Properties of Polypropylene Filled with Synthetic Sodium Aluminum Silicate

R. D. UPADHYAY, D. D. KALE

University Department of Chemical Technology, University of Mumbai, Matunga, Mumbai 400 019, India

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ABSTRACT: The effect of synthetic sodium aluminum silicate (SSAS) on the mechanical, physical, electrical, optical, and rheological properties of two different grades of polypropylene (PP) homopolymer with melt flow indexes (MFIs) of 3 and 11 was studied. Incorporation of SSAS improved the flexural strength and modulus of PP. At a given loading of SSAS, the mechanical properties of MFI 3 PP were better than those of MFI 11 PP. The presence of significant slip at the wall was observed for SSAS filled PP. The addition of a fluoropolymeric processing aid increased the slip effect further.
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Key words: filled polypropylene; synthetic sodium aluminum silicate; slip velocity; processing aid; rheology

INTRODUCTION

The use of fillers in plastics is widely practiced. Incorporation of fillers primarily reduces the cost and/or alters the physical, mechanical, and other properties. The most commonly used fillers in polypropylene (PP) are calcium carbonate or talc. The effect of such fillers on the properties of PP is described in the literature.[1–8]

Talc is a naturally occurring silicate. Most of the natural fillers contain impurities, depending on the geographical location of the mine and the mining process employed. There is also less control of the particle size for natural silicates. Therefore, synthetic silicates are being developed and commercially employed. In recent years one such silicate, synthetic sodium aluminum silicate (SSAS), has shown promising results. Its high refractive index and its specific particle size has led to its use as a partial replacement for TiO_2 in paint formulations.[9] Its pigmentory properties have been used in rubber and paper,[10,11] primarily to improve the whiteness and hiding power. In synthetic paper applications, use of SSAS in polyolefinic resin has been recommended.[10] The loading of filler can be as high as 40–50% by weight for such applications. Thus, there could be areas where PP filled with higher loadings of SSAS may find applications. There are no data available on the effect of SSAS on the properties of PP, and such study is useful. In the present study the effect of incorporating SSAS at different concentrations on the mechanical, electrical, optical, and rheological properties of two different grades of PP is presented.

EXPERIMENTAL

Materials

Two different homopolymer grade PPs (H030SG and H110MA) were supplied by Reliance Industries Ltd., India. The melt flow indices (MFIs) of these two grades were 3.0 and 11 g/10 min, respectively, at 210°C under a load of 2.16 kg.

The SSAS was Zeolex™ 323 grade (J. M. Huber Corporation, USA) procured from market. Its

Correspondence to: D. D. Kale.

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density was 1.9 g/cm^3 and the average particle size was 18 μm. The primary particles were spherical and the secondary or agglomerates can be platy according to the literature supplied by the manufacturer.[7,12] The concentration of the SSAS was varied from 5 to 40% (w/w).

The effect of a processing aid (PA) for compositions containing 30 wt % SSAS was evaluated using a fluoropolymer master batch Dynamer^{TM} 9613, which contained 5% fluoropolymer.

Compounding

Appropriate amounts of SSAS were initially dry blended with PP pellets and then compounded using a Haake counter rotating twin-screw extruder (TW 100) connected to a torque rheometer (RC 9000). The concentration of SSAS was varied up to 40 wt %. The temperature profiles during extrusion were 150°C for zone 1, 170°C for zone 2, 190°C for zone 3, and 210°C for zone 4. The screw speed was 50 rpm.

Testing

The extruded strands were pelletized. The dried pellets were then injection molded using a Boolani microprocessor-based injection molding machine for measuring the tensile strength (ASTM D 638M-91), flexural strength (ASTM 790M-92), and impact strength (ASTM 256). The temperature of the injection molding barrel was kept at 210°C, the injection pressure was 100 kg/cm^2, and the mold temperature was between 35 and 45°C. The MFI was measured using a Davenport model 10 melt flow indexer. The tensile and flexural properties were measured using a universal tensile testing machine (LR50K, Lloyds Instruments). The impact strength was measured for notched samples using an Avery Denison impact tester with a striking velocity of 3.46 m/s. A 5 J striker was used. The notches on the impact specimens were made using a Ray Ran notch cutter (model 1). All the mechanical results were averages of 10 readings. The variation was $\pm$5%. The melt rheology over the shear rate range of 10^{-2}–10^3 s^{-1} was measured using a Haake RT-10 rheometer and a Rosand twin bore capillary viscometer. The diameter of the capillary was 1 mm (L/D = 16).

