

Calcium Carbonate (CaCO₃) Nanoparticle Filled Polypropylene: Effect of Particle Surface Treatment on Mechanical, Thermal, and Morphological Performance of Composites

Manish Kamal,¹ C. S. Sharma,¹ Pradeep Upadhyaya,¹ Vishal Verma,¹ K. N. Pandey,¹ Vijai Kumar,¹ D. D. Agrawal²

¹Central Institute of Plastic Engineering & Technology, Lucknow Uttar Pradesh, India

²Department of Applied Chemistry, Jiwaji University, Gwalior, Madhya Pradesh, India

Received 21 January 2011; accepted 11 May 2011

DOI 10.1002/app.35319

Published online 2 November 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The present study was aimed to see the effect of surface treatment on nanocomposites with different fatty acids (stearic acid and oleic acid) having two different coupling agents (titanate and silane). Nanocomposites were prepared via melt mixing in Haake 90 twin screw extruder. The characterization of nanocomposites had been carried out using various advance analytical techniques such as dynamic mechanical analysis, thermogravimetric analysis, heat distortion temperature, melt flow index, and scanning electron microscopy. The strength and stiffness were also improved with the incorporation of maleic-anhydride grafted ethylene propylene rubber in PP/Nano-CaCO₃ nanocomposites. The tensile, flexural, and

impact strength properties of PP/MA-g-EPR/treated-CaCO₃ and untreated nanocomposites were determined. These studies revealed that stearic acid treated nanofiller filled composites had better properties than those of untreated and oleic acid treated nanofiller filled composites. The SEM studies demonstrated that the dispersion and distribution of Nano-CaCO₃ (nCaCO₃) particles within the polypropylene matrix were dependent on the nature of surface treating agents. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2649–2656, 2012

Key words: polypropylene; stearic acid; oleic acid; MA-g-EPR; titanate and silane coupling agent

INTRODUCTION

Polypropylene (PP) is one of the most important commodity polymers, which is widely used in technical applications, because of its good process-ability, relatively high mechanical properties, great recyclability, and low cost. However, owing to its low modulus, high notched sensibility, and poor impact resistance the usefulness of PP as an engineering thermoplastic is still limited. Continual efforts have been made to enhance mechanical, thermal, and microphase properties. The challenge of increasing the aforementioned properties of polymer provoked considerable interest.¹

In recent years, organic–inorganic nanocomposites have attracted immense interest, both in industry and in academia. These nanocomposites are a class of hybrid materials composed of an organic matrix and an inorganic reinforcement because they often exhibit excellent properties.^{2–5} The main aim of producing such types of nanocomposites is to reduce

industrial cost and modifying the particles of nanoscale dimension is embedded^{6–11} of some characteristics such as stiffness, electrical insulation, thermal stability, and optical properties. However, it has been observed that in most of the cases a loss in mechanical properties like tensile strength and tenacity is observed, due to a lack of affinity between the polymer and the filler resulting in low adhesion. The difference in surface energy between the composites component is thought to be the main reason for the weak affinity between filler and polymer.¹² Some filler can be treated by organic compounds coupling agents to overcome this weak affinity and coupling agents may reduce the surface energy and improve interfacial adhesion.¹³ Weak affinity can be reduced to a greater extent when filler particles are extremely small, like in nanocomposites structure. In this class of composites the fillers like montmorillonites are added, in very low percentage (1–5 wt %) to enhance the physico-mechanical thermal and microphase properties.^{14–16}

The extremely high surface area is one of the most attractive characteristics of nanoparticles because it facilitates creating a great amount of interphase in a composite. Introduction of nanoparticles into a polymer changes the intermolecular interaction of the matrix which is very well documented in

Correspondence to: V. Verma (vishalv_001@yahoo.co.in).

TABLE I
Composition Nomenclature

Sample	Composition
MN-1	SA-nCaCO ₃ /MA-g-EPR/T
MN-2	OA-nCaCO ₃ /MA-g-EPR/T
MN-3	nCaCO ₃ /MA-g-EPR/T
MN-4	SA-nCaCO ₃ /MA-g-EPR/S
MN-5	OA-nCaCO ₃ /MA-g-EPR/S
MN-6	nCaCO ₃ /MA-g-EPR/S

literature.¹⁷ As estimated by Regnaud et al.,¹⁸ an interphase of 1 nm thickness represents roughly 0.3% of the total volume of polymer in the case of microparticles filled composites, whereas, it can be 30% of the total volume in the case of nanocomposites. Uniform distribution of nanoparticles over a polymer matrix has become mandatory to improve nanopartiles/matrix interaction. Tremendous amount of investigations have been conducted in thermoplastic based composites filled with nanofillers.^{19–28}

