Enhancement of Mechanical Properties in PP Nano composites

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Abstract
Nano-clay Compounding using deep-flighted Twin-screw extruders is a promising approach to prepare PP Nanocomposites. PP compounds for molding applications need improved Flexural Modulus without decrease in Impact Strength and increase in specific gravity. Improvement in mechanical properties of PP Nanocomposites, not only depends upon Resin and Compatibilizer, but also greatly depends upon the characteristics of the mixing elements in the extruder. Studies were conducted using X-RD analysis (for dispersion) and testing of Mechanical Properties. Results discuss the selection of extruder configuration and useful data for Nano-clay compounding.

Introduction

Polymer Clay/Nanocomposites have shown significant enhancement in mechanical, thermal and barrier properties of polymers at very low addition level of organically modified clays called Nanoclays. A large number of Polymer/Clay Nanocomposites have been studied including Nylon (1, 2), Polystyrene (3), Poly (Ethylene-co- Vinyl Acetate) (EVA) (4,5), Poly (Methyl methaacrylate) (6), Unsaturated Polyesters (7), Epoxy (8), Polyethylene terephthalate (PET) (9, 10) and Polypropylene(11,16).

Polypropylene Nanocomposites is of current research interest due to its high potential in both molding as well as packaging applications. However, low polarity of Polypropylene limits the dispersion of Nanoclay platelets into polymer resin resulting into less prominent property improvements (11). In recent years progress has been made in the production of Polypropylene Nanocomposites by addition of compatibilizers such as MagPP and melt mixing it into high shear compounding equipments (11-12). It has been found from earlier works that properties of PP Nanocomposites greatly depend upon compatibilizers and processing conditions (15-16). Recently a successful route of preparing PP Nanocomposites has been reported by twostep compounding involving preparation of masterbatch followed by compounding it with neat resin (13-14). Although two step compounding delivers uniform dispersion and better improvement into properties compared to one step process, it increases the cost of Nanocomposites and delivers lesser productivity. One possible way of producing successful Nanocomposites via one step process is by increasing the mixing profile of the compounding extruder. This work is focused on studying the improvement in the mechanical properties of PP Nanocomposites with respect to different screw configuration and operating conditions of the extruder, viz. feed rate and speed of extruder. Twin-screw extruder used in the work is deep flighted twin-screw extruder, which allows for greater flexibility in Mixing. X-RD studies were also conducted to study the dispersion of Nanoclay. Relationship between X-RD values and mechanical property of Nanocomposites are presented.

Experimental Details

Materials

Polymer resin used in the work is REPOL H-110MA (Density =0.90g/cm3, MFI =11 g/10 min. at 2300C, 2.16 Kg load). Nanoclay used in the work is Crysnano 1010P, an organically modified montmorillonite clay having purity level 98.6%, ash content 38% and basal spacing of 24 A0. Compatiilizer used in the work was DuPont MagPP. Grafting level for the MagPP was 0.90.

Equipment & Formulations

A Deep-Flighted Twin-Screw Extruder (STEER Omega 30) was used for compounding the Nanoclay with Polymer resin. The extruder used has a diameter of 30mm, Do/Di of 1.71 and

L/D ratio of 40. Two different screw configurations as shown in Figure 6 and Figure 7 were used. First screw configuration (HS) had more number of neutral mixing elements hence it was expected to deliver more shear than the second (MS) screw configuration. On the HS configuration seven trials named HS 1, HS 2, HS 3, HS 4, HS 5, HS 6 and HS 7 were taken at three different screw rpm (400, 800 and 1200) and three different feed rates (7 Kg/h, 17 Kg/h and 35 Kg/h). On the MS configuration, four trials named MS 1, MS 2, MS 3 and MS 4 were taken at two different screw rpm(400 and 800) and three different fed rates (7 Kg/h, 17 Kg/h and 35 Kg/h). Details of all eleven trials are tabulated in Table 2. All the eleven formulations had final content of 6% Nanoclay, 6% MagPP and 88% PP resin. The temperature profile in extruder for all the formulations was set from 160 oC at first barrel to 190oC at the last barrel. The strands were pelletised and then dried for four hours at 90oC for moisture removal. The dried pellets were injection molded into ASTM specimens for mechanical testing. The temperature profile for the molding machine was 190oC to 215oC and mold temperature was set at 40oC.