Processing aids are known to reduce the apparent viscosity of base polymers by the slip effect. Similarly filled composites may also show the slip effect. Therefore, the evaluation of the possible slip velocity for the compositions containing no PA and 400 ppm of polymeric PA (PPA) was carried out using three different capillaries having the same L/D ratio of 16 but different diameters. The three capillaries used for the measurement of the slip velocity had diameters of 1, 1.5, and 2 mm. The slip velocity was calculated using the software provided by the manufacturer. The pressure drop volumetric flow rate data for all the compounds were recorded using three capillaries with the same L/D ratio but different diameters. When the polymer was flowing out of the capillary, visual inspection of the sample ensured that there was no yellowing. All the experiments were repeated 2–3 times. The slip velocity as calculated by the software was within $\pm$5% for different experiments.

The slip velocity is the additional velocity with respect to the stationary walls of the capillary. After each experiment, the barrel was cleaned thoroughly according to the procedure in the manual of operations supplied by Rosand Precision Ltd., UK.

The dielectric strength and surface resistivity were measured using a Ceast dielectric rigidity tester and Arcvis instruments. The tests were carried out using compression molded sheets of 2-mm thickness.

The yellowness index, brightness index, and opacity over dark and light backgrounds were determined using a Gretag McBeth ColorEye 7000A spectrophotometer. A small strip was punched from the compression molded sheets for these measurements. The measurements at five different places were carried out, and the results were the statistical average of these five readings. The standard deviation was less than 0.2.

RESULTS AND DISCUSSION

Mechanical Properties

Tables I and II show the effect of SSAS on the properties of two different grades of PP.

The tensile strength of MFI 11 PP seemed to decrease continuously with the increase in the percentage of loading. However, for MFI 3.0 PP, it seemed to initially decrease slightly and then rose again. The change in tensile strength of MFI 3 PP due to incorporation of SSAS was only marginal. The extension at break decreased drastically for MFI 11 PP while that for the other grade decreased slowly till the loading was 20%, and for higher loading it decreased rapidly. The flexural strength increased for both grades of PP. How-

Table I Mechanical Properties of MFI 3 PP Filled with SSAS

Properties	Composition (wt % SSAS)					
	0	5	10	20	30	40
Tensile strength (MPa)	33	32	30	27	31	33
Elongation at break (%)	147	101	57	59	22	13
Flexural strength (MPa)	33	35	39	42	43	44
Flexural modulus (MPa)	992	1132	1285	1495	1928	2385
Impact strength (J)	0.45	0.55	0.55	0.6	0.55	0.5

ever, the extent of increase was much higher for MFI 3 PP. The flexural modulus increased with the increase in loading for both grades of PP, although the properties of MFI 3 PP were slightly better. The impact strength of both grades of PP decreased, but the extent of decrease for MFI 11 was much higher than that for MFI 3.

The MFI 11 PP is generally recommended for injection molding. The present results showed that incorporation of SSAS reduced the mechanical properties of this grade considerably. Therefore, it may not be advisable to incorporate SSAS for such applications. However, the MFI 3 grade PP is used for extrusion applications, so it may be possible to incorporate higher loading of SSAS because it did not have much of an effect on the mechanical properties. Such a comparison of the two different grades of PP was not presented before.

If the filler particles do not bond well with the polymer matrix discontinuities can be formed, even at the low rates of deformations. Therefore, the stress transfer at the interface will be improper. The tensile strength and the elongation at break are measured at fairly high rates of deformation. A sudden decrease of the elongation at break for concentrations of SSAS beyond 20% seemed to indicate that the SSAS-PP system could be changing over from the state of a lower stress concentration effect to a system of a higher stress concentration effect, when the concentration of SSAS was beyond 20%. Maiti and Lopez[8] observed this kind of behavior for kaolin filled PP, and the level of concentration at which the mechanism of stress transfer occurred was around 15%. The increase in flexural modulus indicating the increased rigidity accompanied by reduced tensile strength and percentage of elongation seemed to indicate that this property modification may have been due to the restriction in mobility of the PP molecules by the filler particles.

