Proc Indian natn Sci Acad **79** No. 1 March 2013 pp. 11-20

Research Paper

Preparation of Nanoclay/Polypropylene Nanocomposite and Study of its Rheological and Mechanical Properties

VINEETA NIGAM[1], TRIPTI DIXIT[2], G LAL[1], VIJAY KUMAR[2] and A K SAXENA[1*]
[1]*Defence Materials & Stores Research & Development Establishment, DMSRDE Post Office, G.T. Road, Kanpur 208 013, India*
[2]*Central Institute of Plastic Engineering & Technology, Lucknow 110 042, India*

(Received 20 July 2012; Revised 29 May 2012; Accepted 11 June 2012)

Polypropylene (PP)/Clay nanocomposites (PPNCs) were prepared using a single screw extruder. The dynamic rheological properties were measured using a capillary rheometer. Effect of shear rate (100-8000 sec^{-1}) on shear viscosity of PPNC's at varied nanoclay content was measured. At 6000 sec^{-1} shear rate the shear viscosity of PP+Na^+ MMT is higher than that of PP+ Cl 20A but above that the amount of clay loading shows a negligible role in effecting the shear viscosity. Die swell, which is an important parameter during extrusion for governing the process control was also studied. Effect of shear rate and nanoclay content on die swell behaviour of PPNC's with different percentage of nanoclay loading was measured at 200°C. At lower shear rates up to 5000 sec^{-1}, PP with nanoclay showed higher die swell in comparison to pure PP, whereas at shear rates beyond that, the same blend showed lower die swell compared to pure PP. It may be inferred that the shear rate controls the die swell behaviour of PP nanoclay nanocomposites. A marginal yet distinct change in shear viscosity and shear stress with addition of nanoclay at different shear rates (100 to 8000 sec^{-1}) was also observed. However, the power law index (n) indicates that the polymer melt shows less shear thinning with increasing nanoclay loading. Shear viscosity decreased with increasing shear rate for all PPNCs showing their pseudo-plastic non-Iewtonian behaviour.

Key Words: Polypropylene; Nanoclay; Nanocomposites; Single Screw Extruder; Rheology

Introduction

The easy processability and high performance mechanical properties make polypropylene (PP) an important commodity polymer and its demand is continuously increasing at a rate of 3.7 % per year. PP is also competing in international markets with other engineering grade plastics owing to its blendability with a host of polymers and reinforcements at a relatively low cost. Its properties could be tailored as per requirement with other polymers and several additives. Therefore, PP is often filled with organic or inorganic fillers such as wood and flour [1], talc [2], mica [3], calcium carbonate [4, 5] etc. to enhance the mechanical properties and reduce cost. Over last few years, PP is extensively blended with nanoclay to prepare PP-Clay nanocomposites (PPNCs) which offer a wide array of properties to suit large number of applications [6-10] with large commercial opportunities in both automobiles and packaging industries.

Though a large number of polymers with varying degree of polarity and chain rigidity have been used as base polymers for polymer nanocomposites, which include polystyrene [11], polyamide [12], polyimide [13], epoxies [14] and polypropylene [15-17], these nanocomposites present remarkable prospects for newer applications of conventional polymeric materials. Now a days, polypropylene nanocomposites have become an area of interest of the researchers because of dramatic

*Author for Correspondence: E-mail: arvsaxena@gmail.com

improvements in their thermal, gas barrier and mechanical properties [18-21] at very low filler loadings (1 to 5% by weight) compared to conventional particulate micro-composites.

The properties of these nanocomposites are dependent on several processing variables and aids like dispersion, distribution, surface modification of additives, nature of compatibilizers, functionalization of polymer and processing methods etc. Therefore, out of several methods for mixing of nanoclay in PP, melt mixing is one of the most preferred method as it provides high yield with sufficient process control and marginal batch to batch variations.

Keeping in view, of our continued interest in the area of nanocomposites, [22-31] in the present investigation, we wish to report our studies on the effect of shear rate on shear viscosity and effect of nanoclay content (1 to 4%) on die swell/power law index of PP clay nanocomposites (PPNC's) of Cloisite 20A and Na^+ nanoclay and compare the results with that of pure PP.

Experimental

Materials

Polypropylene (Repol 110MA) manufactured by Reliance India Ltd. (MFI = 11g/10min) was taken as the base polymer. Unmodified nanoclay (Na^+ MMT) and Cloisite 20A from Southern Clay Product Inc. U.S.A. were used as the nanofiller. OPTIM P-425 manufactured by Pluss Polymer, India is used as compatibilizer. B225 manufactured by Nurchem, China was used as an antioxidant.

Mixing and Compounding

Nine batches of (1 kg each) PPHP/Nanoclay were compounded on Brabender, Germany Single Screw Extruder (Screw Dia = 19 mm; L/D = 25mm) at a temperature profile of 80 rpm with formulations appended in Table 1. The PP clay nanocomposites were obtained as strands of 2mm diameter, which were palletized online in a strand cutter to form pellets. These pellets were dried for 3 hours at 80°C before carrying out any further experiments. After formulations, the compositions are further processed to obtain the desired samples.

