

# PROPERTIES OF POLYPROPYLENE COMPOSITES FABRICATED USING TWIN-SCREW EXTRUSION

Gang Sui, Weihong Zhong, Mike A Fuqua and Chad A Ulven

Department of Mechanical Engineering  
North Dakota State University, Fargo, ND 58105, USA

**Keywords:** *Composites, Sunflower, Polypropylene, Mechanical property, Thermal property*

## **Abstract**

Sunflower hull sanding dust (SHSD) filled polypropylene (PP) composite was prepared using a twin-screw extruder. Mechanical and thermal properties of the SHSD/PP composite were characterized contrasting to organically modified clay /PP composite. Differential scanning calorimetry (DSC) analysis showed that the crystallization temperature and the degree of crystallinity of PP exhibited changes with addition of SHSD. Mechanical properties of the PP were obviously enhanced by adding SHSDs. Flexural strength and flexural modulus of PP composite containing 5wt% SHSD are higher than that of the organically modified clay reinforced PP. Scanning electron microscopy (SEM) observation showed that no obvious agglomeration of SHSD existed in PP composites. Compared to the neat PP and organo-clay/PP, the SHSD/PP composites exhibited a relatively decreasing rate of thermal degradation with the increase of temperature. Experimental results suggest that SHSD, as a sunflower processing byproduct, may find promising applications in composite materials.

## **1. Introduction**

Polymer composites are an important approach in improving physical properties of polymeric materials for high-tech applications. Natural fillers, such as clay, silica, calcium carbonates, hemp fibers and wood fibers have been used in polymer composites displaying some desirable properties [1-5]. By further exploring the potential use of recycled and

waste byproducts, utilizing natural fibers has become an important approach to resolve resource shortage and environmental pollution issues. Some plant processing byproduct, such as sunflower oil cake, have been attempted to produce composite material, and evoke wide attention of researchers [6].

As an effective processing method for thermoplastic composites, twin-screw extrusion has been used gradually in recent years. Twin-screw extrusion provides high shear compounding for polymer melts to obtain a uniform composite microstructure. It was shown that twin-screw extruder compounded composites had higher mechanical properties than those compounded in a two-roll mill or a high-speed mixer [7-10].

In this work, a new plant fiber – sunflower seed hull sanding dust (SHSD), was comminuted and compounded with PP using a micro-18mm twin screw extruder. After a great deal of exploratory experiments, the optimal processing parameters for extruding SHSD/ PP composites were obtained. The effects of SHSD on the crystallization, mechanical and thermal properties of the PP matrix were studied. The resulting composites were compared against neat PP and organo-clay reinforced PP composites.

## **2. Experimental**

### **2.1 Materials**

PP with a density of 0.91kg/m<sup>3</sup> was supplied by Formosa Plastics Corporation, USA under the trade name Formolene 5100H. SHSD were obtained from the Agricultural Experiment Station, North Dakota State University. To

analyze the blending and bonding potential of the unprocessed SHSD on the polymer matrix, the fiber surface did not undergo any chemical treatments. An organo-clay, Cloisite 15A, which is montmorillonite modified with a dimethyl, dehydrogenated tallow quaternary ammonium ion, was purchased from Southern Clay Products, Gonzales, TX.

## 2.2 Preparation of the PP composites

The SHSD and clay 15A were dried prior to use for 24 h in a vacuum oven to remove moisture. The SHSD and clay loading of all specimens was set at 5wt%. Then SHSD/PP and clay/PP were melt-compounded in a co-rotating Leistritz Micro-18/GL-40D twin-screw extruder manufactured by Brabender Technologie Inc, Germany. The screw rotation rate was set at 75 rpm, and the temperature profile from hopper to die was as follows: 182°C, 188°C, 193°C, 199°C, 204°C, 210°C, 210°C, 210°C. The extruded PP and composites were pelletized and then compression molded at 200°C to obtain test specimens.

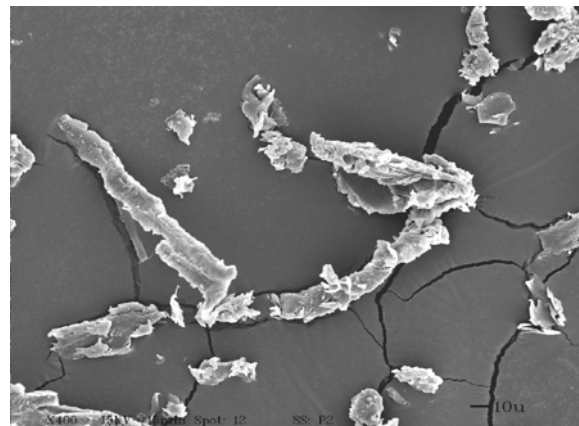
## 2.3 Characterizations of the materials