In the present communication, an attempt has been made to see the influence of coupling agents and compatibilizer on treated and untreated nanocomposites based on PP-CP/CaCO₃ and also to analyze the behavior of CaCO₃ nanoparticles and their effect on overall properties of the resultant nanocomposites so derived. Various macroscopic properties such as thermal, mechanical, and morphology at nanometer regime have been analyzed and correlated with the overall performance of nanocomposites. More over in recent years, in addition to traditional modifiers, such as rubber particles and micro, nanosize fillers have also been introduced to improve physical, thermal, and mechanical properties.^{29–34}

EXPERIMENTAL

Materials

The material used in this study was impact copolymer polypropylene (PP-ICP) grade MI3530 supplied by Reliance Polymer, compatibilizer (MA-g-EPR) OPTIM P-613 with MFI 4.0 g/10 min at 190°C temperature and 2.16 kg weight according to ASTM D 1238 supplied by Pluss Polymers Pvt. India, and coupling agents titanate grade EB-1019A supplied by industrial Products Mfg., India and Silane (3-Aminopropyl triethoxy silane, 98%), grade RM6592 supplied by Himedia (India). Surface modifiers stearic acid and oleic acid of 98% purity were procured from Loba Cheme Pvt., India and Qualigen Pvt., India, respectively. Nano-CaCO₃ (grade-CC 301) particle size 40 nm without surface modification was supplied by Yuncheng Chemical Industrial (Taiwan).

Nano-CaCO₃ particle surface treatment

Physical treatment of nano-CaCO₃ (nCaCO₃) by stearic acid and oleic acid has been performed by dry

method. High speed mixer having high shear rate was used to disperse the stearic acid and oleic acid consistently. The powdered form of nCaCO₃ was mixed with stearic acid in the mixer for 1 h at a speed of 3500 rpm. Heat generated due to friction then acid melted (above 80°C) and gave a uniform coating on CaCO₃. The same process was adopted for oleic acid coating on CaCO₃ nanoparticles.

Composite preparation

Prior to mixing the PP copolymer and surface treated and untreated nCaCO₃ were dried at 80°C for 12 h in vacuum oven. The nanocomposites were prepared with the help of Haake Rheocord 90 corotating twin screw extruder at 170–210°C at a screw speed of 100 rpm with using surface treated and untreated (2–10%) nCaCO₃ and MA-g-EPR (5%) followed by mixing 1% silane/titanate. The standard size specimens were prepared by Texair-40 semiautomatic injection molding machine at 170–210°C and the sheets were prepared by Nuchem semiautomatic compression molding machine.

Formulations

All batches comprised of 100% PP, 5% MA-g-EPR, 1% coupling agent and 2–10% nCaCO₃.

Maleic anhydride grafted EPR (MA-g-EPR), Titanate coupling agent (T), Silane coupling agent (S); Stearic acid surface treating agent (SA) and Oleic acid surface treating agent (OA) have been used in the preparation of nano-composites. The compositions with their nomenclatures are given in Table I.

Mechanical testing

The tensile and flexural testing of composites were determined by using INSTRON 3382 Universal testing machine at room temperature. The tensile tests (ASTM D 638) were performed at a crosshead speed of 50 mm/min. For Flexural tests (ASTM D 790), a three point loading system was used, and the support span length was adjusted to 100 mm, the crosshead speed was 5 mm/min. According to ASTM D256, the notched izod impact strength was performed. The result reported were the average of five individual measurements.

Differential scanning calorimetry

Diamond DSC manufactured by Perkin-Elmer (New Jersey, USA) was used to study the melting behavior of PP/nCaCO₃ nanocomposite at temperature range 0–220°C in nitrogen atmosphere at heating rate: 20°C/min and cooling rate: 15°C/min. The percentage crystallinity was calculated from the DSC traces as follows:

$$\% \text{ Crystallinity} = \frac{\Delta H_c (\text{observed})}{\Delta H_c (100\% \text{ crystalline})} \times 100$$

