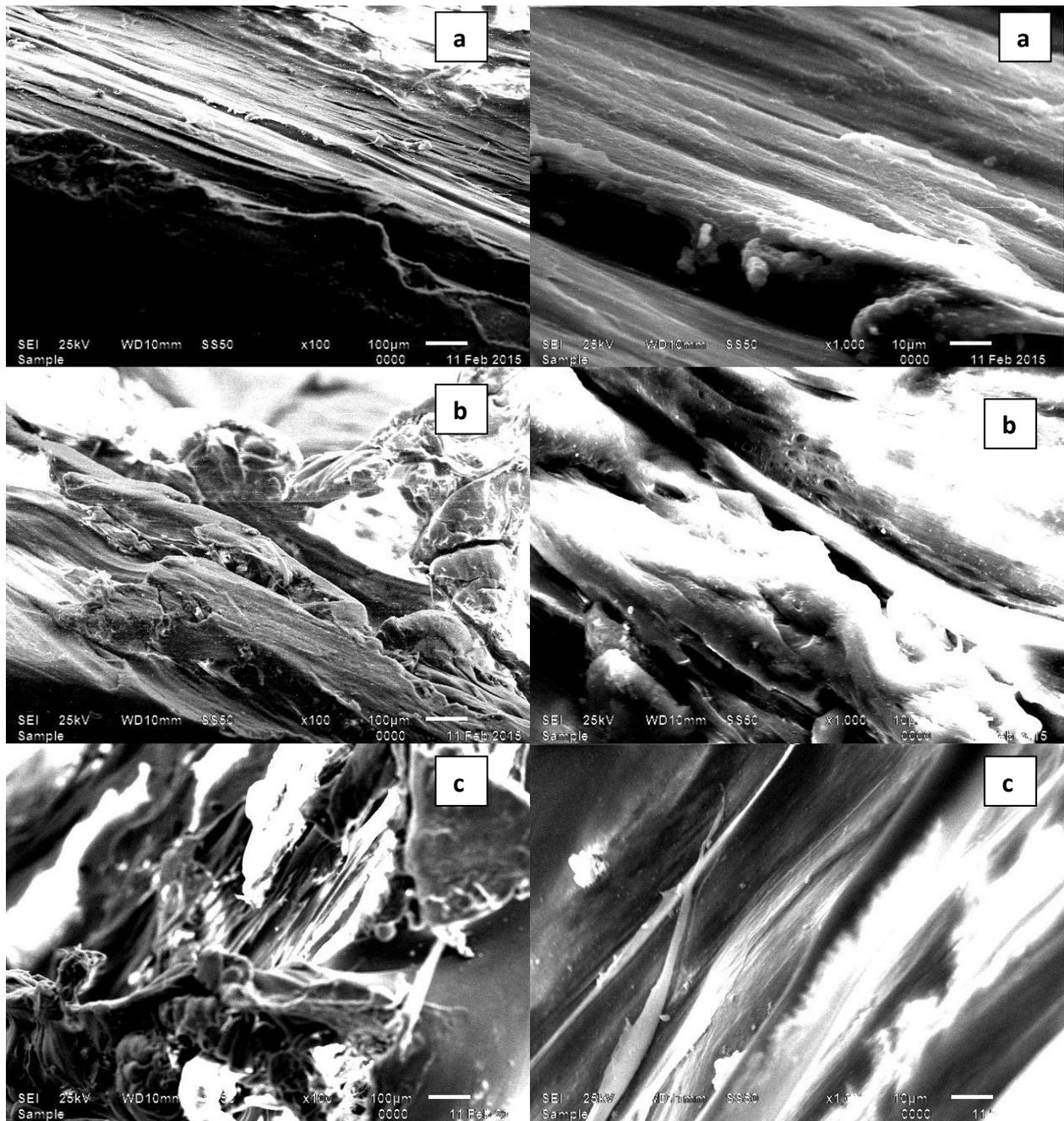


Figure 7. SEM micrographs: (a) pure PVC (100x and 1000x), (b) PVC/CaCO₃ (1phr) nanocomposite (100x and 1000x), and (c) PVC/CaCO₃ (5 phr) nanocomposite ((100x and 1000x).

Morphological description demonstrated that the efficacy of modified CaCO₃ nanoparticles, which supported the formation of PVC nanocomposite structure; the CaCO₃ nanoparticles look as it finely and homogeneously dispersed in the PVC matrix when compared with pure PVC without modified CaCO₃ nanoparticles. Actually, nanoparticles generally pulled out, leaving holes on the surface of polymer matrix and, therefore, establishing the absence of bonding and compatibility between the polymer and CaCO₃ nanoparticles. In conclusion, the presence of the sole stearic acid, while preventing the nanoparticle pull out, at the same time, was not able to prevent the agglomeration phenomena. Furthermore, stearic acid could not be considered a proper coupling agent, but the occurrence of an organic layer (such as stearic acid) on the surface allowed to lower the surface energy, but at the same time, it did not result in compatibility with PVC matrix as shown in Figure 7 (b and c).