Table 1: Composition of Polypropylene Nanocomposites (1 Kg Batch)

S.No.	Nomen-clature	PP % (gm)	PP-g-MA % (gm)	Clay % (gm)	Antioxidant % (gm)
1.	PPHP	100 (1000)	0 (0)	0 (0)	0 (0)
2.	1% 20A	97.5 (975)	1 (10)	1(10)	0.5 (5)
3.	2% 20A	95.5 (955)	2 (20)	2 (20)	0.5 (5)
4.	3% 20A	93.5 (935)	3 (30)	3 (30)	0.5 (5)
5.	4% 20A	91.5 (915)	4 (40)	4 (40)	0.5 (5)
6.	1% Na	97.5 (975)	1 (10)	1 (10)	0.5 (5)
7.	2% Na	95.5 (955)	2 (20)	2 (20)	0.5 (5)
8.	3% Na	93.5 (935)	3 (30)	3 (30)	0.5 (5)
9.	4% Na	91.5 (915)	4 (40)	8 (40)	0.5 (5)

Rheological Experiments

Advanced Twin Bore Capillary Rheometer (RH7) supplied by Malvern Instrument Ltd. U.K. fitted with a single axis laser instrument was used for recording the die swell in the shear rate range from 100 sec^{-1} to 8000 sec^{-1} at 200°C. 1 mm x 16 mm x 180 mm die was used to measure the die swell of pure PP and PP clay nanocomposites.

Die-swell is an important parameter for characterization of elastic properties during extrusion of polymeric melts, and the degree of swell is usually expressed by die-swell ratio (Ds).

$$\text{Die Swell (Ds)} = De/D \quad (1)$$

where, De is the diameter of extruder and D is the diameter of capillary.

The power law denoted by 'n' in eq. 2 is a measure of deviation from Newtonian fluid behaviour where λ is the shear stress, τ is the shear rate and K is a constant. When $n < 1$, shear thinning (psuedoplastic behaviour) occurs and if $n > 1$, shear thickening (dilatant behaviour) occurs. If $n = 1$ then the fluid behaves like an ideal Newtonian fluid. The larger the deviation of n from 1, more is the shear thinning or shear thickening behaviour of the fluid.

$$\eta = (\tau / r')^n. \quad (2)$$

Rate of extrusion of a resin in molten condition under specified temperature and pressure through a specified size of die in 10 min is defined as Melt Flow Index (MFI). Ceast 7027 Melt Flow Index tester was utilized to measure the MFI.

Tensile strength was performed as per ASTM-D 638 on INSTRON 3382 model tensile machine.

Results and Discussion

Shear Viscosity with Shear Rate

A rheological evaluation was performed to compare the effect of shear rate on shear viscosity at 200°C (Fig. 1) for PPHP, PP+ Cl 20A and PP+ Na^+ MMT nanocomposites at varied clay concentration. In the present study, shear viscosity decreases with increasing shear rates for all PPNCs showing psuedoplastic non-Newtonian behaviour at 200°C. At lower shear rates, i.e., below 6000/sec, the shear viscosity of PP+ Na^+ MMT is higher than that of PP+ Cl 20A whereas the amount of clay loading beyond that shows a negligible role in effecting the shear viscosity. Therefore, shear viscosity of PPHP and PPNC's are similar at high shear rates.

Shear Stress with Shear Rate

Polypropylene nanocomposites (PPNCs) were studied for the evaluation of effect of varied shear rate on shear stress and were compared with PPHP (Fig. 2). In all the cases, shear stress increases with increasing shear rate. Pure PP have higher stress value than nan oclay filled PP. This is because the pp matrix gets separated by nano clay particles and also covers the surface of each particle. Due to encapsulation of nano clay particles, stress of PP molecules becomes weak and hence, the shear rate does not change in proportion to the shear stress. Also the packing fraction plays a role in flow behaviour which defines the volume occupied by solid particles over the total volume. In a shear thinning fluid a simple plot of shear stress *vs* shear rate results in a curve that bends as it approaches the origin. Thus, it may be inferred that the viscosity is not constant. The input shear energy tends to align anisotropic molecules or particles and disaggregate any large clumps of particles, thereby reducing the overall hydrodynamic clumps, which in turn reduces the dissipation of energy in the fluid and the viscosity.