TABLE II
Mechanical Properties Test Results

Properties	nCaCO ₃ (in %)	MN-1	MN-2	MN-3	MN-4	MN-5	MN-6
Tensile strength (MPa)	2	21.20	20.98	24.12	20.84	20.64	23.98
	6	21.53	21.21	24.32	21.02	20.98	24.11
	8	22.48	21.63	24.56	21.53	21.25	24.33
	10	21.83	21.48	24.89	21.22	21.12	24.49
Tensile modulus (MPa)	2	330.00	317.00	490.38	310.00	300.00	457.32
	6	354.00	351.00	512.52	347.00	338.00	493.54
	8	389.00	364.00	599.35	358.00	345.00	515.43
	10	339.00	348.00	537.86	343.00	339.00	505.13
Flexural strength (MPa)	2	51.51	51.26	46.50	50.98	40.73	43.44
	6	52.63	52.55	47.91	51.47	50.89	44.79
	8	53.52	52.36	48.85	53.07	52.59	46.12
	10	53.15	53.06	50.15	52.37	51.92	48.66
Flexural modulus (MPa)	2	1096.00	1084.00	1039.22	1059.00	1006.00	995.54
	6	1163.00	1148.00	1097.21	1068.00	1027.00	1029.40
	8	1268.00	1217.00	1129.70	1145.00	1089.00	1114.86
	10	1232.00	1196.00	1195.33	1115.00	1063.00	1130.73
Impact strength (J/m)	2	192.00	186.00	152.89	180.00	184.00	130.35
	6	212.00	197.00	169.46	186.00	189.00	133.00
	8	236.00	218.00	178.23	195.00	193.00	137.32
	10	228.00	205.00	187.50	192.00	191.00	138.55

where ΔH_c (observed) is the enthalpy associated with melting of the material and ΔH_c (100% crystalline) is the enthalpy of 100% crystalline PP having value 146.5 J/g.³⁵

Melt flow index

Melt flow index studies were conducted as per ASTM D 1238 by Y. Rosand (UK) melt flow tester at 2.16 kg load and 230°C temperature.

Heat distortion temperature

Heat distortion temperature (HDT) was studied according to ASTM D 648 by Wallace (UK) HDT apparatus. Specimens used were rectangular bar in shape having dimensions 127.0 × 12.3 × 36.0 mm³ at 0.45 MPa load.

Thermo gravimetric analysis

Thermo gravimetric analysis was carried out in nitrogen atmosphere at a heating rate of 20°C/min. in the temperature range of 0–850°C.

Scanning electron microscopy

Microphase properties were analyzed from LEO-430 (UK) scanning electron microscope. Prior to SEM analysis specimens were gold coated for 2 min with the help of gold sputtering unit to avoid the charging effect and to enhance the emission of secondary electrons.

Dynamic mechanical analysis

Dynamic mechanical thermal properties were determined on a TA Instrument (Q-800) New Castle, DE,

USA, under nitrogen atmosphere. The temperature dependence frequency is taken 1 Hz in temperature range (–) 50–120°C at a heating rate of 3°C/min.

X-ray diffraction

XRD studies were performed using SIETRONICS XRD SCAN model with a diffraction angle 20–60° and intensity in the range of 0–400 cps.

The particle size distribution of nCaCO₃ was measured with Scherrer's formula.

$$\text{Particle size } d(A0) = K \times \lambda / \Delta 2\theta \cos\theta$$

where K = order of reflection,

λ (Wave length) = 1.542 and θ = diffraction angle.

RESULTS AND DISCUSSION

Mechanical properties

It is well established fact that fillers are added in plastic materials to enhance the mechanical properties. It is also a bare fact that the compatibility between filler and polymer improves when the filler surface is treated with organic materials.

Tensile strength of nanocomposite changes slightly with increase of nCaCO₃ percentage. Tensile strength of nCaCO₃ with titanate coupling agent shows higher value than that of surface treated nCaCO₃. It has also been observed that tensile modulus is a direct function of amount of nCaCO₃ upto 8% and beyond that it shows decline behavior in its value data given in Table II. This observation indicates greater affinity of nCaCO₃ particles towards