The other popular filler used in PP is calcium carbonate. The data presented by Baker et al.[13] showed that even when $CaCO_3$ was added up to a 40% load, the increase in flexural modulus was only 40%. The percent increase in the flexural modulus for SSAS filled PP was 140%. Thus, SSAS imparted better flexural modulus than $CaCO_3$. The talc filled PP showed improvement in the flexural modulus[5] similar to SSAS.

Optical Properties

Table III shows the optical properties of filled PP. It is interesting to see that for MFI 3 PP, the yellowness index initially increased quite significantly up to 20% loading and then decreased at higher loadings. At 40% loading the yellowness index was comparable to that of virgin PP. It was surprising that there was an increase in the yel-

Table II Mechanical Properties of MFI 11 PP Filled with SSAS

Properties	Composition (wt % SSAS)				
	0	5	10	20	30
Tensile strength (MPa)	32	32	31	29	27
Elongation at break (%)	385	108	21	19	12
Flexural strength (MPa)	31	32	35	42	40
Flexural modulus (MPa)	923	1029	1120	1531	1756
Impact strength (J)	1.25	1.0	0.8	0.6	0.4

Table III Optical Properties of MFI 3 and 11 PP Filled with SSAS

		Filler (%)					
Base Polymer	Properties	0	5	10	20	30	40
MFI 3 PP	YI	13	45	49	45	24	13
MFI 11 PP	YI	18	27	25	28	25	—
MFI 3 PP	BI	15	19.5	16.3	17.7	26.3	27.8
MFI 11 PP	BI	36.7	26.7	25.1	20.5	23.5	—
MFI 3 PP	RO	—	54	58	60	60	60
MFI 11 PP	RO	—	50	52	60	60	—

YI, yellowness index, ASTM D 1925; BI, brightness index, TAPPI Brightness I 452 (1982); RO, relative opacity, Opacity I 425.

lowness index, although the SSAS filler particles were snow white. It is well known that SSAS particles primarily fill the interparticle voids of TiO_2 in a paint film and thus SSAS acts as a partial substitute of TiO_2 in paints only. The particle size of the SSAS used in the present work, which was much larger than the particle size of TiO_2, could be causing a different internal reflectance–transmittance of the light different that imparted the yellowness effect at a lower concentration of this filler. At a higher concentration the effect of the yellowness could be masked. This is the first report of this type of behavior for any filler.

The MFI 3 PP had a much lower brightness index than MFI 11 PP. The addition of SSAS into MFI 3 PP increased the brightness index while that of MFI 11 PP decreased considerably. The relative percent opacity, however, was the same for both grades. The comparison of the mechanical and optical properties suggested that incorporation of SSAS in MFI 3 PP seemed to give better properties. Therefore, the electrical and rheological properties were measured for compounds made from MFI 3 PP only.

Electrical Properties

Table IV shows the variation of the electrical properties. The dielectric strength decreased slightly until 20% loading and at higher loading it decreased significantly. Similarly, the surface resistivity was marginally reduced until about 20% loading while at higher loading it decreased considerably. Thus, it seemed that the electrical properties of SSAS filled PP depended upon the concentration of filler. Up to a loading of 10% SSAS, the electrical properties of PP were not seriously affected. However, at higher concentrations the resistivity was reduced.

Rheology

Figure 1 shows the variation of the viscosity at 210°C with shear rate for different compositions of filled PP. All the compounds showed a well-defined limiting viscosity at low shear rates and non-Newtonian shear thinning behavior at high shear rates. The melt viscosity of the compounds containing 5 and 10% filler showed significantly lower viscosity than that of virgin PP at low shear rates. The viscosity of both these compounds at high shear rates was however higher than that of virgin PP. The viscosity of compounds containing higher loading showed higher viscosity than that of virgin PP at low shear rates. However, at higher shear rates they showed much higher viscosity than PP.