Power Law Property of Material

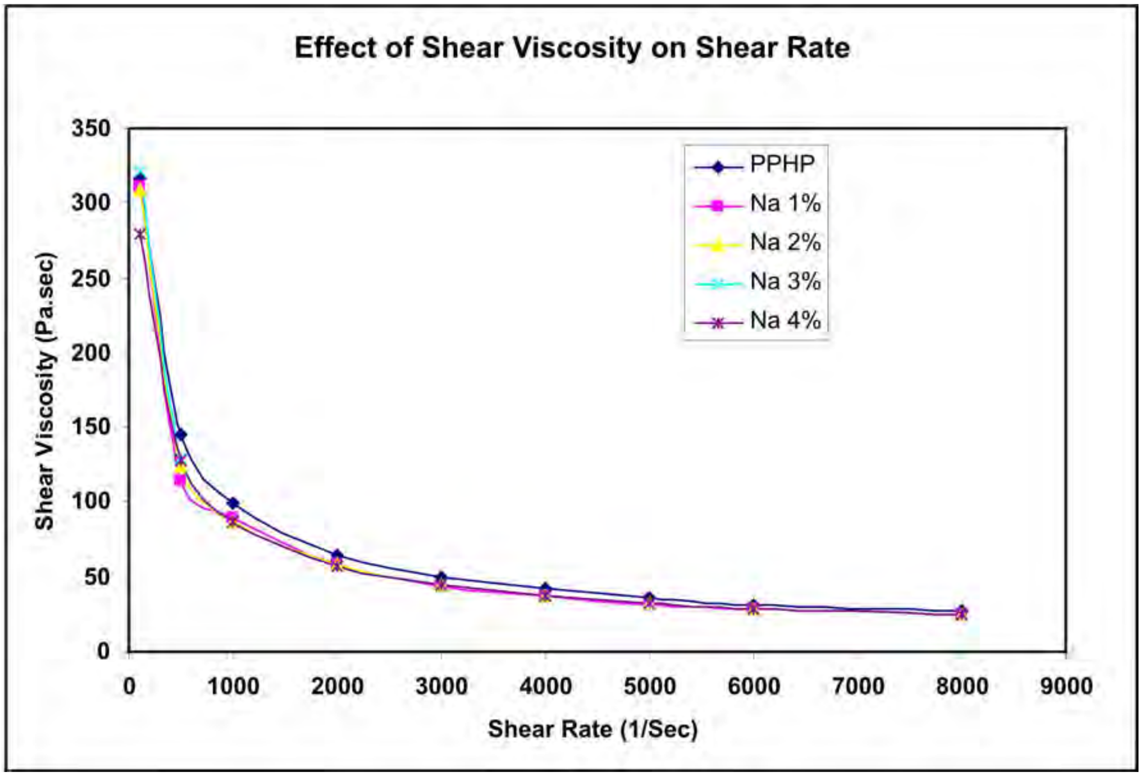
The above facts were supported by non-linear model to describe the change in viscosity with shear rate. A log-plot of shear stress *vs* shear rate as shown in Fig. 3, results in a straight line. The flow behaviour index 'n' can be used as a measure of the degree of shear thinning character, which was measured using linear regression method and the computed value which to less than unity. A small decrease in flow behavior index with an increase in clay content suggests that PPNCs become more shear thinning as compared to PPHP.

Die Swell

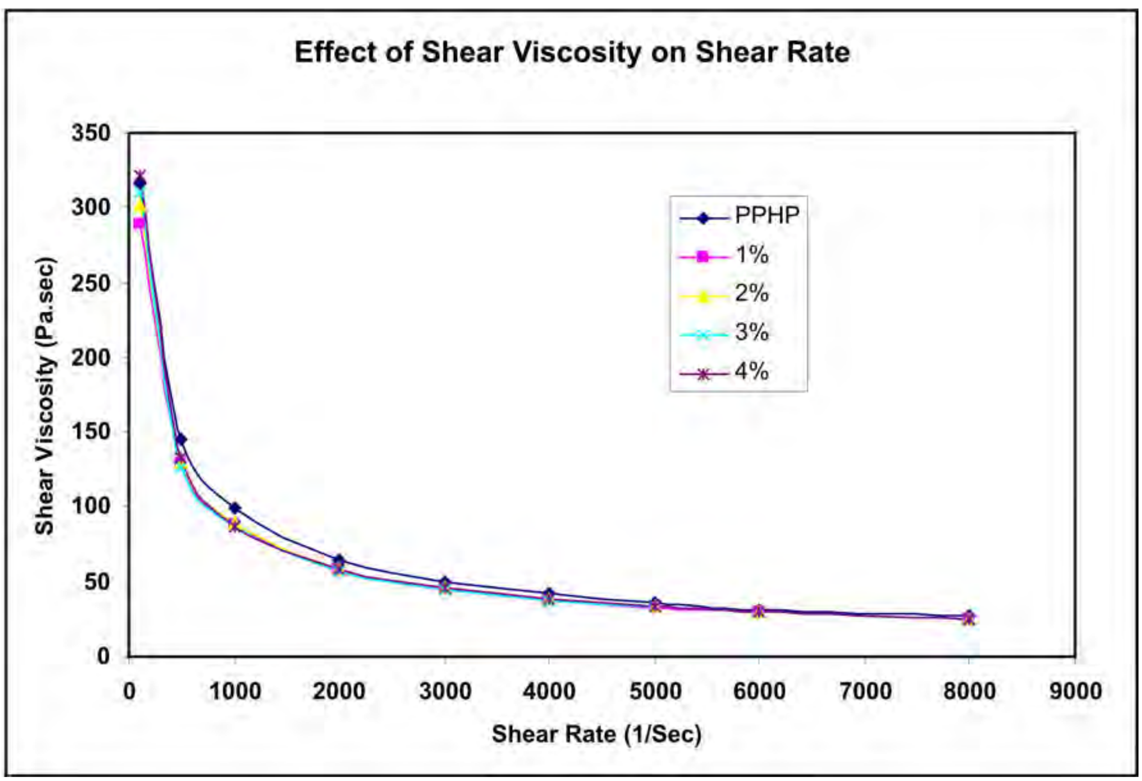
Effect of extrusion on die swell behaviour of PPNCs was studied at 200°C and compared with pure PP and the results are shown in Fig. 4. The dependence of the die-swell ratio of PPHP/PPNCs on shear rate at the channel wall was also studied. Die-swell ratio of PPHP/PPNCs melts was observed to present a non-linear increase with increase in shear rate, thus showing higher value of PPHP than nano clay filled PPHP. This suggested that filling of clay content in the polymer matrix does not affect the flow property. When the extrudate comes out of the die exit, a PP molecule tends to recoil, leading to the phenomena of die-swell. When the clay is mixed with PPHP, the amount of recoil is restricted. The restriction depends on the amount of clay loading as well as interaction between clay and PP molecules. In case of organically modified clay based PPNCs there is a reduction in die-swell with increasing wt% of clay content whereas unmodified clay based PPNCs do not show any significant variation in the reduction of die-swell with increasing clay loading. These effects may be attributed to better intercalation/exfoliation of modified clay in PP matrix due to better interaction between organically modified platelets and PP chains.