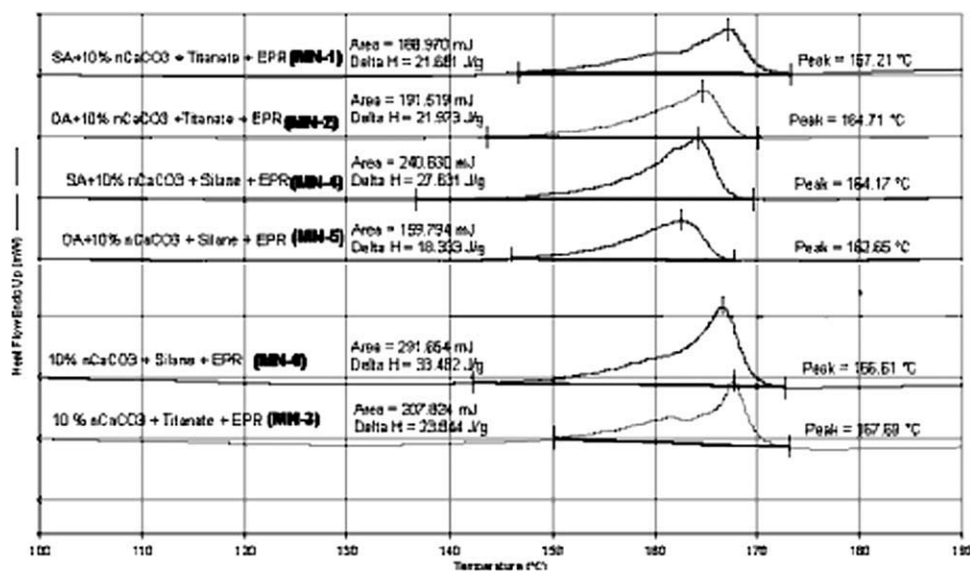


Figure 1 DSC graphs of different samples.

the matrix in every stage of loading. With titanate modulus of elasticity increases than silane coupled nanocomposites because of the fact that it is a good coupling agent than silane. It can be concluded that SA surface treated $n\text{CaCO}_3$ nanocomposite with titanate coupling agent shows best mechanical properties as depicted in Table I. This might be due to increase in surface energy and there by felicitating good wettability resulting in good interfacial adhesion between matrix and filler.

Differential scanning calorimetry

Effect of the surface treatment on thermal properties of nanocomposites have been analyzed by DSC. The change in melting behavior of PP/Ma-g-EPR/ $n\text{CaCO}_3$ nanocomposite with compatibilizer and different surface treating agent has been studied at a heating rate of $20^\circ\text{C}/\text{min}$. The results are shown in Table III and Figure 1.

Nanocomposite of PP/MA-g-EPR/ $n\text{CaCO}_3$ shows increased melting temperature. In the presence of compatibilizer (MA-g-EPR), the compatibilizer also acts as nucleating agent thus leading to an increase of the crystallization.³⁶ The change in crystallization behavior of nanocomposite with different surface modifiers in combination with different coupling agents are shown in Table II. The value of crystallinity is highest for untreated $n\text{CaCO}_3/\text{Ma-g-EPR/S}$ because of excellent arrangement of chains while among surface treated nanocomposites SA- $n\text{CaCO}_3/\text{Ma-g-EPR/S}$ show the highest crystallinity. The crystallinity decreases as well as the dispersion of filler increases. Thus the arrangement of chains is reduced.

Melt flow index

MFI of nanocomposites changes with varying percentage of $n\text{CaCO}_3$ and modifiers. MFI also depends on the nature of modifiers. The surface treated $n\text{CaCO}_3$ nanocomposites have higher MFI than untreated $n\text{CaCO}_3$ nanocomposite due to fatty acids which acts as flow promoters. SA treated $n\text{CaCO}_3$ has higher MFI as compared to OA treated. Because of better coupling between matrix and filler, titanate increases MFI value higher than silane. The results depicted in Table IV reveal that flow rate increases upto 8 wt % of surface treated $n\text{CaCO}_3$ but above this value the flow rate is reduced. It has also been observed that in the case of nanofilled composites the value of MFI increases upto 8 wt % and above it reduces because of $n\text{CaCO}_3$ does not disperse in adequate manner as the filler concentration increases.

Heat distortion temperature

HDT of PP increases with addition of $n\text{CaCO}_3$, whereas, slight declination in HDT value is observed in the case of surface treated $n\text{CaCO}_3$ as compared

TABLE III
Differential Scanning Calorimetric Results

Composition	T_m (°C)	ΔH (J/g)	REA (mJ)	Crystallinity (%)
MN-1	167.21	21.681	188.970	14.7993
MN-2	164.71	21.973	191.519	14.9986
MN-3	167.69	23.644	207.824	16.1392
MN-4	164.17	27.631	240.800	18.8607
MN-5	162.65	18.333	159.794	12.5139
MN-6	166.69	33.644	291.654	22.9651

TABLE IV
Melt Flow Index Results

Sample	MFI at 2.16 kg and 230°C (g/10min), % nCaCO ₃			
	2	6	8	10
MN-1	3.36	3.56	4.01	3.87
MN-2	3.04	3.17	3.28	3.25
MN-3	2.56	2.33	2.03	1.82
MN-4	3.12	3.18	3.27	3.23
MN-5	3.02	3.08	3.20	3.15
MN-6	2.10	1.95	1.80	1.32