The increase in viscosity with increasing filler loading was documented for a number of fillers.[14]

Table IV Electrical Properties of MFI 3 PP Filled with SSAS

	Composition (wt % SSAS)					
Properties	0	5	10	20	30	40
Dielectric strength (kV/mm)	33	27.8	27.7	28.0	9.1	9.5
Surface resistivity $\times 10^{14}$ (ohm)	4.3	4.3	4.3	1.7	0.086	ND

ND, it could not be detected on the instrument.

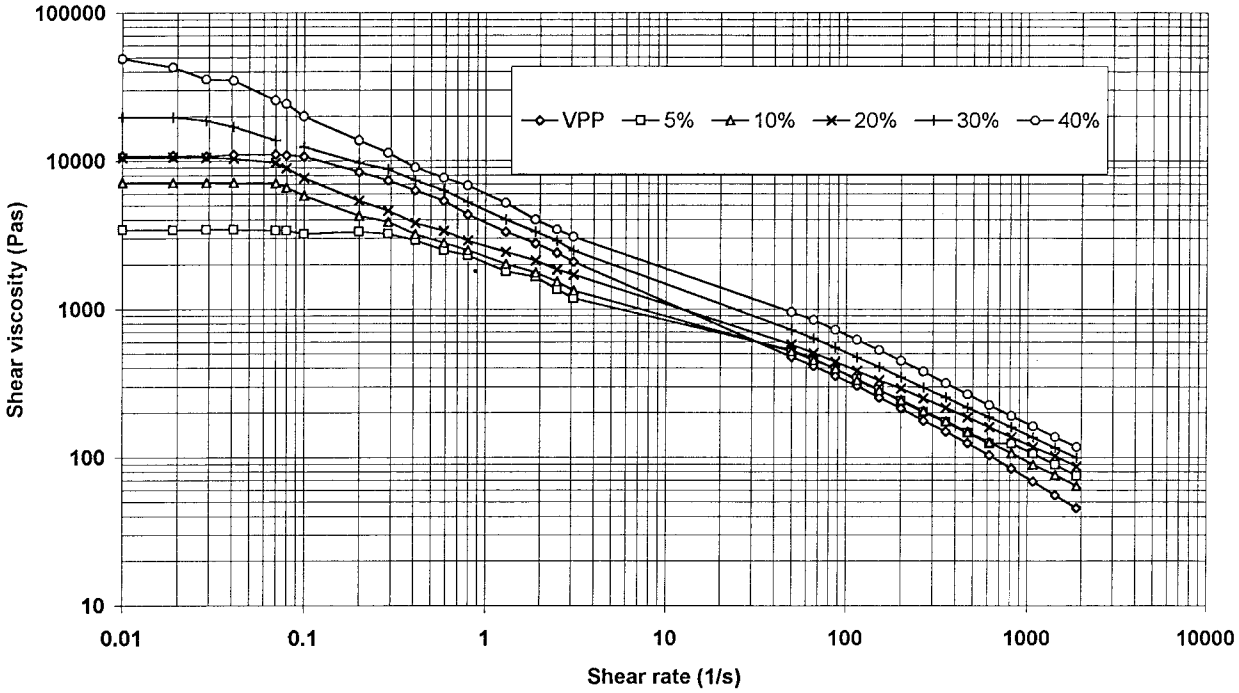

Figure 1 The effect of SSAS on the shear viscosity of the filled PP composition at 210°C: (◇) virgin PP (VPP), (□) 5%, (△) 10%, (×) 20%, (+) 30%, and (○) 40%.

However, a lower viscosity of filled compounds may indicate slip between the filler particles and polymer matrix or noncompatibility. Therefore, the presence of possible wall slip was measured.