Characterization

Wide angle X-ray diffractometer (X-RD) manufactured by Shimadzu, Japan was used to study the dispersion of Nanoclay platelets into polymer resin. The diffractogram were scanned in 2q ranges from 2 to 100 at scanning rate of 10/min. Nanoclay powder was also scanned under same conditions for comparing the peak shift in Nanocomposites with Nanoclay. Flexural modulus of the specimens was measured by universal testing machine of Instron (Model No. 3365) and Izod impact strength was measured using impact tester of Ceast, Italy.

Result and Discussion

X-RD studies were conducted to evaluate dispersion of Nanoclay platelets into polymer resin and to further study the correlation of dispersion with mechanical property improvement. Based on X-RD data the clay interlayer distance (A0) of all the samples were determined and is reported in Table 3. A 24 A0 basal d-spacing was observed for Nanoclay powder. Basal d spacing for all the Nanocomposite samples was found to be in the range of 28-32 A0. Increase in basal spacing indicates the partial exfoliation of clay platelets into polymer resin. It can also be noted from Table 3 that all the Nanocomposites showed different values of basal spacing.

In order to study the correlation of increase in basal spacing with degree of improvement into mechanical properties, a graph was drawn between basal spacing and flexural modulus of all the samples as shown in Figure 1. It is observed from Figure 1 that increase in basal spacing is not directly co-related to increase in flexural modulus. Hence, X-RD analysis of PP/Nanocomposite gave qualitative inferences about exfoliation of clay platelets into polymer resin while it is not possible to relate the same with degree of improvement into properties.

In order to relate the mechanical properties of Nanocomposites with operating parameters of extruder, trials were conducted at different feed rate, screw speed and screw configuration. Polypropylene being non-polar in nature, it was expected that higher shear energy would lead to greater improvement into properties. In order to study the effect of shear energy on mechanical property improvement, the energy input was calculated for all the samples. Specific energy (SpE) defined as the Drive Mechanical Energy consumed by extruder per Kg of product produced is used as the basis. Table 3 reports details of specific energy, flexural modulus and impact strength values for all the samples. Further in order to study the correlation of SpE with Flexural modulus at different screw speeds and screw configuration graph between specific energy and flexural modulus has been drawn as shown in Figure 2, 3, 4 and 5. Figure 2 shows graph between SpE and flexural modulus at different screw speed, feed rate and screw configuration. It is seen from Figure 3, 4 and 5 that flexural modulus strongly depends upon SpE in all the cases. In all the cases, flexural modulus increases sharply with increase in SpE. It is seen that degree of improvement into flexural modulus is more prominent in lower SpE ranges but at higher SpE values graphs starts flattening towards X-axis. It is not yet obvious at what stage a state of complete dispersion is achieved. It is clear that a point of saturation will be soon reached since there is a trend that further increase into SpE did not result into similar degree of improvement in flexural modulus.

Figure 2 shows graph between SpE and flexural modulus at different screw speeds, feed rates and screw configurations. It is interesting to note the localized negative trend at certain places due to changes in Screw speed, Feed rate and configuration. On matching the respective values from Table 3, it can be seen that the configuration with a higher shear was providing better results at a higher speed and feed-rate compared to medium shear at lower feed rates and speed. It is therefore indicated that improvement into flexural modulus was also a function of screw speed. Further work is required to extend the relationship specifically to individual parameter.

Impact strength of these Nanocomposites are reported in Table 3. Impact strength does not vary greatly with changes in operating parameters of extruder and in most cases impact values are close to the impact strength of neat resin. However, studying the flexural modulus and impact strength data together for all the samples it was found that impact strength showed negative trend with flexural modulus improvement. The mechanisms contributing to this trade-off also needs further investigation.