Differential scanning calorimetry (DSC) analysis was performed using TA Instruments Q1000 in a nitrogen atmosphere. In the non-isothermal experiments the specimens were heated at a rate of 10°C/min to 250°C to eliminate any previous thermal history and then cooled down to -40°C at a rate of 10°C/min. Following this, specimens were again heated to 250°C at a rate of 10°C/min. A load frame, manufactured by MTS Co. was used for the three-point bending test according to the ASTM-D790. The speed of the cross-head was 1 mm/min. The morphology of the fracture interface of the neat PP and composite specimens was observed by scanning electron microscopy (SEM) with a model JEOL JSM-6300. The thermal stability of specimens was tested using Thermogravimetric Analysis (TGA) (TA Instrument, model 2960) from room temperature to 600°C at a heating rate of 20°C/min under nitrogen purge.

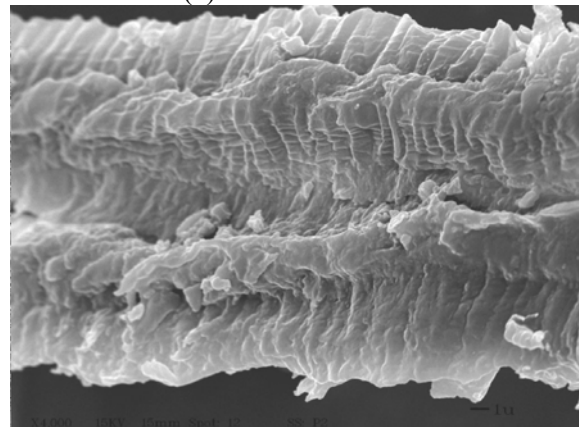
## 3 Results and discussion

### 3.1 Structural characteristics of the SHSD

The microstructure of the SHSDs used in this work is shown in Fig.1. It can be found that the SHSDs consist of micron-scale fibers and fragments from Fig.1 (a). In higher resolution image (Fig.1 (b)), it can be seen that there are many grooves on the surface of the SHSDs, which can improve the specific surface areas of the fibers and facilitate the adhesion with a polymer matrix.



(a) Low resolution



(b) High resolution

Fig.1 The microstructure of SHSDs

FTIR spectrum of SHSDs used in this experiment was tested and shown in Fig.2. Characteristic peaks related to the functional groups in the SHSDs were obtained from FTIR spectrum. The peak at 2911  $\text{cm}^{-1}$  confirms the appearance of O-H groups on the SHSD surface. The peak at 3410  $\text{cm}^{-1}$  is the characteristic

vibration of C-H bonds. The appearance of peak at  $1740\text{ cm}^{-1}$  indicated the existing of C=O bond. The peak at  $1615\text{ cm}^{-1}$  is attributed to the N-H or C=C bonds. The peak at  $1056\text{ cm}^{-1}$  is due to the characteristic vibration of C-O bonds. It is clear that functional groups such as hydroxyl, carbonyl, amino group exist in SHSDs, which may result in good interaction in SHSDs and polymers.

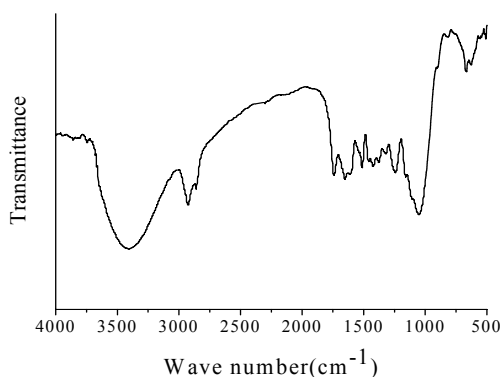
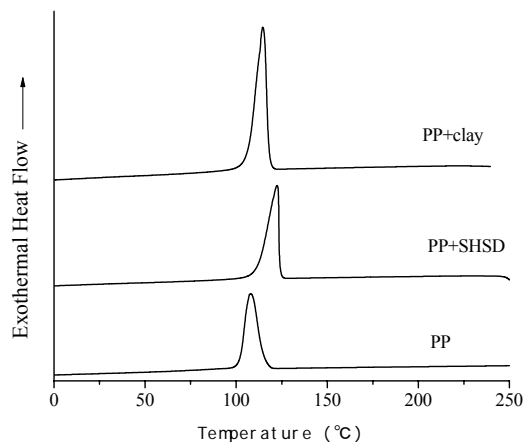