Melt Flow Index (MFI)

The MFI was measured for PPHP/PPNCs and results are depictd in Fig. 5. MFI increases with increase of

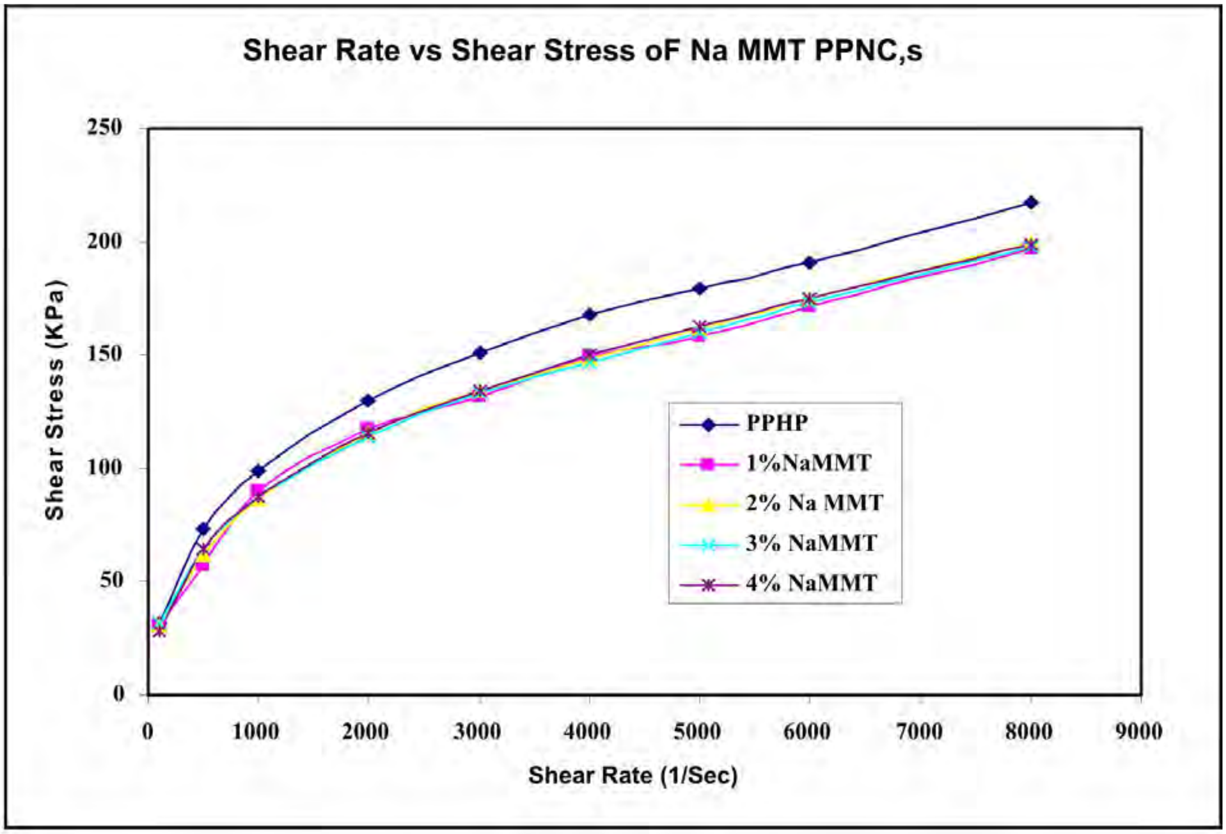


(a)