TABLE V
Heat Distortion Temperature Results

Sample	HDT (°C) % nCaCO ₃			
	2	6	8	10
MN-1	112	114	116	118
MN-2	110	113	115	116
MN-3	114	118	120	121
MN-4	108	111	113	115
MN-5	107	109	112	113
MN-6	110	112	114	116

to untreated nCaCO₃ nanocomposites. With titanate coupling agent because of better bonding between filler and PP matrix, the HDT value is higher than silane treated nanocomposites. The change in HDT generates with surface modification by two different fatty acids. HDT data as given in Table V, shows increasing trend with increase of nCaCO₃ upto 10% in both surface treated and untreated composites.

Thermo gravimetric analysis

Figure 2 shows that the surface treated nCaCO₃ nanocomposites have higher thermal stabilities than untreated nCaCO₃. During thermal degradation, the TGA plots depict a double step degradation behavior. The first step shows the degradation of PP,

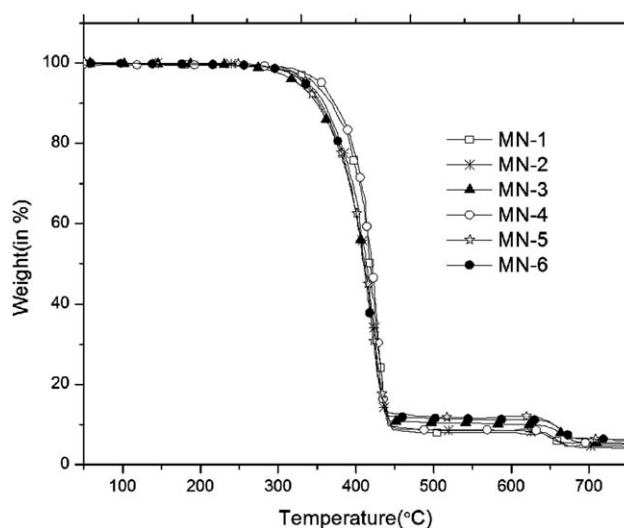


Figure 2 TGA graphs of samples.

while the second one shows the degradation of additives. TGA plots show no change in weight upto 300°C while above 300°C weight loss is observed. The improvement in the thermal stability PP/nCaCO₃ nanocomposites is because of formation of char residues (at 690°C), which hinders the out-diffusion of the volatile decomposition products. The stability after surface treatment increases appreciably due to better dispersion of filler and better coupling within PP matrix.

Scanning electron microscopy

SEM micrographs in Figure 3 indicate that agglomeration can be reduced significantly by surface treatment using different modifiers in presence of different coupling agents. The SEM micrographs show homogeneous dispersion of the nanofiller within the polymer matrix. It is also observed that MA-g-EPR domain size is decreased as the percentage of filler is increased. It is clearly evident from micrographs

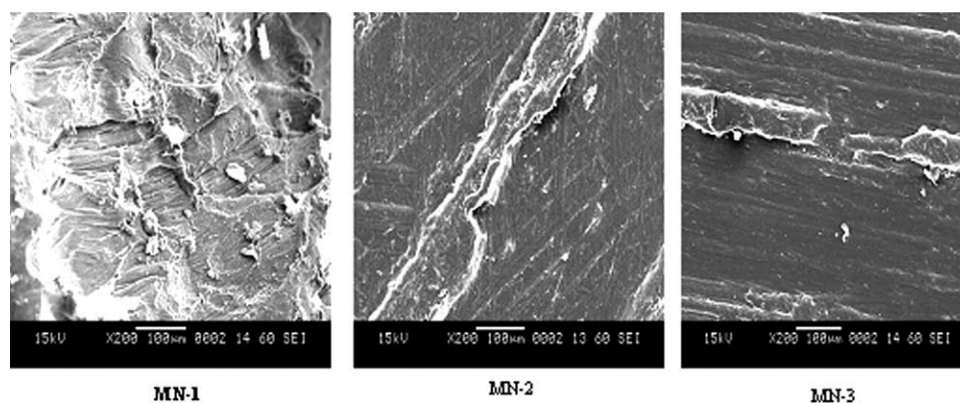


Figure 3 SEM Images at 200 magnifications.

TABLE VI
DMA Results

Sample	Tan Delta (J/g)
MN-1	32.59
MN-2	32.02
MN-3	35.58
MN-4	32.21
MN-4	32.21
MN-5	31.75
MN-6	34.47

that addition of surface modification enhances the surface morphology of nanocomposite. SA treated nCaCO₃ shows better dispersion than OA treated nCaCO₃ as is evident from the SEM micrographs depicted in Figure 3.

