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Wollastonite in Polypropylene
Size, Shape and Surface Modification

Rubber and Plastics Department
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A Versatile Functional Filler

Wollastonite is a versatile functional filler for plastics because it is available in a range of particle sizes, particle aspect ratios and surface treatments unequaled by other minerals. When it is used as a reinforcing agent in polypropylene (PP), and in other plastics, these size, shape and surface chemistry options allow the compounder to control compound stiffness and toughness to a degree that might otherwise be impossible.

In filled systems, reinforcement is obtained by the transfer of applied stress from the polymer to the filler. Stress transfer is promoted by the intimacy of polymer-filler contact and by filler-polymer adhesion - the extent to which the polymer will remain anchored on the filler surface. Stress transfer is also a function of filler size and shape.

With most fillers, the requirements for impact resistance generally result in this property being sacrificed as strength and stiffness are improved, or vice versa. A compound becomes more resistant to bending as the filler's surface area, aspect ratio and resin adhesion restrict the ability of polymer chains to move relative to its surface. A filler-stiffened compound is, however, in most cases more brittle, and therefore more prone to crack initiation and propagation at points of stress concentration, such as notches, bends and voids. A filler that is truly coupled to the polymer generally provides the most stiffening, but at the expense of impact resistance.

Compound stiffness is measured by flexural modulus, but compound toughness is related to several aspects of impact testing. Notched testing, with a stress concentrator under tension, allows for little or no plastic deformation and produces brittle failure. Reversed notch testing, with the stress concentrator under compression, and unnotched testing allow for polymer deformation and ductile failure.

Size and Shape

The calcium silicate structure of wollastonite grows naturally as a chain, resulting in needle-like crystals. These high aspect ratio needles are retained by appropriate milling, or broken into lower aspect ratio fragments as required for particular applications. For the reinforcement of plastics, smaller and higher aspect ratio particles expose greater surface area to better intercept stress propagation.

This study compares the effect on stiffness and impact strength of wollastonite's particle size and shape, using **VANSIL® W-50**, **VANSIL HR-325** and **VANSIL HR-1500**, the physical properties of which are summarized in Table 1.

Table 1.
Physical Properties of Wollastonite

VANSIL:	W-50	HR-325	HR-1500
Median particle size*, micrometers	2.8	2.3	9.0
Average particle length**, micrometers	8	20	60
Average aspect ratio**	4:1	12:1	14:1
BET surface area, m^2/g	4.2	3.7	1.6

*sedimentation **microscopy

Surface Modification

Resin-filler contact is improved by surface modification with organic treatments and additives. The surface treatment most commonly used with wollastonite is organosilane. When the filler is pretreated with silane, the silicon end of the structure becomes covalently bound to the surface of the mineral. The organic end of the structure acts as a wetting agent, making it easier for the resin to contact and coat the mineral surface. When the organic functionality is not reactive toward the resin, as with aminopropylsilane in the presence of PP, it may provide improved compound physicals through improved wetting. Certain organic functionalities, such as the alkyl group of alkylsilanes, serve as both a wetting agent and lubricant, reducing polymer drag across filler surfaces. This tends to make the compound less stiff, but more impact resistant (see Vanderbilt Report No. 701). If the organic functionality of the silane is reactive toward the PP resin, as with methacryloxypropylsilane or vinylsilane, true coupling can occur.

A current approach to maximizing the benefits of silicates in polypropylene is to use an aminosilane treated filler along with a maleated polypropylene (MAPP) additive. In this system the silane and MAPP cooperatively enhance interaction between the mineral and polypropylene. The silane binds the mineral to the anhydride groups on MAPP via amide linkages. The polypropylene chain of MAPP can be visualized as becoming entangled and co-crystallizing with the bulk polypropylene matrix, thus forming a continuous interface between the mineral and resin. This allows for greater adhesion of polymer to filler than is obtained with nonreactive silanes.

MAPP can also react with silicate surfaces, acting as an *in situ* wetting and semi-coupling agent. In this case, MAPP couples with the mineral surface directly, while the polypropylene functionality becomes entangled with the bulk matrix as described above. In addition to particle size and shape, therefore, this study compares the results of the aminosilane/MAPP combination to those from simple MAPP addition, and to the use of aminosilane treatment alone.

Experimental

Materials: A portion of each of the three wollastonite products - **VANSIL W-50**, **VANSIL HR-325** and **VANSIL HR-1500** - was treated with sufficient aminopropyltriethoxysilane to result in 0.3% aminopropylsilane on the mineral surface after reaction and drying.* Polybond® 3200 (Crompton), with 1% maleic anhydride, was used as the maleated polypropylene. The resin was 4 MF HB 9200 polypropylene (BP Polypropylene Americas).

