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VANDERBILT *Report*

Micro-Acicular Wollastonite in Thermoplastics

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Fillers in Plastics

In the world of functional mineral fillers for plastics - fillers that in some way improve the mechanical properties of the plastic - reinforcement is promoted by several factors:

- Smaller particle size
- Higher particle aspect ratio
- Better matrix-filler contact
- Uniform filler dispersion
- Matrix-filler adhesion

Reinforcement in this context means improving the engineering value of the composite as measured by properties such as tensile and flexural strength, flexural modulus (stiffness), impact resistance, and resistance to heat deformation or distortion.

The purpose of using mineral fillers is to lower the composite cost by replacing part of the resin while maintaining or even improving physical properties. While many polymers have inherent mechanical strength, they can be improved by adding certain fillers. Some flexible plastics, for instance, are made stronger and stiffer by talc and wollastonite. A major challenge for compounders today is to find the right balance between stiffness and impact resistance.

Wollastonite, A Functional Filler

The function of reinforcing fillers is to transfer applied stress from the polymer matrix to the strong and stiff mineral. This stress transfer will be better effected if the mineral particles are smaller, because greater mineral surface is thereby exposed for a given mineral concentration. If these particles are needle-like or platy in shape, they will better intercept the stress propagation through the plastic matrix. Likewise, intimate adhesion of the matrix onto mineral particles is essential, since air gaps represent points of zero strength. Thus, composite strength can be further enhanced if the matrix adheres to the mineral surface by means of chemical coupling agents.

Wollastonite is a commonly used functional filler in thermoplastics, particularly in polyamides and polypropylene, because it is available

- in grades with very fine particle size
- in grades with high aspect ratio, containing acicular or needle-like particles
- with mineral surface modifiers for good matrix "wetting": silane hydrophobes and titanates
- with coupling agents for matrix-mineral adhesion: reactive silanes

Many combinations of particle size, acicularity and coating chemistry have been readily available, except for ultrafine particle size together with high aspect ratio.

Wollastonite is a naturally-occurring metamorphic mineral, usually formed from the reaction of calcium carbonate and silica under intense heat and pressure. Its calcium silicate structure grows as a chain, resulting in needle-like crystals. Careful milling can retain the needle shape, as shown in the photomicrograph of VANSIL® WG (Figure 1), a standard high aspect ratio product. However, the acicularity of wollastonite particles tends to diminish in proportion to the energy used to mill successive smaller sizes. Non-acicular or so-called powder grades do, nevertheless, contain a substantial fraction of acicular particles, as seen in the photomicrograph of VANSIL W-50 (Figure 2), a nominal 1250 mesh product. These ultrafine acicular particles are short, averaging less than a 5:1 aspect ratio.

All untreated wollastonite produced by R.T. Vanderbilt Company is sold under the VANSIL trade name. Treated wollastonite is sold under the VANCOTE® trade name, with the suffix letters indicating the type of treatment.



Figure 1. VANSIL WG (170X)



Figure 2. VANSIL W-50 (1700X)

VANSIL HR-325

VANSIL HR-325 is a new micro-acicular wollastonite that provides ultrafine particle size while substantially retaining acicular particle shape, thereby extending the utility of wollastonite as a functional filler. VANSIL HR-325 has a 12:1 average aspect ratio, a 12 micron top size and a median equivalent spherical diameter of 2.3 microns. A photomicrograph of this product is shown in Figure 3.

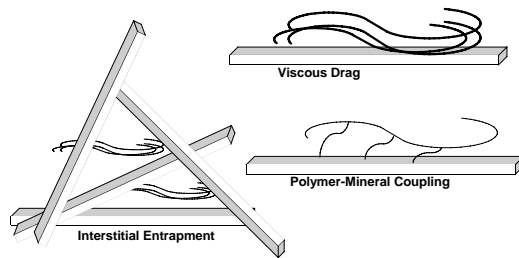
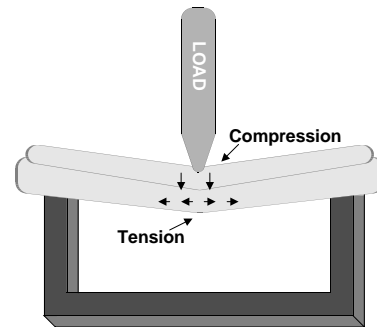