Dynamic mechanical analysis

A gradual decrease in storage modulus is observed with increasing temperature from 50 to 120°C. DMA studies show that the storage modulus drastically decreases about 20% in case of surface treated nCaCO₃ nanocomposite. The glass transition temperature (T_g) steadily increases from 163 to 167°C as a function of nCaCO₃ loading due to the reinforcing influence of nCaCO₃ particulates into the PP matrix. As expected, storage modulus (E') of PP/nCaCO₃ with titanate and silane coupling agent is higher than that of virgin PP-CP matrix during the entire range of testing temperature.

It has been noted that at low temperature stearic acid treated nCaCO₃ with titanate coupling agent shows higher storage modulus. In the presence of nCaCO₃, displacement of the relaxation peaks towards lower temperature shows that the presence of the nCaCO₃ filler increases the mobility of polymer chains. The loss factor represents mechanical damping or internal friction in a viscoelastic system. The increase in storage modulus shows that the reinforcement increases and compatibilizer *m*-g-EPR facilitates to increase the surface area and reinforcement. It is observed that stearic acid treated nCaCO₃ nanocomposites show higher values than oleic acid treated nCaCO₃. The DMA results are depicted in Table VI and Figure 4(a–c).

XRD of untreated/treated nCaCO₃

The XRD pattern of untreated and treated (stearic acid and oleic acid) nCaCO₃ is shown in Figure 5(a–c). XRD pattern of stearic acid and oleic acid treated nCaCO₃ shows an increase in interlayer spacing (d_{001}) from 14.29 to 22.39 Å which is an indicative of the fact that after surface treatment the nCaCO₃

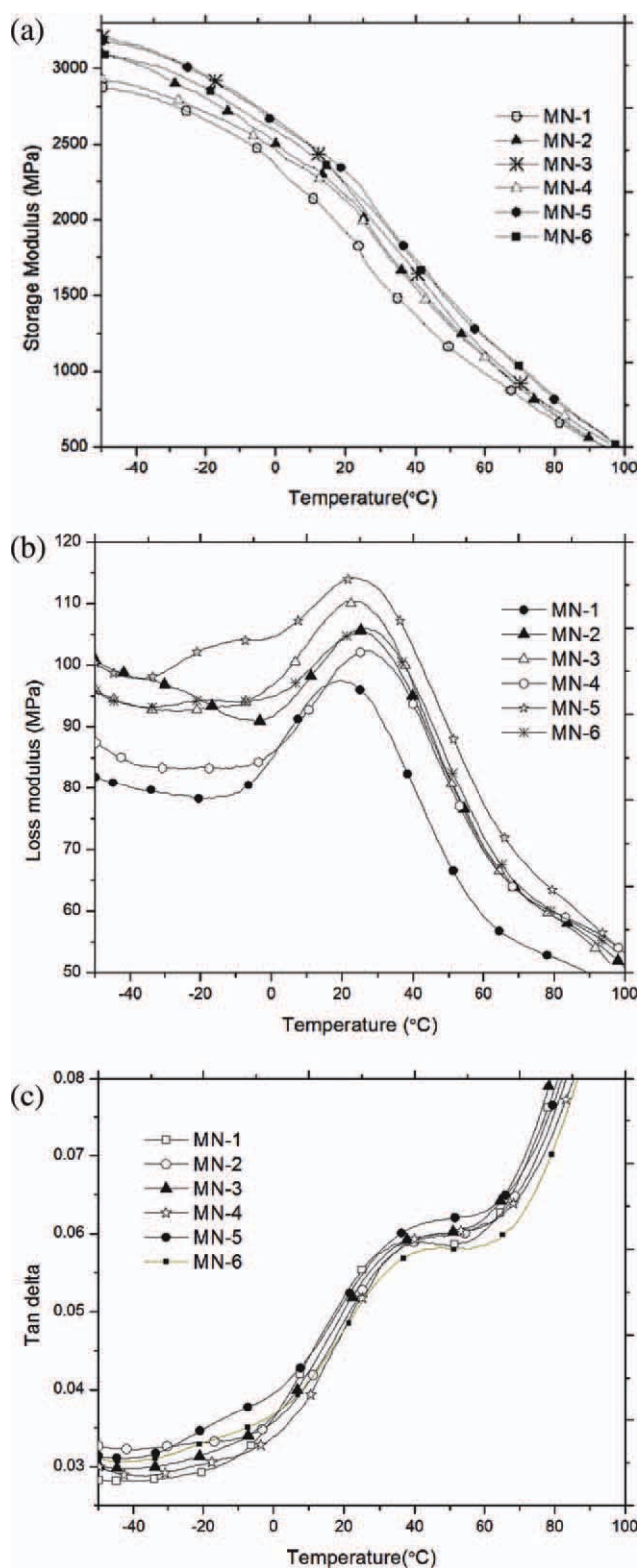


Figure 4 (a) DMA storage modulus graph, (b) DMA Loss modulus graph, and (c) DMA Ten delta graph. [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.wiley.com].