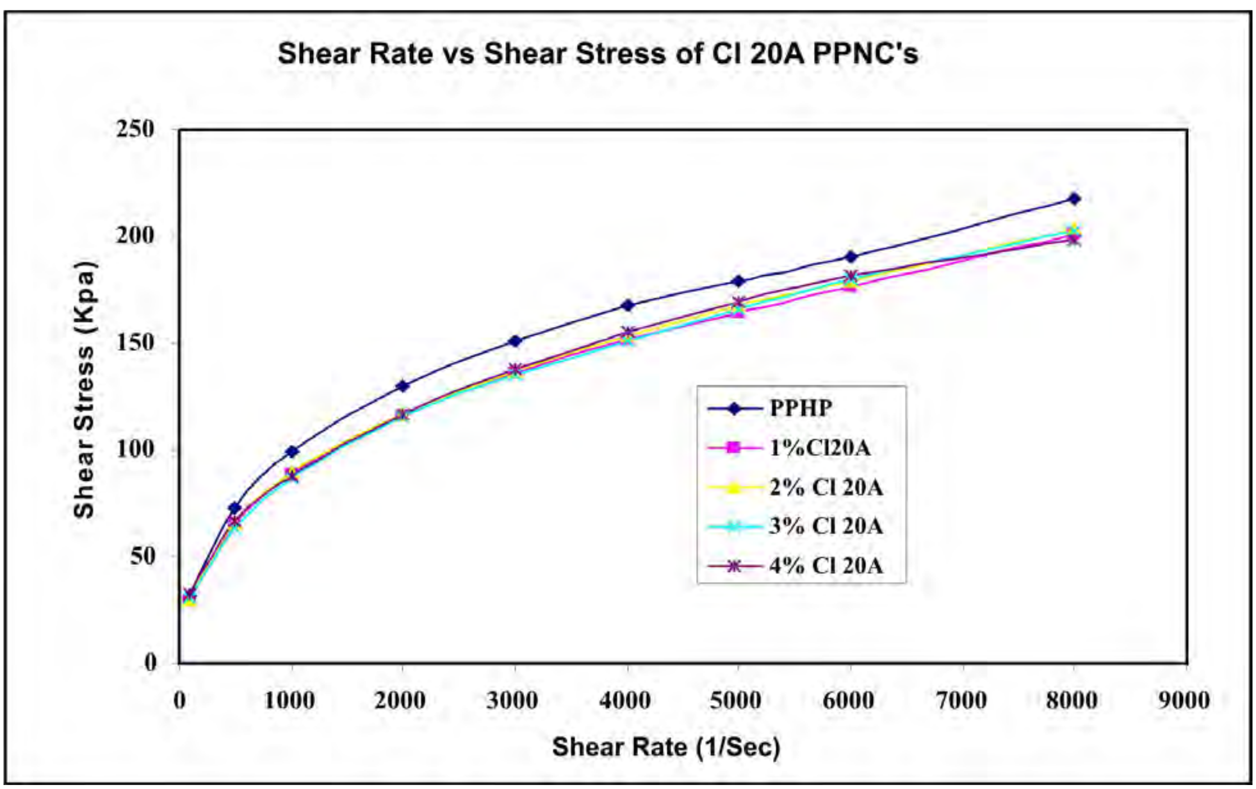


(b)

Fig. 1: Effect of Shear Viscosity on Shear Rate of PPNCs. (a) Na^+ MMT and (b) Cl 20 A



(a)



(b)