Figure 3. VANSIL HR-325 (1700X)

In order to determine the effects of enhanced acicularity on compound properties, 30% loadings of VANSIL HR-325 and VANCOTE HR-325AS (aminosilane-treated) were compared to 40% loadings of the corresponding ultrafine low acicularity VANSIL W-50

and VANCOTE W-50AS (12 micron top size, 2.8 micron median) in nylon 6,6 and nylon 6. A 40 mm twin screw extruder was used for compounding, with test specimens injection molded to appropriate dimensions. Properties of interest were flexural modulus and flexural strength (ASTM D790); tensile strength, elongation and Young's modulus (ASTM D638); Izod impact (ASTM D256); and heat deflection temperature (ASTM D648). The significance of each of these tests in assessing the effect of fillers in composites can be summarized as follows.

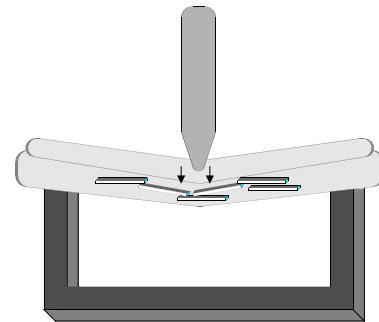
Flexural modulus is a measure of compound stiffness determined by the resistance to bending when a perpendicular force is applied to a test bar of the plastic. For the plastic to bend, the polymer chains at the point of contact must be compressed, while the polymer chains on the opposite side of the bar must stretch and move past each other.



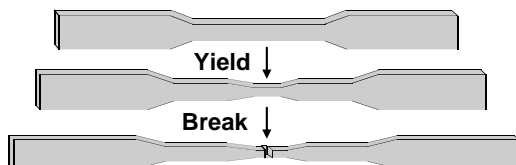
Functional fillers generally act to reduce the mobility of the polymer chains in several ways:

- through viscous drag on their surfaces.
- through bonding, as when coupling agents are used.
- through restriction of the polymer within the small interstitial spaces between filler particles.

The high surface area exposed by very fine particle size fillers and the high aspect ratio provided by needle-shaped and platy fillers restrict polymer motion. High aspect ratio fillers are particularly effective in increasing flexural modulus because they tend to align parallel to plastic flow during molding and thus expose their lengths or faces to the bending force.

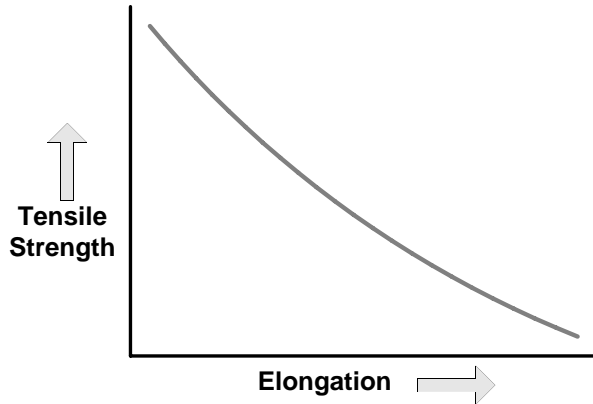
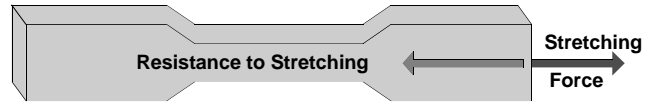


Flexural strength is an extension of flexural modulus testing and is a measure of the resistance to rupture of the outer surface of the test specimen. Since the outer surface is under tension, considerations of filler effects are similar to those for tensile strength.