become hydrophobic in nature due to increase in interlayer spacing between the galleries nCaCO₃. This facilitates the PP matrix to enter into the

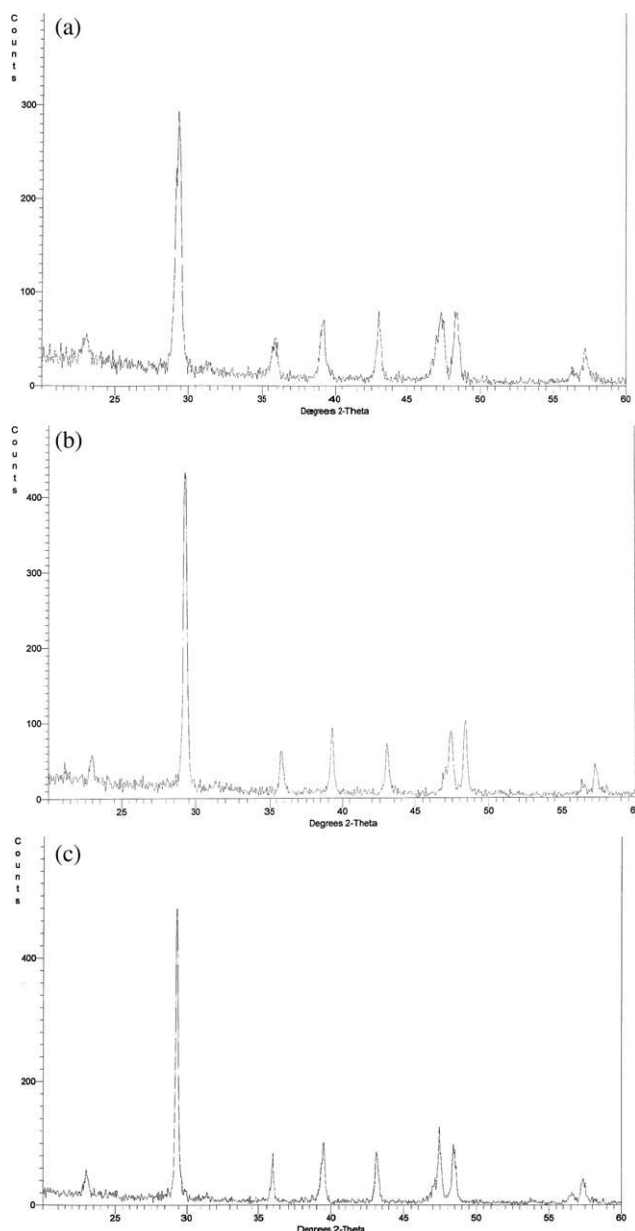


Figure 5 (a) XRD Pattern of nCaCO₃, (b) XRD Pattern of SA-nCaCO₃, and (c) XRD Pattern of OA-nCaCO₃.

interlayer spacing and creating an intercalation or exfoliation structure of nanocomposites.

CONCLUSIONS

The Stearic acid and oleic acid surface treated nCaCO₃ nanoparticles were prepared via chemical surface modification method with two different coupling agents. Uses of surface treated nCaCO₃ and MA-g-EPR increase the mechanical properties of nanocomposites.

The coupling agents show the significant effect on nanocomposites properties; titanate gave the best properties compared to silane.

It has been exposed that the phase morphology of nanocomposites increases with surface modification. The dispersion of nCaCO₃ in the PP matrix depends on the nature of coating (stearic acid or oleic acid). Stearic acid treated nCaCO₃ effectively improves the mechanical properties. Tensile properties show significant changes in untreated nanocomposites, while notched impact strength increases significantly with surface treated nCaCO₃ at 8% the value increase upto 21%. TGA results show that the thermal stability increases with surface treated nCaCO₃. SEM reveals that adequate homogeneous dispersion is seen in surface treated nCaCO₃. The overall results reveal that stearic acid treated gives fairly good properties than those of the oleic acid treated nanocomposites.