Conclusion

The result obtained here shows a quantum jump in flexural modulus without loss of impact strength. The improvement into flexural modulus greatly depends upon operating parameter of extruder that controls the Specific Energy. X-RD analysis gives qualitative analysis about degree of dispersion but fails to co-relate the improvement into Nanocomposite properties with increase into basal spacing. High-speed and High-flight depths are providing considerable advantage in greatly enhance the mechanical properties. Future work has to be conducted to determine the nature of the process causing this improvement.

References

1. G.M. Kim, D.H. Lee, B. Hoffmann, J. Kressler, and Stoppelmann, *Polymer*, **42**, 1095 (2001).
2. J.W. Cho and D.R. Paul, *Polymer*, **42**,1083(2001).
3. X. Xu. And S. Qutibuddin, *Polymer*, **42**, 807(2001).
4. M. Zanetti, G. Camino, R. Thomann, and R. Mulhaupt, *Polymer*, **42**, 4501(2001).
5. M. Alexandre, G. Beyer, C. Henrist, R. Cloots, A.Rulmont, R. Jerome, and P.Dubios, *Macromol.Rapid.Comm*., **22**, 643(2001).
6. X. Huang and W. J. Brittain, *Macromolecules*, **34**, 3255(2001).
7. D. J. Suh, Y.T. Lim, and O.O. Park, *Polymer*, **41**, 8557(2000).
8. T. Lan, P. D. Kaviratna, and T. J. Pinnavaia, *J. Phys. Chem. Solids*, **57**, 6(1996).
9. Jin-Hae Chang , Sung Jong Kim, Yong Lak Joo, Seungsoon Im, *Polymer*, **45**, 919(2004).
10. Guozhen Zhang, Tetsuya Shichi, Katsuhiko Takagi, *Material letters*, **57**, 1858,(2003).
11. Kawasumi, M., Hasegawa, N., Kato, M., Usuki, A., and Okada, A., *Macromolecules*, **30**, 6333(1997)
12. N. Hasegawa, M. Kawasumi, M. Kato, A. Usuki, and A. Okada, *J. Appl. Polym. Sci*., **67**, 87 (1998).
13. T. Lan and G. Qian, *Proceeding of additive' 00 Clearwater Beach, FL*.(2000).
14. G. Qian, J. W. Cho and T. Lan, *Polyolefins 2001*, Houstan, TX, February 25-28(2001).
15. Linjie Zhu, M. Xanthos , *J. Appl. Polym. Sci*., **93**, 1891(2004).
16. M.-T. Ton-That *, F. Perrin-Sarazin, K. C. Cole, M. N. Bureau, J. Denault, *Polm. Engg. and Sci*.,**44**, 1212(2004).