Fig. 2: Shear Stress *vs* Shear Rate of PPNCs. (a) Na^+ MMT and (b) Cl 20 A

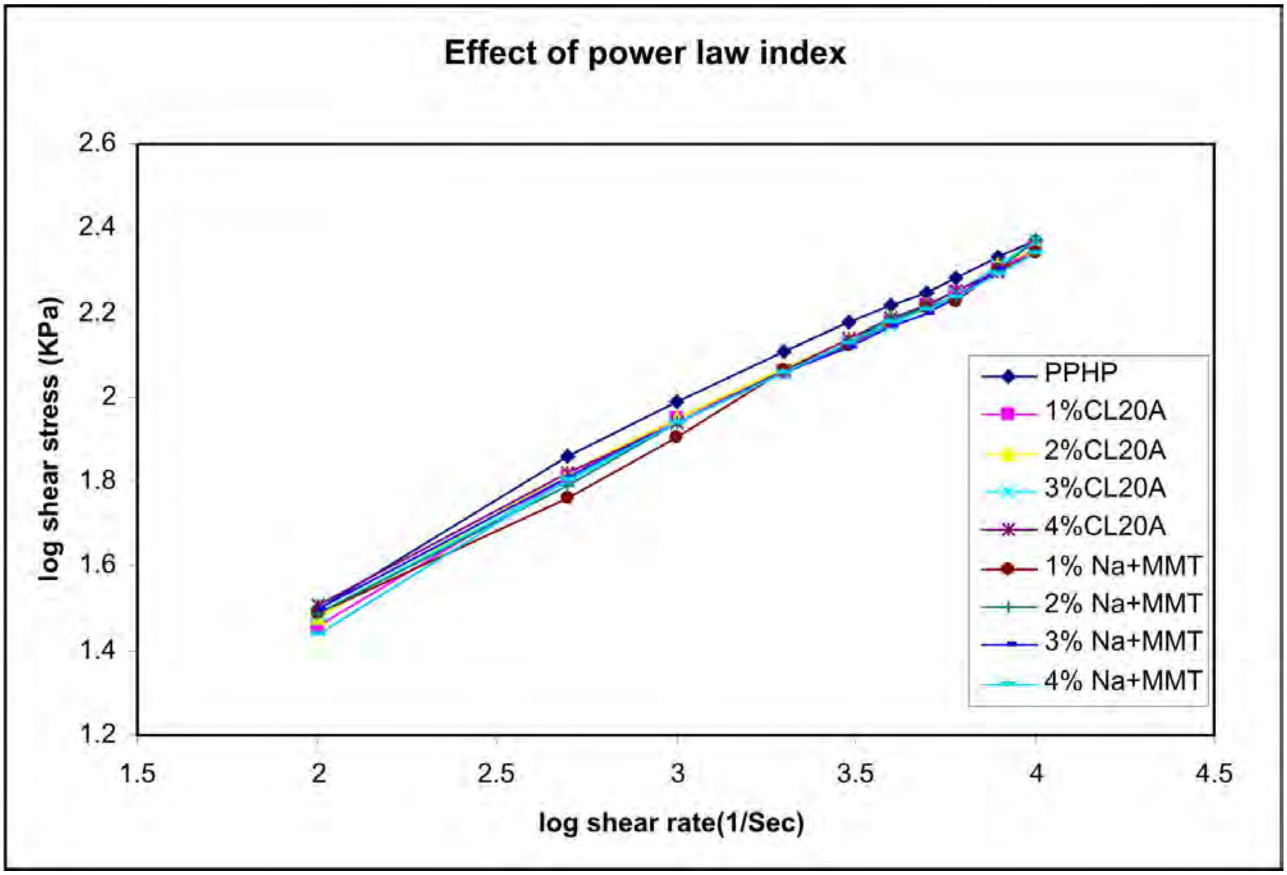


Fig. 3: Power Law Index of PPNCs

Table 2: Rheological characteristics of polypropylene nanocomposites (Log Shear Stress *vs* Log Shear Rate)

Shear Rate (1/sec)	Shear Stress (KPa)								
	PPHP	1% CL20A	2% CL20A	3% CL20A	4% CL20A	1% Na MMT	2% Na MMT	3% Na MMT	4% Na MMT
2	1.5	1.46	1.48	1.49	1.51	1.49	1.49	1.5	1.44
2.7	1.86	1.81	1.82	1.8	1.82	1.76	1.79	1.81	1.808
3	1.99	1.95	1.95	1.94	1.94	1.905	1.94	1.94	1.94
3.3	2.11	2.06	2.07	2.06	2.062	2.062	2.06	2.06	2.06
3.48	2.18	2.13	2.14	2.13	2.14	2.124	2.13	2.12	2.13
3.6	2.22	2.18	2.19	2.17	2.19	2.178	2.187	2.17	2.177
3.7	2.25	2.22	2.22	2.22	2.22	2.214	2.214	2.2	2.21
3.78	2.28	2.25	2.25	2.25	2.254	2.23	2.24	2.24	2.24
3.9	2.33	2.3	2.31	2.31	2.296	2.3	2.3	2.3	2.292
4	2.37	2.35	2.35	2.37		2.34	2.37		2.34