References

1. Young, K.; Young, Q.; Li, G.; Sun, Y. *Polym Compos* 2006, 27, 443.
2. Zhaoxy, H. *Polymer* 2004, 45, 3819.
3. Kawasumi, M.; Hasegawa, N.; Kato, M.; Okada, A. *Macromolecules* 1997, 30, 6333.
4. Le Baron, P. C.; Wang, Z.; Pinnavaia, T. J. *Appl Clay Sci* 1999, 15, 11.
5. Lee, H. S.; Fishman, D.; Kim, B.; Weiss, R. A. *Polymer* 2004, 45, 7807.
6. Messersmith, P.; Giannelis, E. *J Polym Sci Part A: Polym Chem* 1995, 33, 1047.
7. Usuki, A.; Kojimay, Y.; Kawasumi, M.; Okada, A. *J Mater Res* 1993, 8, 1179.
8. Kojima, Y.; Usuki, A.; Kawasumi, M.; Fukushima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1185.
9. Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 2493.
10. Vaia, R. A.; Jandit, K. D.; Kramer, E. J.; Giannelis, E. P. *Macromolecules* 1995, 28, 8080.
11. Bascil, A. M.; Ruggeri, G.; Ciardelli, F. *Polymer* 1994, 35, 3295.
12. Lee, J. Y.; Lee, H. K. *Mater Chem Phys* 2004, 85, 410.
13. Kazak, M.; Domka, L. J. *Phys Chem Solid* 2004, 65, 441.
14. Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
15. Gorrasi, G.; Tartoram, M.; Vittoria, V.; Kaempfer, D. *Polymer* 2003, 44, 3679.
16. Gilman, J. W. *Appl Clay Sci* 1999, 15, 31.
17. Jurga, J.; Nowicki, M.; Bula, K.; Susla, B.; Rejeibi, S. S. E. *Mol Cryst Liq Cryst* 2000, 354, 43.
18. Reynaud, E.; Gauthier, C.; Perex, J. *Rev Metallurgic* 1999, 96, 169.
19. Rong, M. Z.; Zhang, M. Q.; Zheng, Y. X.; Zheng, H. M.; Watter, R. *Polymer* 2001, 42, 167.
20. Wu, C. L.; Zhang, M. Q.; Rang, M. Z.; Friedrich, K. *Compos Sci Technol* 2002, 62, 1327.
21. Rong, M. Z.; Zhang, M. Q.; Zheng, Y. X.; Zheng, H. B.; Friedrich, K. *Polym Eng Sci* 2003, 43, 490.
22. Wong, G.; Chen, X. Y.; Huang, R.; Zhang, L. *J Mater Sci Lett* 2002, 21, 985.
23. Zang, M. Q.; Rong, M. Z.; Pan, S. L.; Friedrich, K. *Adv Compos Lett* 2002, 11, 293.
24. Rong, M. Z.; Zhang, M. Q.; Zheng, Y. X.; Zeng, H. M.; Watter, R.; Friedrich, K. *J Mater Sci Lett* 2000, 19, 1159.
25. Chung, S. C.; Hahm, W. G.; Im, S. S.; Oh, S. G. *Macromol Res* 2002, 10, 221.

26. Zhang, J.; Wang, X.; Lu, L.; Li, D.; Yang, X. *J Appl Polym Sci* 2003, 87, 381.
27. Xiong, M. N.; Wu, L. M.; Zhou, S. X.; You, B. *Polym Int* 2002, 51, 693.
28. Jana, S. C.; Jain, S. *Polymer* 2001, 42, 6897.
29. Yang, K.; Yang, Q.; Li, G. *Mater Lett* 2006, 60, 805.
30. Hanim, H.; Zarina, R.; Ahamad, M. Y. *Malaysian Polym J*, 2008, 3, 38.
31. Liang, J. Z. *Compos A* 2007, 38, 1502.
32. Ma, C. G.; Mai, Y. L.; Ruan, W. H. *Compos Sci Technol* 2007, 67, 2997.
33. Khosh, L. R.; Bagheri, R.; Zokaei, S. *J Appl Polym Sci* 2008, 110, 4040.
34. Esfandiari, A.; Nazokdast, H. *J Appl Sci* 2008, 8, 545.
35. Lonkar, S. P.; Morlat-Therias, S.; Caperaa, N.; Leroux, F.; Gardette, J. L.; Singh, R. P. *J Polym* 2009, 50, 1505.
36. Modesti, M.; Lorenzetti, A.; Bon, D.; Besco, S. *Polym Degrad Stab* 2006, 91, 672.