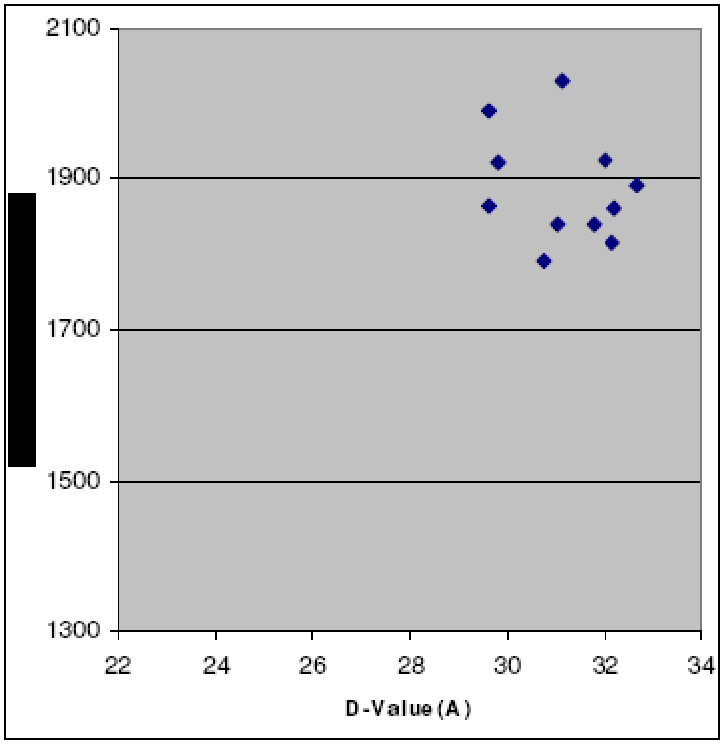

Figure 1. Influence of Basal spacing on flexural modulus

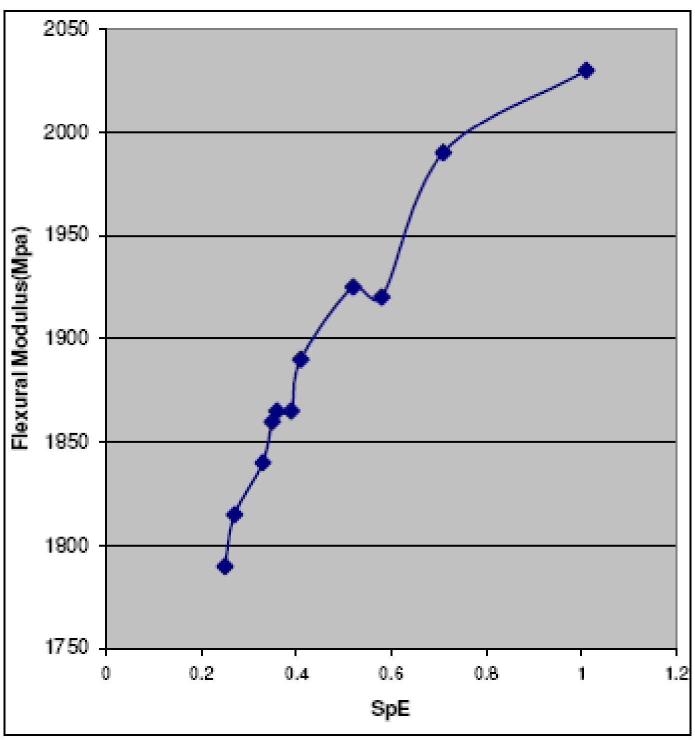

Figure 2. Flexural modulus, SpE curve at various screw speeds, feed rates and screw configuration.

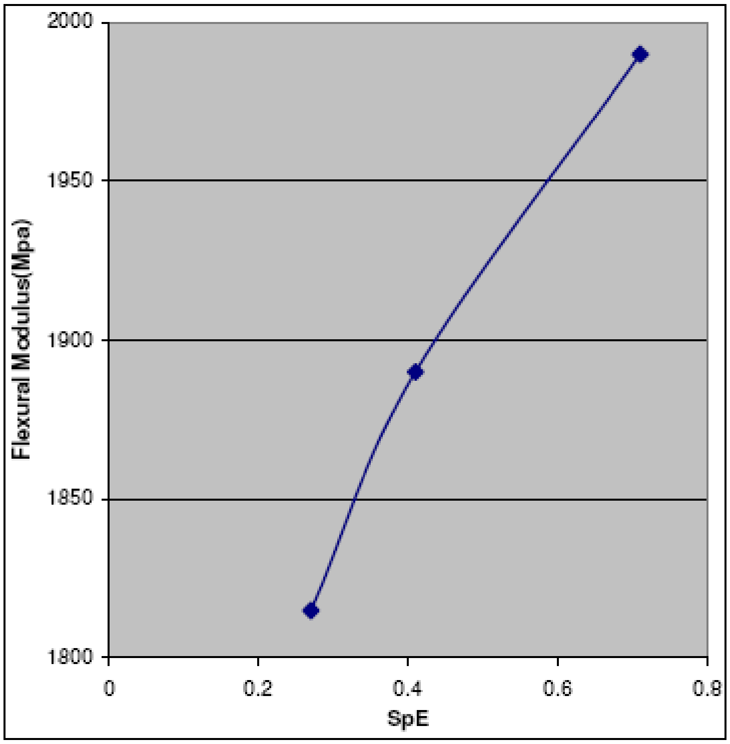

Figure 3. Flexural modulus, SpE curve at 800 rpm and high shear screw configuration