Table V shows the variation of the wall slip effect with the wall shear stress for PP filled with SSAS. It was interesting to see that all the compositions clearly showed the presence of wall slip over some range of shear stresses. As the concentration of filler increased, the wall slip effect initially increased and then became zero at higher shear stress levels. As the concentration of filler increased, the shear stress level at which the slip effect became zero also increased. The presence of slip over a short range of shear stress can explain the lower apparent viscosity compared to PP at lower shear rates. As the shear rate increased, the slip effect vanished and the viscosity of the filled system became higher than that of virgin PP.

Because the viscosity of filled plastics increases at high shear rates that are of interest for polymer processing, the use of PPA may be useful. Upadhyay et al.[15] studied the effect of PA on virgin PP in terms of the slip velocity. They showed that the concentration of PA at 400 ppm

Table V Variation in Wall Slip Effect of PP Filled with SSAS at 210°C

	Wall Slip Velocity (m/s)				
Shear Stress (kPa)	0% SSAS	5% SSAS	10% SSAS	20% SSAS	30% SSAS
80	0.017	0.005	0	0	0
100	0.017	0.014	0.002	0.004	0
120	0.017	0.024	0.004	0.005	0.002
140	0.017	—	0.167	0.007	0.006
160	0.017	0.506	0	—	—
180	0.017	1.125	0	—	—
200	0.017	—	—	0.711	0.266
250	0.017	—	—	—	1.250

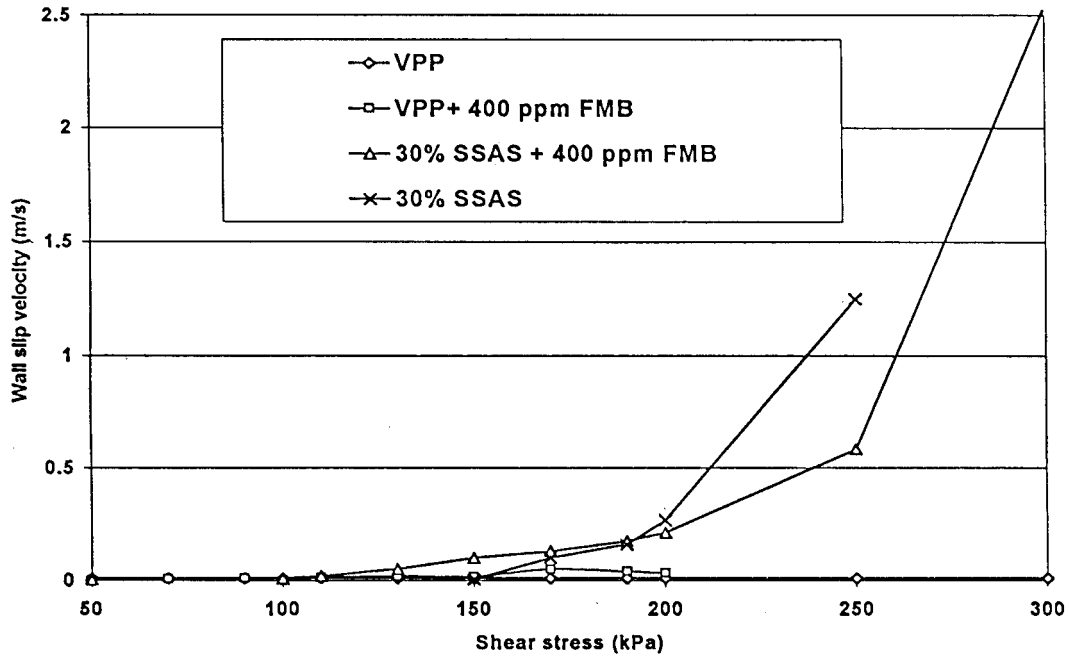

Figure 2 The variation of the wall slip velocity of MFI 3 PP filled with SSAS with a processing aid: (◇) virgin PP (VPP), (□) VPP + 800 ppm fluro master batch (FMB), (△) 30% SSAS + 800 ppm FMB, and (×) 30% SSAS.

caused maximum slip for MFI 3 PP. Therefore, the rheological data were collected to study the combined effect of PA at 400 ppm and the filler on the slip effect.