Fig.2 FTIR spectrum of SHSD

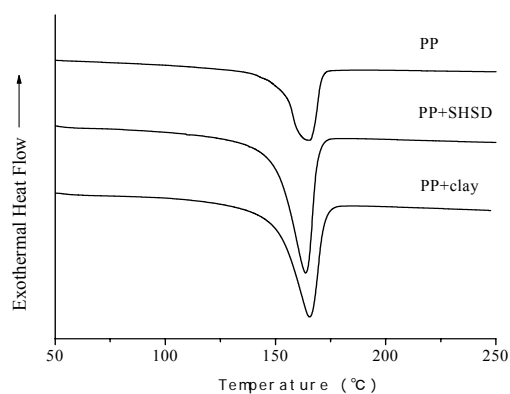
### 3.2 DSC analyses

The crystallization and melting patterns of the PP and PP composites were obtained during the cooling and heating processes of non-isothermal DSC measurements. From the DSC thermogram of the cooling process (Fig.3(a)), the  $T_p$  (peak temperature of crystallization),  $T_c$  (temperature at the intercept of the tangent at the baseline and the high temperature side of the exotherm peak) and  $\Delta W$  (width at half-height of the exotherm peak) were obtained and listed in the Table 1. The cooling process shows an increase in the crystallization temperature of PP with the addition of fillers. This phenomenon may be attributed to that the fillers being dispersed in PP matrix, promoting the heterogeneous nucleation. Meanwhile, the value of  $T_c - T_p$  shows a decrease for the SHSD composites when compared to neat PP, which indicates the crystallization rate of the PP matrix was increased. The width at half-height of the exotherm peak,  $\Delta W$ , also shows a slight

decrease denoting that the crystallite size distribution in the SHSD reinforced PP composites is narrower than that of neat PP.



(a) Cooling process



(b) Heating process

Fig.3 DSC curves of the PP and composites

Table 1 Non-isothermal crystallization parameters in cooling process

Specimen	$T_p$ (°C)	$T_c$ (°C)	$T_c - T_p$ (°C)	$\Delta W$ (°C)
Neat PP	108.07	115.14	7.07	8.2
PP+SHSD	117.44	118.67	1.23	7.1
PP+ clay	114.47	117.96	3.49	7.5

DSC thermogram for the second heating process is shown in the Fig.3 (b). The  $T_m$  (peak temperature of crystallization melting),  $\Delta H_m$  (melting heat of crystallization) were obtained and listed in the Table 2. From these data, the degree of supercooling (the difference in the melting peak temperature and crystallization peak temperature) were obtained. The degree of crystallinity of specimens was calculated from the melting heat of crystallization according to the following equation:  $X_c = \frac{\Delta H_m}{\Delta H_0}$ , where  $\Delta H_0 = 207.1$  J/g is the melting heat of 100% crystalline PP [11].

Table 2 Non-isothermal crystallization parameters in heating process

Specimen	$T_m$ (°C)	$T_m-T_P$ (°C)	$\Delta H_m$ (J/g)	$X_c$ (%)
Neat PP	165.39	57.32	87.46	42.23
PP+SHSD	163.66	46.22	75.04	36.23
PP+ clay	165.47	51.00	63.52	30.67

There was no marked change seen for the peak temperature of crystallization through the different specimens. The degree of supercooling required for the crystallization of PP reduces with the presence of the fillers, which is found to be consistent with others analyses[12]. As the 5wt% fillers were added into PP matrix, the fillers were found to obstruct the mobilization of the PP macromolecular chain and prevent the macromolecular segment from obtaining ordered alignment of the crystal lattice. Thus, the degree of crystallinity of the specimens decreased accordingly, although this was observed to occur to a greater extent for the clay composite compared to the SHSD composites. It is speculated that not only the fillers themselves, but also the crystalline structures will affect the mechanical properties.