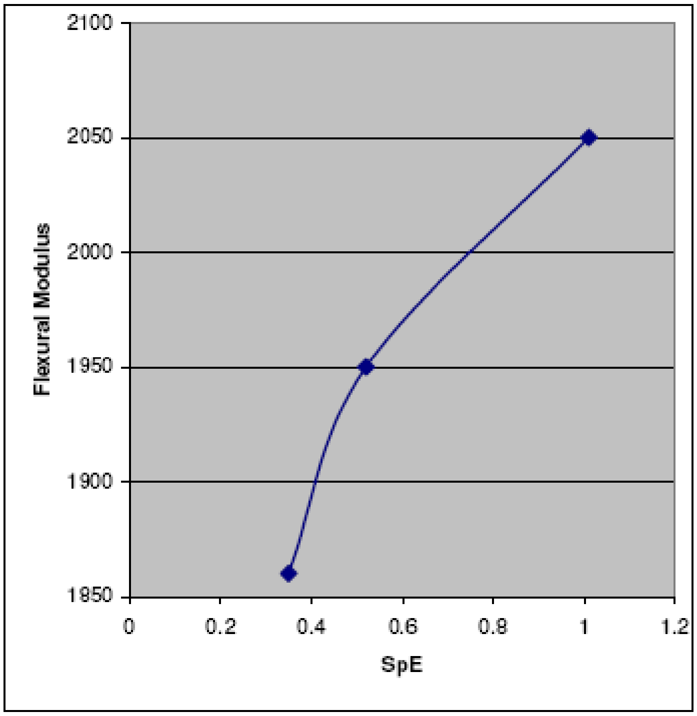

Figure 4. Flexural modulus, SpE curve at 1200 rpm and high shear screw configuration

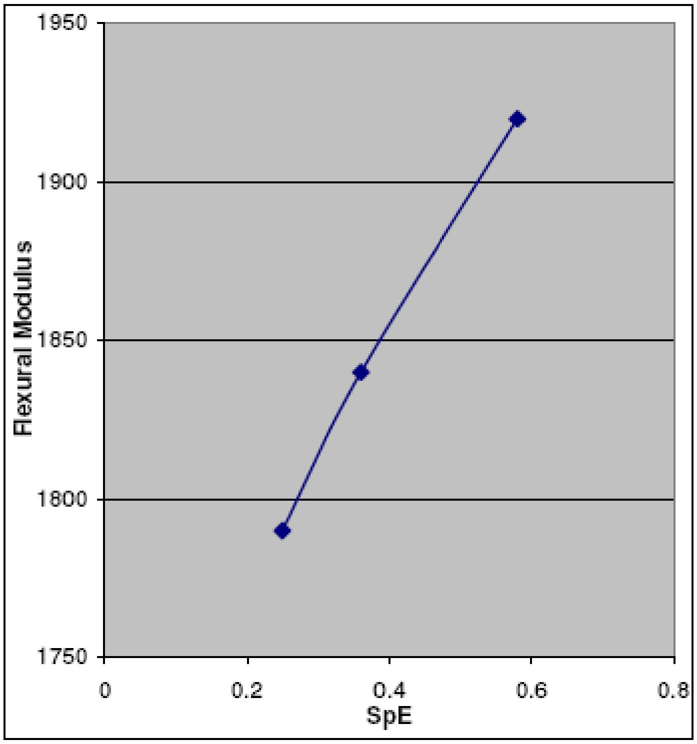

Figure 5. Flexural modulus, SpE curve at 800 rpm and medium shear screw configuration