Compounding and Testing: A Werner & Pfleiderer ZSK 30mm co-rotating twin screw extruder was used at 300 rpm with 190°C zone temperatures, 200°C die temperature, 210°C melt temperature and the vacuum port open. Compound components were preblended and added to the hopper of the extruder. The extruded strand passed through a water bath before being cut into 5mm pellets. The pellets were dried before specimens were molded on a BOY 15S injection molder. Tensile, flexural and impact properties were measured using ASTM procedures.

*Silane-treated wollastonite products are available under the **VANCOTE®** trade name.

Effect of Particle Size and Shape

Table 2 compares the effect of wollastonite size and shape on compound properties:

- **VANSIL HR-1500**, the highest aspect ratio and longest needle product, provided the greatest stiffness and the correspondingly lowest overall impact resistance.
- **VANSIL W-50**, the finest particle size, low aspect ratio product, provided the least stiffness, but the highest overall impact strength.
- **VANSIL HR-325**, offering both small particle size and high aspect ratio, provided a favorable balance of stiffness and impact resistance, as well as the greatest tensile and flex strength.

Table 2.
Untreated Wollastonite

VANSIL W-50	30.0	---	---
VANSIL HR-325	---	30.0	---
VANSIL HR-1500	---	---	30.0
Phenol/Phosphite Antioxidant	0.175	0.175	0.175
4 MF Polypropylene	69.825	67.825	69.825
Tensile:			
Modulus, MPa	2491	3148	3075
Peak Stress, MPa	33.2	36.7	35.1
Elongation at Break, %	11.8	10.1	8.9
Flexural:			
Modulus, MPa	2786	3276	3498
Strength, MPa	58.6	61.5	60.4
Impact:			
Notched Izod, J/m	20.3	21.9	21.9
Reversed Notched Izod, J/m	418	397	252
Unnotched Charpy, J/m	681	626	596

Tables 3, 4 and 5, representing the three chemical modifications that improve filler functionality, also show that **VANSIL HR-1500** provides the greatest stiffness, but that **VANSIL HR-325** provides the best balance of stiffness and impact resistance.

Table 3.
Aminosilane-treated Wollastonite

VANSIL W-50, AS-treated	30.0	---	---
VANSIL HR-325, AS-treated	---	30.0	---
VANSIL HR-1500, AS-treated	---	---	30.0
Phenol/Phosphite Antioxidant	0.175	0.175	0.175
4 MF Polypropylene	69.825	67.825	69.825
Tensile:			
Modulus, MPa	2496	2939	3051
Peak Stress, MPa	36.0	38.4	38.3
Elongation at Break, %	15.0	18.3	12.3
Flexural:			
Modulus, MPa	2914	3319	3330
Strength, MPa	61.1	64.4	65.3
Impact:			
Notched Izod, J/m	30.4	32.0	25.6
Reversed Notched Izod, J/m	582	633	446
Unnotched Charpy, J/m	953	893	818

Table 4. MAPP Additive

VANSIL W-50	30.0	---	---
VANSIL HR-325	---	30.0	---
VANSIL HR-1500	---	---	30.0
MAPP	2.0	2.0	2.0
Phenol/Phosphite Antioxidant	0.175	0.175	0.175
4 MF Polypropylene	67.825	67.825	67.825
Tensile:			
Modulus, MPa	2483	2933	2978
Peak Stress, MPa	36.3	38.6	38.1
Elongation at Break, %	13.5	15.5	12.9
Flexural:			
Modulus, MPa	2884	3246	3348
Strength, MPa	62.1	64.1	65.2
Impact:			
Notched Izod, J/m	31.5	35.2	29.9
Reversed Notched Izod, J/m	704	690	410
Unnotched Charpy, J/m	1224	1131	1004

Table 5. Aminosilane-treated Wollastonite with MAPP Additive

VANSIL W-50, AS-treated	30.0	---	---
VANSIL HR-325, AS-treated	---	30.0	---
VANSIL HR-1500, AS-treated	---	---	30.0
MAPP	2.0	2.0	2.0
Phenol/Phosphite Antioxidant	0.175	0.175	0.175
4 MF Polypropylene	67.825	67.825	67.825
Tensile:			
Modulus, MPa	2402	2834	2961
Peak Stress, MPa	35.8	38.3	38.8
Elongation at Break, %	18.7	23.9	16.3
Flexural:			
Modulus, MPa	2881	3196	3323
Strength, MPa	62.0	64.5	66.0
Impact:			
Notched Izod, J/m	31.0	37.4	32.6
Reversed Notched Izod, J/m	775	954	397
Unnotched Charpy, J/m	1380	1254	1029

Effect of Compatibilizers

Tables 6, 7 and 8 are an alternate presentation of the data, comparing the three methods of chemical modification with each wollastonite product:

- In all cases the chemical modifications improved impact properties, but provided little, if any, improvement in stiffness.
- For all three **VANSIL** products, impact strength and elasticity, as measured by tensile modulus and elongation, were maximized by the aminosilane/MAPP combination.
- MAPP alone was more effective than AS treatment in improving impact properties.
- The contribution of the chemical modifications to stiffness was inversely related to the stiffening ability of the untreated filler. The finest particle size, low aspect ratio product, untreated **VANSIL W-50**, contributed the least of the three fillers to stiffness, and benefited the most from the chemical modifications. Untreated **VANSIL HR-1500** provided the greatest stiffness.
- The filler modifier that contributed the best overall balance of stiffness, strength and impact resistance was MAPP.

Table 6.
Modified VANSIL W-50

VANSIL W-50	30.0	30.0	---	---
VANSIL W-50, AS-treated	---	---	30.0	30.0
MAPP	---	2.0	---	2.0
Phenol/Phosphite Antioxidant	0.175	0.175	0.175	0.175
4 MF Polypropylene	69.825	67.825	69.825	67.825
Filler Modification	None	MAPP	AS	AS/MAPP
Tensile:				
Modulus, MPa	2491	2483	2496	2402
Peak Stress, MPa	33.2	36.3	36.0	35.8
Elongation at Break, %	11.8	13.5	15.0	18.7
Flexural:				
Modulus, MPa	2786	2884	2914	2881
Strength, MPa	58.6	62.1	61.1	62.0
Impact:				
Notched Izod, J/m	20.3	31.5	30.4	31.0
Reversed Notched Izod, J/m	418	704	582	775
Unnotched Charpy, J/m	681	1224	953	1380

Table 7.
Modified VANSIL HR-325

VANSIL HR-325	30.0	30.0	---	---
VANSIL HR-325, AS-treated	---	---	30.0	30.0
MAPP	---	2.0	---	2.0
Phenol/Phosphite Antioxidant	0.175	0.175	0.175	0.175
4 MF Polypropylene	69.825	67.825	69.825	67.825
Filler Modification	None	MAPP	AS	AS/MAPP
Tensile:				
Modulus, MPa	3148	2933	2939	2834
Peak Stress, MPa	36.7	38.6	38.4	38.3
Elongation at Break, %	10.1	15.5	18.3	23.9
Flexural:				
Modulus, MPa	3276	3246	3319	3169
Strength, MPa	61.5	64.1	64.4	64.5
Impact:				
Notched Izod, J/m	21.9	35.2	32.0	37.4
Reversed Notched Izod, J/m	397	690	633	954
Unnotched Charpy, J/m	626	1131	893	1254

Table 8.
Modified VANSIL HR-1500

VANSIL HR-1500	30.0	30.0	---	---
VANSIL HR-1500, AS-treated	---	---	30.0	30.0
MAPP	---	2.0	---	2.0
Phenol/Phosphite Antioxidant	0.175	0.175	0.175	0.175
4 MF Polypropylene	69.825	67.825	69.825	67.825
Filler Modification	None	MAPP	AS	AS/MAPP
Tensile:				
Modulus, MPa	3075	2978	3051	2961
Peak Stress, MPa	35.1	38.1	38.3	38.8
Elongation at Break, %	8.9	12.9	12.3	16.3
Flexural:				
Modulus, MPa	3498	3348	3330	3323
Strength, MPa	60.4	65.2	65.3	66.0
Impact:				
Notched Izod, J/m	21.9	29.9	25.6	32.6
Reversed Notched Izod, J/m	252	410	446	397
Unnotched Charpy, J/m	596	1004	818	1029

Conclusion

- The chemical modifications significantly affected impact strength regardless of filler size and shape. The order of effectiveness was **AS/MAPP>MAPP>AS**.
- Filler size and shape had a more significant influence on stiffness than the chemical modifications. The order of effectiveness was from the longest high aspect ratio particles to the smallest low aspect ratio particles: **VANSIL HR-1500**>**VANSIL HR-325**>**VANSIL W-50**.
- **VANSIL HR-1500** with no modification provided the greatest stiffness, although it also provided the least impact strength.
- Aminosilane-treated **VANSIL HR-325**, in combination with maleated polypropylene, provided the greatest impact strength.
- **Untreated VANSIL HR-325, in combination with maleated polypropylene, provided the best overall balance of stiffness and impact strength.**

Acknowledgement

The contribution of Crompton Corporation to the silane treatment of the wollastonite samples and to the compounding and testing of the compounds examined in this study is gratefully acknowledged. For more information on Polybond® maleic anhydride functionalized polyolefins, please see www.cromptoncorp.com or call 1-800-322-3243.

Additional Information

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