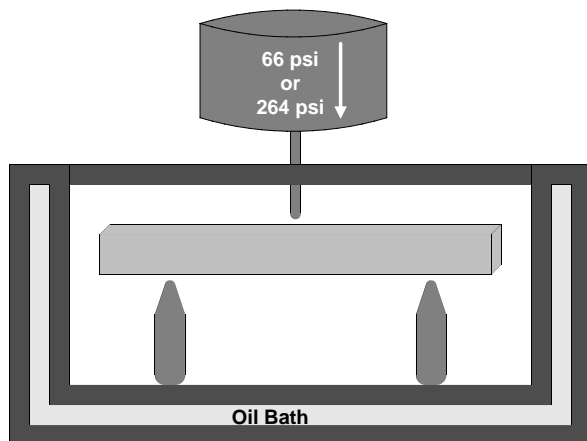
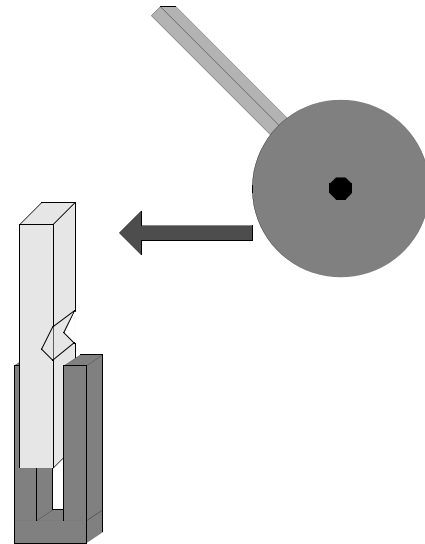
Tensile strength reflects a test specimen's resistance to rupture under tension or stretching force. Smaller particles move more readily than larger particles as the polymer chains move and extend under tension. Since high aspect ratio particles tend to align in the direction of mold flow, they are usually parallel to the stretching polymer chains, and thus do not greatly differ from similarly sized non-acicular particles in their interaction with the matrix.

Young's modulus, also called elastic modulus, is indicative of a specimen's resistance to stretching, as opposed to flexural modulus, which measures resistance to bending. It is conventionally expressed as the slope of the line obtained by plotting stress (the amount of force used to pull on or stretch the sample) vs. strain (the corresponding change in the length of the sample) while the composite is still behaving as an elastic material. An elastic material is one that will regain its original length/shape when the force is removed, i.e. before tensile yield has occurred. For a given amount of force, a plastic with high elastic modulus will stretch less than one with a low elastic modulus.



A functional filler will reduce the ability of a piece of plastic to stretch (elongate) commensurately with its ability to influence polymer chain movement. Accordingly, particle size, matrix-mineral wetting and matrix-mineral adhesion are important factors in composite elongation. Reinforcing fillers such as wollastonite usually reduce elongation as they improve tensile strength.

Impact strength is a measure of the energy required to break a test specimen with a single sharp blow. The specimen is clamped at one end and the impact force is applied near the opposite end. The test specimen is usually notched in the center to provide localized stress concentration for a clean break. The effect of a functional filler on impact strength is related to its contribution to the brittleness of the composite. The less flexible and elastic the composite, the lower its impact resistance. On a comparative basis, fillers that contribute to higher modulus and restricted elongation tend to reduce impact strength. Fibrous fillers are a notable exception: they can distribute the impact stress over a larger area perpendicular to the force of impact.



Heat deflection temperature is a measure of the softening of the composite on short term exposure to heat, and is given as the temperature at which a standard test bar deflects 0.010 inch under a fixed load. Functional fillers generally raise the softening point of plastics by restricting the motion of polymer chains. This is furthered by small particle size, high aspect ratio, and the use of coupling agents.

The micro-acicular and ultrafine powder (low acicularity) grades of wollastonite are compared in nylon 6,6 and in nylon 6 in Tables I and II. In nylon 6,6, the advantages of acicular particle shape and silane treatment are apparent when compared to the corresponding powder grades of wollastonite:

- VANSIL HR-325 at 30% loading provides flex and tensile strength equal to that from the higher loading of the ultrafine low acicularity VANSIL W-50. Stiffness (flex mod) is not quite as high with the reduced loading of the micro-acicular wollastonite, but impact strength is superior.
- The aminosilane treatment on VANCOTE HR-325AS further enhances the impact benefits of the micro-acicular product and reduces the difference in stiffness compared to VANCOTE W-50AS.