### 3.3 Mechanical properties

Mechanical properties of the SHSD composites were examined through three-

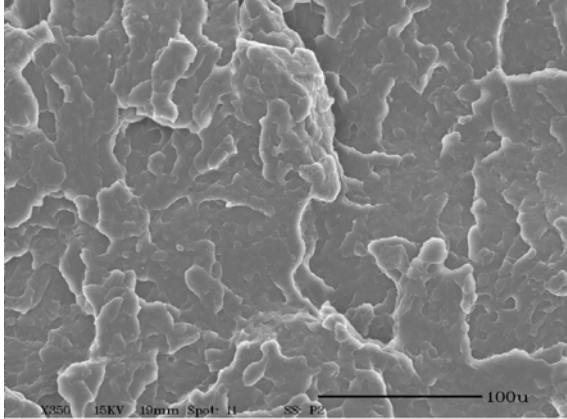
point bending tests. The bending test results of the neat PP and PP composites are shown in Table 3. It can be seen that the SHSDs provided significant reinforcing effects to the PP matrix, comparable to PP reinforced with organo-clay. After the addition of the fillers, the flexural strength and modulus of the PP composites were noticeably improved. Enhancements of 27% and 13% in flexural strength and flexural modulus for the PP matrix, respectively, were obtained after adding 5wt% SHSD, which are higher than the enhancements gained from composites containing 5wt% organo-clay. As well-known, the raw clay is very cheap, but almost inertia for reinforcing polymer matrices. In order to achieve a reinforced effect in polymer composites, it needs complicated treatment procedures with chemicals involved in, which results in increased cost. Therefore, these levels of enhancement in flexural strength and modulus incurred by the SHSDs are significant for a polymer material loading with an agricultural processing byproduct without any chemical treatment involved.

Table 3 Flexural properties of PP and composites

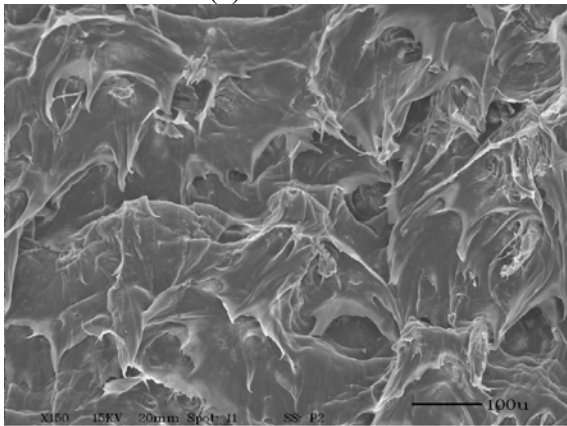
	$\sigma_f$ / MPa	$E_f$ / GPa
Neat PP	40.7±0.7	1.39±0.12
PP + SHSD	51.5±2.1	1.57±0.09
PP + clay	49.4±3.9	1.51±0.07

The fracture surface morphology of the PP, SHSD/PP and organo-clay/PP composites after the three-point bending tests are shown in Fig. 4. Compared to the characteristic features of neat PP material, obvious plastic deformation was found in the fracture morphology of the PP composites. The reason for this phenomenon is speculated to be the strong reinforcing effect of the fibers in the polymer, as well as higher amorphous portions of the PP inside the composites, which allowed increased deformation beyond the elastic behavior. At the same time, no obvious agglomerations of the fillers were found in the composites

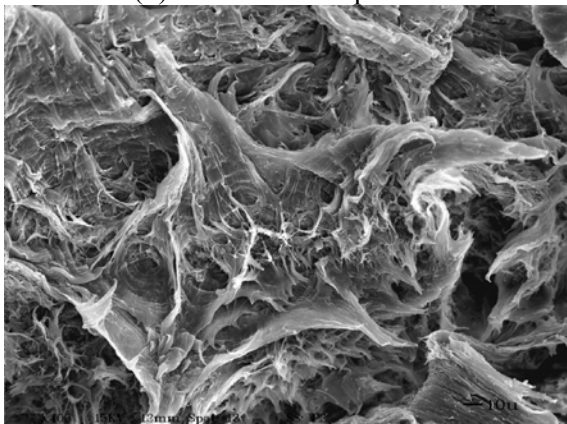
indicating that mixing through a twin-screw extruder, which is an industry friendly method, is effective for dispersing the SHSD fillers uniformly in the PP matrix.



(a) Neat PP



(b) PP/SHSD composite



(c) clay/PP composite

Fig.4 Fracture morphology of the PP and composites after three-point bending tests

### 3.4 Thermal stability

Thermal stability of the composites was studied by TGA. Fig.6 shows TGA curves of the neat PP and PP composites. By comparing the weight loss as a function of temperature, the effects of the two kinds of fillers, SHSD and organo-clay, on the thermal stability of the PP material were analyzed. There was a slight decrease at the onset temperature of thermal degradation for SHSD-filled specimens compared to the neat PP. With the increasing temperature, the thermal degradation rate of the SHSD-filled specimens was gradually decreasing compared to that of the neat PP. The SHSD composites exhibited the highest temperature for entire thermal degradation. Generally, the SHSD composite has similar thermal stability level to the organo-clay reinforced composite. As well known, the adhesion between clay and polymer is poor if no compatibilizer and/or surface treating agent would be involved.