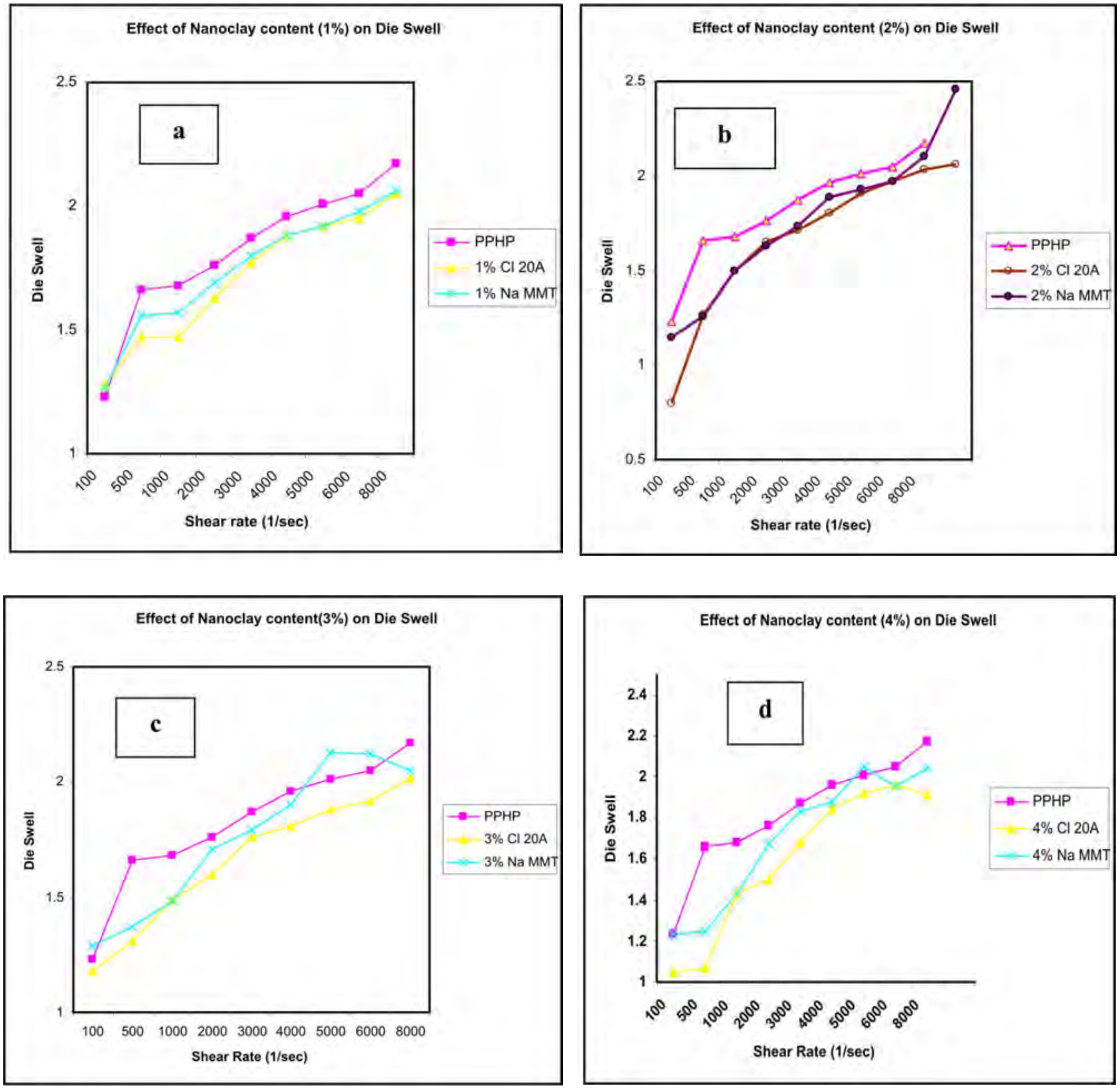


Fig. 4: Die Swell *vs* Shear Rate of PPNCs; (a) 1 wt. %, (b) 2 wt. %, (c) 3 wt. % and (d) 4 wt. %

nano clay contents in the material, which indicate ease of melting and easy processability. This study suggests that processing of PPNCs are better than PPHP. It is also suggested that dispersion of clay in polymer matrices usually results into a product (polymer/clay composite) with combined properties of the polymer and filler and hence, material of an enhanced property may be obtained. The most essential factor that leads to optimized composite properties is good dispersion (intercalation and exfoliation) and spatial distribution of filler in the matrix.

Tensile Strength

The tensile test was carried out on PPNCs prepared with different wt. % and results are shown in Fig. 6. The composite PPNCs samples with cloisite 20A showed improved tensile strength, with reference to