CONCLUSIONS

In this paper, the characteristic of PVC/CaCO₃ nanocomposites were successfully prepared based on modified CaCO₃ nanoparticles using stearic acid. In particular, the commercial acrylic impact modifier was replaced by modified CaCO₃ nanoparticles and compared with the properties of the prepared PVC/CaCO₃ nanocomposites. A significant improvement in the thermal stability of PVC nanocomposites compared to pure PVC matrix was stabilized with the addition of stearic acid modified CaCO₃ nanoparticles at different loadings. Also the morphology of the prepared PVC/CaCO₃ nanocomposites was evaluated. Moreover, the mechanical properties were estimated at low and high modified CaCO₃ nanoparticles loadings. Finally, the addition of modified CaCO₃ nanoparticles to the PVC instead of acrylic impact modifier provides good PVC/CaCO₃ nanocomposites properties and reduces the products price.

REFERENCES

- [1] Youssef AM, El-Gendy A and Kamel S. *Materials Chemistry and Physics* 2015; 152: 26–33.
- [2] Pukanszky B. *Polypropylene: Structure, Blends and Composites, Composites*; Karger-Kocsis, J., Ed.; Chapman & Hall: London, 1995; 3: pp1-70
- [3] Baker R A, Koller L L and Kummer P E. *Handbook of Filler for Plastics*; Katz HS, Milevski J V, Eds.; Van Nostrand Reinhold: New York, 2nd^{ed}1987, Chapter 6, p 119-3
- [4] Moussa M A, Ghoneim AM, Abd el-Hakim A A and Turky G M. *Advances in Polymer Technology* 2009, 28: 257-266
- [5] Abd El-Hakim A A. *Colloid and polymer science* 1991; 269 (6): 628-632
- [6] Youssef A M, Abou-Yousef H, El-Sayed S M and Kamel S. *International Journal of Biological Macromolecules* 2015; 76: 25–32.
- [7] Youssef A M. *RSC Advances* 2014; 4: 6811–6820,
- [8] Khaled E, Kamel M S, Hassan H N A, Haroun A A, Youssef A M, Aboul-Enein H Y. *Talanta* 2012; 97: 96–102.
- [9] Bonadies, Avella M, Avolio R, Carfagna C and Errico M. *Journal of Applied Polymer Science* 2011; 122(6): 3590-3598.
- [10] Chen N, Wan C and Zhang Y, Zhang Y X. *Polymer Testing* 2004; 23(2):169-174.
- [11] Kemal I, Whittle A, Burford R and Vodenitcharova T. *Polymer* 2009; 50(16): 4066-4079.
- [12] Wu D, Wang X, Song Y and Jin R. *Journal of Applied Polymer Science* 2004; 92(4): 2714-2723.
- [13] Chen C-H, Teng C, Su S, Wu W-C and Yang C-H. *Journal of Polymer Science Part B: Polymer Physics* 2006; 44(2): 451-460.
- [14] Zhu A P, Cai A Y and Zhou W D. *Applied surface science* 2008; 254(13): 3745-3752.
- [15] Lorenzo D, Errico M M and Avella M. *Journal of Materials Science* 2002; 37(11): p. 2351-2358.
- [16] Nassar M A, Youssef A M. *Carbohydrate Polymers* 2012; 89:269-274
- [17] Chen N, Wan C Y, Zhang Y, Zhang Y X, Zhang C. *J Appl Polym Sci* 2005; 95; 953-961.
- [18] Xiong Y, Chen G and Guo S. *J Appl Polym Sci* 2006; 102: 1084-1091.
- [19] Yang L, Hu Y, Guo H, Song L, Chen Z and Fan W. *J Appl Polym Sci* 2006; 102: 2560-2567.
- [20] Wan C Y, Qiao X Y, Zhang Y and Zhang Y X. *Polymer Testing* 2003; 22: 453–461.
- [21] Reynaud E, Jouen T, Gaunthier C, Vigier G and Varlet J. *Polymer* 2001; 42: 8759–8768.
- [22] Chan C M, Wu J S, Li J X and Cheung Y T. *Polymer*; 43: 2981-2992.
- [23] Avella A, Errico M E and Martuscelli E. *Nano Lett* 2001; 1:213-217.
- [24] Cao Y M, Sun J and Yu D H. *J Appl Polym Sci* 2002; 83: 70-77.
- [25] Djidjelli H, Martinez-Vega J J, Farenc J, Benachour D. *Macromol Mater Eng* 2002; 287: 611-618