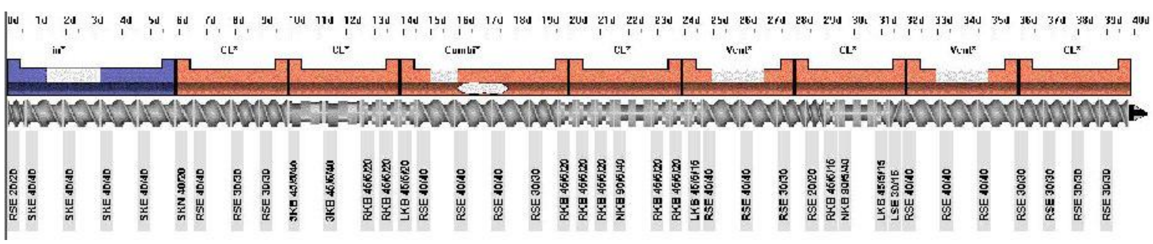

Figure 6. High shear screw configuration

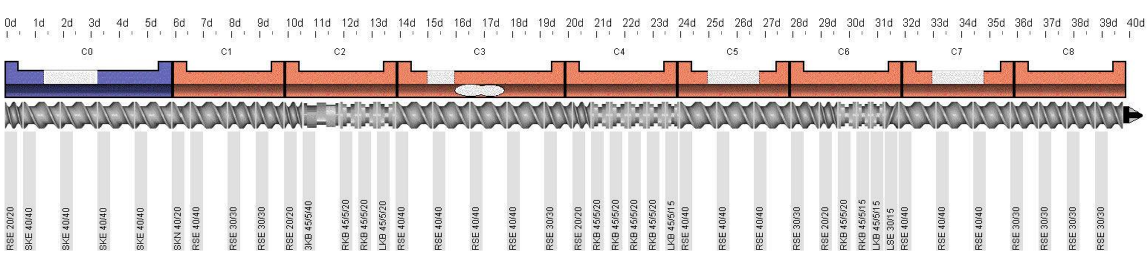

Figure 7. Medium shear screw configuration

Table 1. Detailed Compounding formulation

Resin	MFI	Resin (wt.%)	Nanoclay (wt.%)	MagPP (wt.%)
HomoPolypropylene	11	88	6	6

Table 2. Trial Details

Trial No.	Extruder Profile	Screw Speed RPM	Feed Rate Kg/h	Power kW
HS 1	High Shear	400	7.0	2.74
HS 2	High Shear	800	7.0	5.0
HS 3	High Shear	800	17.5	7.24
HS 4	High Shear	800	35.0	9.3
HS 5	High Shear	1200	7.0	7.05
HS 6	High Shear	1200	17.5	9.11
HS 7	High Shear	1200	35.0	12.42
MS 1	Medium Shear	400	7.0	2.29
MS 2	Medium Shear	800	7.0	4.05
MS 3	Medium Shear	800	17.5	6.30
MS 4	Medium Shear	800	35.0	8.8

Table 3. Results

Trial No.	RPM	Feed Rate Kg/h	Specific Energy(SpE)	Flexural Modulus (MPa)	Impact Strength (J/m)	X-RD (A^0)
Neat				1300	32.10	
HS 1	400	7.0	0.39	1865	32.35	29.6
HS 2	800	7.0	0.71	1990	30.50	29.64
HS 3	800	17.5	0.41	1890	31.24	32.66
HS 4	800	35.0	0.27	1815	32.05	32.16
HS 5	1200	7.0	1.01	2030	28.01	31.12
HS 6	1200	17.5	0.52	1925	30.10	32.02
HS 7	1200	35.0	0.35	1860	33.10	32.20
MS 1	400	7.0	0.33	1840	32.67	31.77
MS 2	800	7.0	0.58	1920	30.23	29.82
MS 3	800	17.5	0.36	1840	32.50	31.02
MS 4	800	35.0	0.25	1790	33.34	30.73