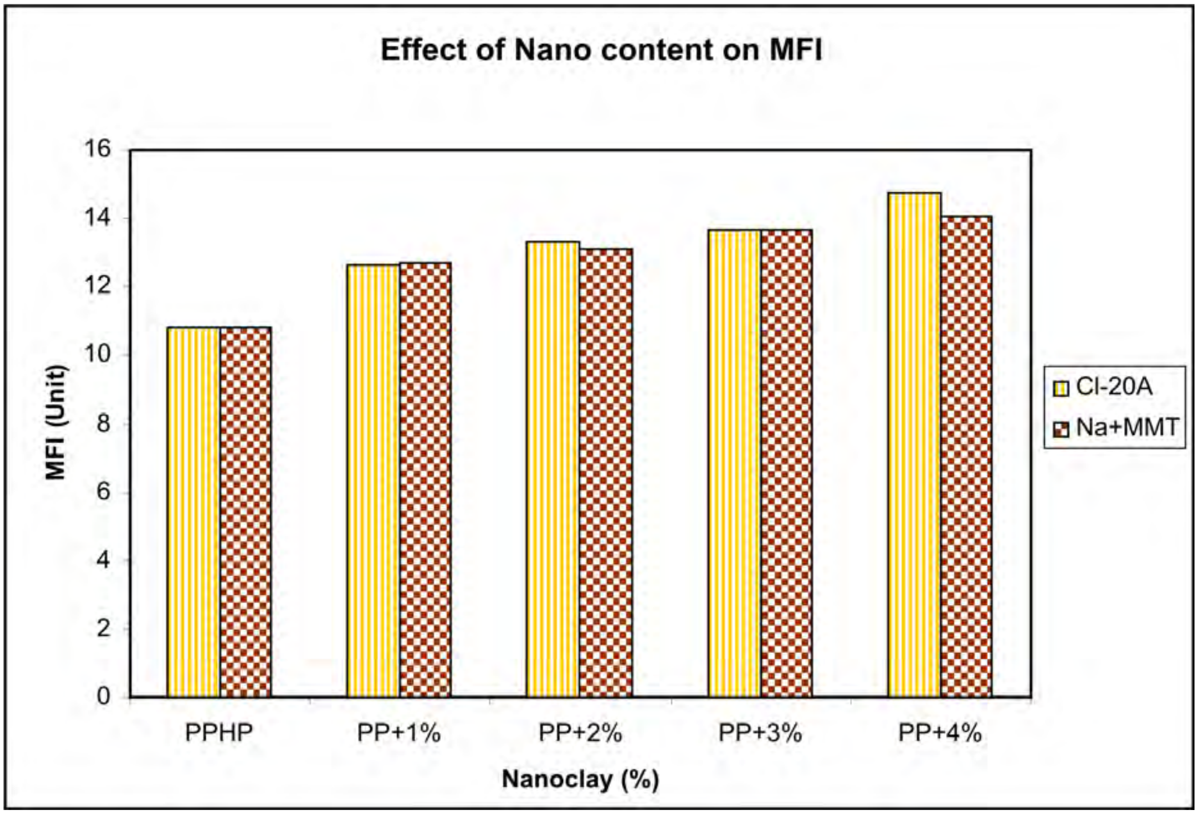


Fig. 5: Melt Flow Index *vs* Filler conc Histogram of PPNCs

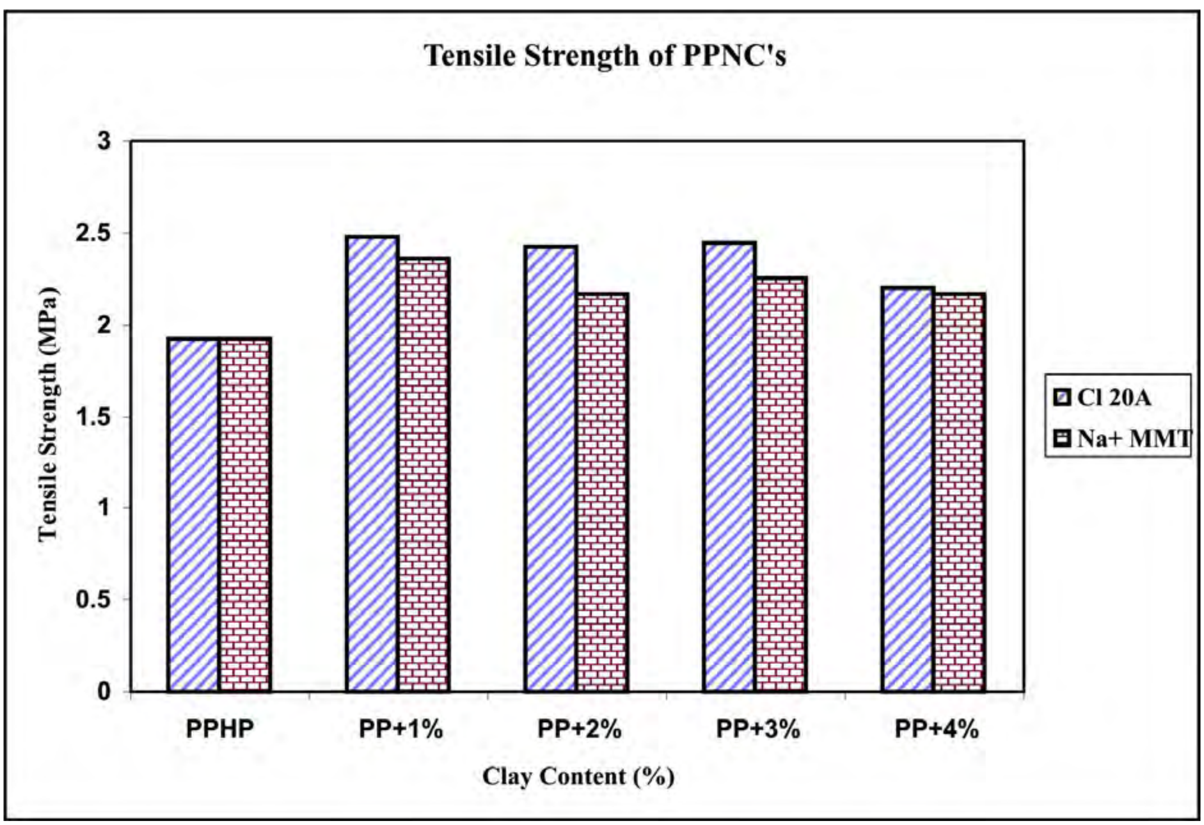


Fig. 6: Tensile Strength *vs* Filler conc Histogram of PPNCs

Na^+ MMT nanocomposites. PPNCs indicate increase in crystallinity in the presence of modified clay at small loadings (1 to 4%) thus responsible for higher strength. Tensile strength of PP+Cl 20A is higher as compared to PP Na^+ MMT. Both the nanocomposites have much higher value than pure PP. 4% nano clay filled PPNCs showed slight decrease in tensile strength which indicates the utility of optimum loading concentration of nano clay into the polymer matrix. This is because, augmentation of the clay content above the optimum value results in agglomeration, which tends to reduce strength properties of the PPNCs.

Conclusion

A Rheological study shows that PP nanocomposite has the same flow characteristics as neat PP, indicating the new technology can drop in the single extruder set up, without adding additional cost to end users. PPNCs do allow for improved mechanical properties to the base resin, but very intensive dispersionary mixing is required to make sure that organoclay particles are uniformly and thoroughly dispersed and distributed throughout the molten polymer before it enters the die. Tensile study shows that its mechanical property extensively increased as compared with pure PP. PPNCs made from master batch with single extruder showed better mechanical properties of the composites as compared to the batch obtained from the direct compounding.

Acknowledgement

The authors are thankful to Dr. AK Saxena, Director, Defence Materials & Stores Research & Development Establishment, Kanpur, for providing all support and encouragement.

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