Figure 2 compares the combined effect of PA and 30% filler. It is very clear that the wall slip effect increased when PA was incorporated. These results therefore suggested that synthetic sili-

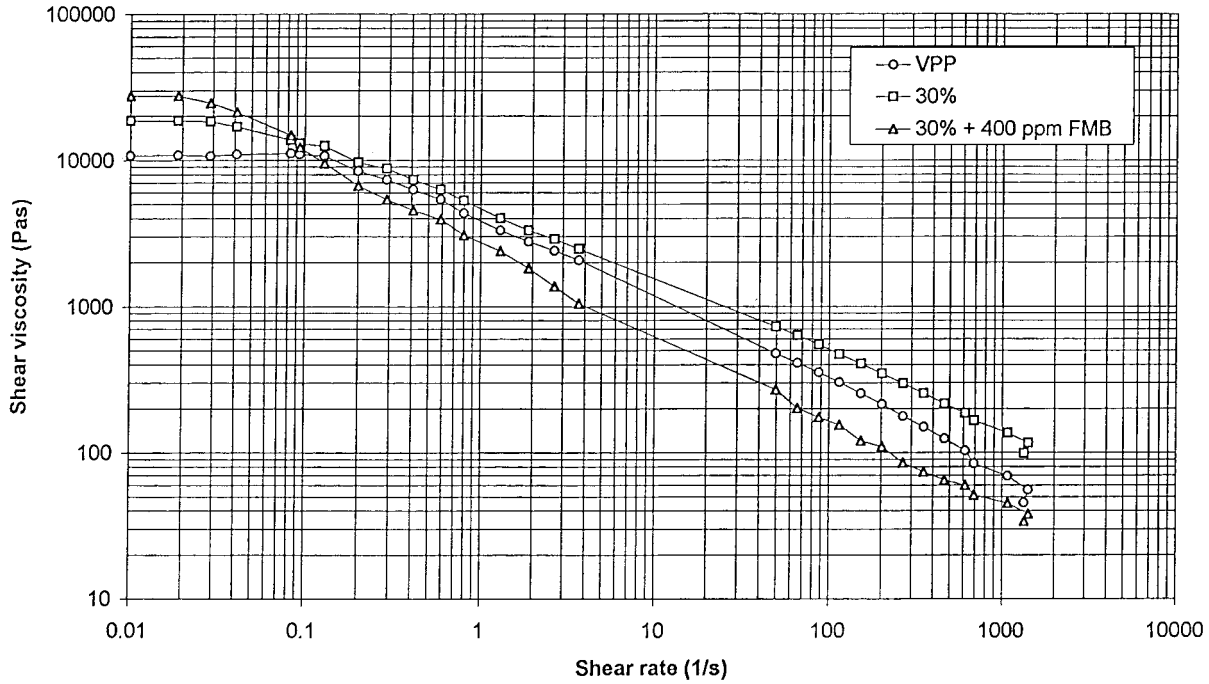

Figure 3 The effect of SSAS on the shear viscosity of the filled PP composition at 210°C: (○) virgin PP (VPP), (□) 30% SSAS, and (△) 30% SSAS + 400 ppm FMB.

cates caused slip between the filler particles and PP matrix and incorporation of fluoropolymeric PA helped to increase the slip effect further, thereby further reducing the apparent viscosity. Figure 3 compares the flow curves for virgin PP, PP containing 30% SSAS, and 400 ppm of PPA. It is interesting to see that the viscosity of PP filled with 30% SSAS was further reduced when 400 ppm of PPA was added. Therefore, using PA for highly filled PP with SSAS may be helpful. The presence of a significant slip effect between PP and SSAS even at a lower concentration of 5% may explain the poor bonding between the SSAS particles and PP, because PP is nonpolar in nature while SSAS is polar. The presence of the slip effect supports this reasoning.

CONCLUSIONS

The tensile strength of MFI 3 PP filled with SSAS seemed to be marginally affected, even up to 40% loading. However, the properties of MFI 11 PP were reduced because of the incorporation of SSAS. The flexural modulus increased with an increase in the concentration of SSAS. The SSAS caused a wall slip effect up to a certain level of shear stress, which increased with an increase in loading of the filler. The PA and SSAS caused a synergistic increase in the slip effect.

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