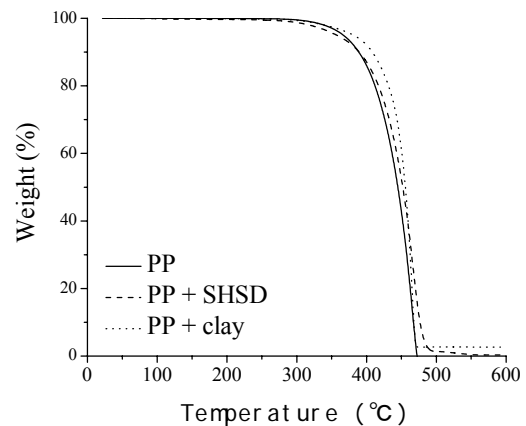


Fig.5 TGA curves of PP and composites

Therefore, it is considered that the SHSD, a natural agricultural processing byproduct, can be used as a good, environmental benign reinforcement agent with lower cost for polymers.

### 4. Conclusions

The sunflower hull sanding dust was dispersed uniformly throughout the PP

matrix by melt mixing using a twin-screw extruder. After adding the SHSDs, the crystallization behavior of the PP matrix was affected. Although the degree of crystallinity of PP exhibited a decrease with addition of SHSDs, the mechanical properties of the SHSD composites were enhanced obviously. The flexural strength and modulus of PP were improved by adding SHSDs by 27% and 13%, respectively. Compared to the neat PP, the SHSD/PP composites displayed a better thermal stability at high temperature stage. The use of the processing byproduct, SHSD, shows a potential for promising applications in cost-effective composites but with enhanced mechanical and thermal properties.

#### Acknowledgements

The authors gratefully acknowledge the support from NSF through NIRT grant 0506531 and DMR Instrumentation grant 0413967. This work is also partially supported by NASA through grant NNM04AA62G.

#### References

- [1] Vladimirov V., Betchev C., Vassiliou A., Papageorgiou G. and Bikiaris D. 2006. "Dynamic mechanical and morphological studies of isotactic polypropylene/fumed silica nanocomposites with enhanced gas barrier properties". *Composites Science and Technology* Vol.66, pp2935-2944,2006.
- [2] Ray D., Sengupta S., Sengupta S. P., Mohanty A. K. and Misra M. "Preparation and Properties of Vinylester Resin/Clay Nanocomposites". *Macromolecules Materials and Engineering*, Vol. 291, pp1513–1520, 2006.
- [3] Karmarkar A., Chauhan S.S., Modak J. M. and Chanda M. "Mechanical properties of wood–fiber reinforced polypropylene composites: Effect of a novel compatibilizer with isocyanate functional group". *Composites Part A* Vol.38, No.2, pp 227-233, 2007.
- [4] Pickering K.L., Beckermann G.W., Alam S.N. and Foreman N.J. "Optimising industrial hemp fibre for composites". *Composites Part A*, Vol. 38, No. 2, pp 461-468. 2007.
- [5] Zuiderduin W.C.J., Westzaan C., Hue'tink J. and Gaymans R.J. "Toughening of polypropylene with calcium carbonate particles". *Polymer*, Vol. 44, pp. 261-275, 2003.
- [6] Rouilly A., Orliac O., Silvestre F. and Rigal L. "New natural injection-moldable composite material from sunflower oil cake". *Bioresource Technology*, Vol. 97, pp 553-561, 2006.
- [7] Modesti M., Lorenzetti A., Bon D. and Besco S. "Effect of processing conditions on morphology and mechanical properties of compatibilized polypropylene nanocomposites". *Polymer*. Vol. 46, pp 10237-10245, 2005.
- [8] Zhuang G.S., Sui G.X., Meng H., Sun Z.S. and Yang R. "Mechanical properties of potassium titanate whiskers reinforced poly(ether ether ketone) composites using different compounding processes". *Composites Science and Technology*, Vol. 67, No. 6, pp 1172-1181, 2007.
- [9] Fang L., Leng Y. and Gao P. "Processing and mechanical properties of HA/UHMWPE nanocomposites". *Biomaterials*, Vol. 27, No. 20, pp 3701-3707, 2006..
- [10] Yang H. S., Wolcott M. P., Kim H. S., Kim S. and Kim H. J. "Properties of lignocellulosic material filled polypropylene bio-composites made with different manufacturing processes". *Polymer Testing*, Vol. 25. No. 5, pp 668-676, 2006.
- [11] Wunderlich B. "Thermal analysis". New York: Academic Press, 1990.
- [12] Li J., Zhou C. and Gang W. "Study on nonisothermal crystallization of maleic anhydride grafted polypropylene / montmorillonite nanocomposites". *Polymer Testing*, Vol. 22, pp 217-223, 2003.