In nylon 6, VANSIL HR-325 at 30% loading, whether untreated or treated, as VANCOTE HR-325AS provides comparable or improved reinforcement overall, with both improved stiffness and significantly greater impact resistance as compared to the higher loading of the corresponding powder grades.

Table I

In Nylon 6,6	VANSIL		VANCOTE	
	HR-325	W-50	HR-325AS	W-50AS
Filler Loading	30%	40%	30%	40%
Flexural Modulus, kpsi	708	821	724	791
Flexural Strength, kpsi	23.0	22.5	23.3	24.1
Tensile Strength @ Yield, kpsi	14.3	13.6	14.2	14.2
Tensile Strength @ Break, kpsi	14.2	13.3	14.1	14.2
Yield Elongation, %	4.2	2.2	4.3	4.5
Break Elongation, %	4.4	2.3	5.8	3.2
Young's Modulus, kpsi	877	950	810	856
Izod Impact, ft-lb/in	0.83	0.48	1.05	0.59

Table II

In Nylon 6	VANSIL		VANCOTE	
	HR-325	W-50	HR-325AS	W-50AS
Filler Loading	30%	40%	30%	40%
Flexural Modulus, kpsi	701	635	658	622
Flexural Strength, kpsi	21.0	20.7	20.0	20.2
Tensile Strength @ Yield, kpsi	12.6	12.7	12.4	12.6
Tensile Strength @ Break, kpsi	11.4	12.3	10.5	11.6
Yield Elongation, %	3.5	3.4	3.5	3.4
Break Elongation, %	10.5	5.2	19.3	8.2
Young's Modulus, kpsi	758	813	714	789
Izod Impact, ft-lb/in	1.04	0.65	1.27	1.01

Polypropylene Compounds

Given its performance in nylon, the balance of stiffness and impact strength imparted by micro-acicular wollastonite to polypropylene was of particular interest. In this case, 30% loadings of VANSIL HR-325 and VANCOTE HR-325HS, (treated with an alkylsilane wetting agent and dispersant) were compared to 40% loadings of VANSIL W-50 and VANCOTE W-50AS (aminosilane-treated). The results in Table III show that VANSIL HR-325 imparts a beneficial combination of greater stiffness, elasticity and impact strength than that exhibited by VANSIL W-50 or VANCOTE W-50AS. The alkylsilane on VANCOTE HR-325HS reduced stiffness, but further increased elasticity and impact strength.

Table III

In Polypropylene	VANSIL HR-325	VANCOTE HR-325HS	VANSIL W-50	VANCOTE W-50AS
Filler Loading	30%	30%	40%	40%
Flexural Modulus, kpsi	467	407	373	378
Flexural Strength, kpsi	8.4	7.9	7.9	8.0
Tensile Strength @ Yield, kpsi	4.6	4.3	3.8	3.9
Tensile Strength @ Break, kpsi	0.5	0.6	2.4	2.6
Yield Elongation, %	5.9	7.8	4.5	4.4
Break Elongation, %	86.2	100.4	57.0	29.0
Young's Modulus, kpsi	173	121	255	370
Izod Impact, ft-lb/in	0.51	0.7	0.41	0.37

Conclusion

In nylon, VANSIL HR-325, a new ultrafine high aspect ratio wollastonite, and VANCOTE HR-325AS, its aminosilane-treated form, provide equivalent or improved performance at 30% loadings compared to ultrafine low aspect ratio wollastonite at 40% loadings. Of particular value is the improvement in nylon 6 of both stiffness and impact strength, which are usually inversely related.

In polypropylene, VANSIL HR-325 offers similar benefits, providing better impact strength and substantially greater stiffness at a lower loading. Impact strength is further improved by the alkylsilane wetting agent on VANCOTE HR-325HS.

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