



APPLIED MINERALS INC.

December 7th, 2011



DRAGONITE™

Halloysite – The Natural Reinforcement for
Elastomeric Systems

Presented by: Dr. Chris DeArmitt – CTO
Silicone Elastomers 2011



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Agenda

- Introduction to fillers
- What is Halloysite?
- Mechanical properties
- Flame retardance
- Sustained release of actives
- Availability and pricing
- Conclusions



Markets Addressed

Plastics

Productivity +20%
Mechanicals +20%
Flame retardance

Coatings & Adhesives

UV cure speed +20%
Mechanicals +20%
Improved adhesion

Environment

Oil clean-up
Soil remediation
Water purification

Elastomers

Reinforcement
Flame retardance
Thermal stability



Markets Addressed

- Additive for plastics, elastomers and coatings
- Global fillers for plastics market is > \$13 BN (> 9 Million tons)¹
 - Elastomers 50%
 - Thermoplastics 35%
 - Thermosets 15%
- Global market for fillers in coatings > \$1.8 BN²
- Global controlled release market > \$21 BN (for drugs alone)³
- Global soil remediation market \$25-30 BN⁴

1. Strategic Analysis of the Global High Performance Fillers Market, Frost & Sullivan 2008
2. World Inorganic Filler Market, Acmite Market Intelligence 2009
3. Controlled-Release Drug Delivery Analysis, Epsicom 2008
4. Advances in Applied Bioremediation, Springer 2009 ISBN 978-3-540-89620-3



Reinforcements Market

Filler	Millions of Tons	Billions of Euros
Carbon Black	4.5	3.96
Natural CaCO ₃	2.3	0.17
Precipitated CaCO ₃	0.2	0.12
Precipitated Silica	0.3	0.3
Al(OH) ₃	0.3	0.17
Talc	0.3	0.14
Kaolin	0.2	0.03
Others	0.8	0.12
Total	8.9	5.01

Source: Rothon Consultants

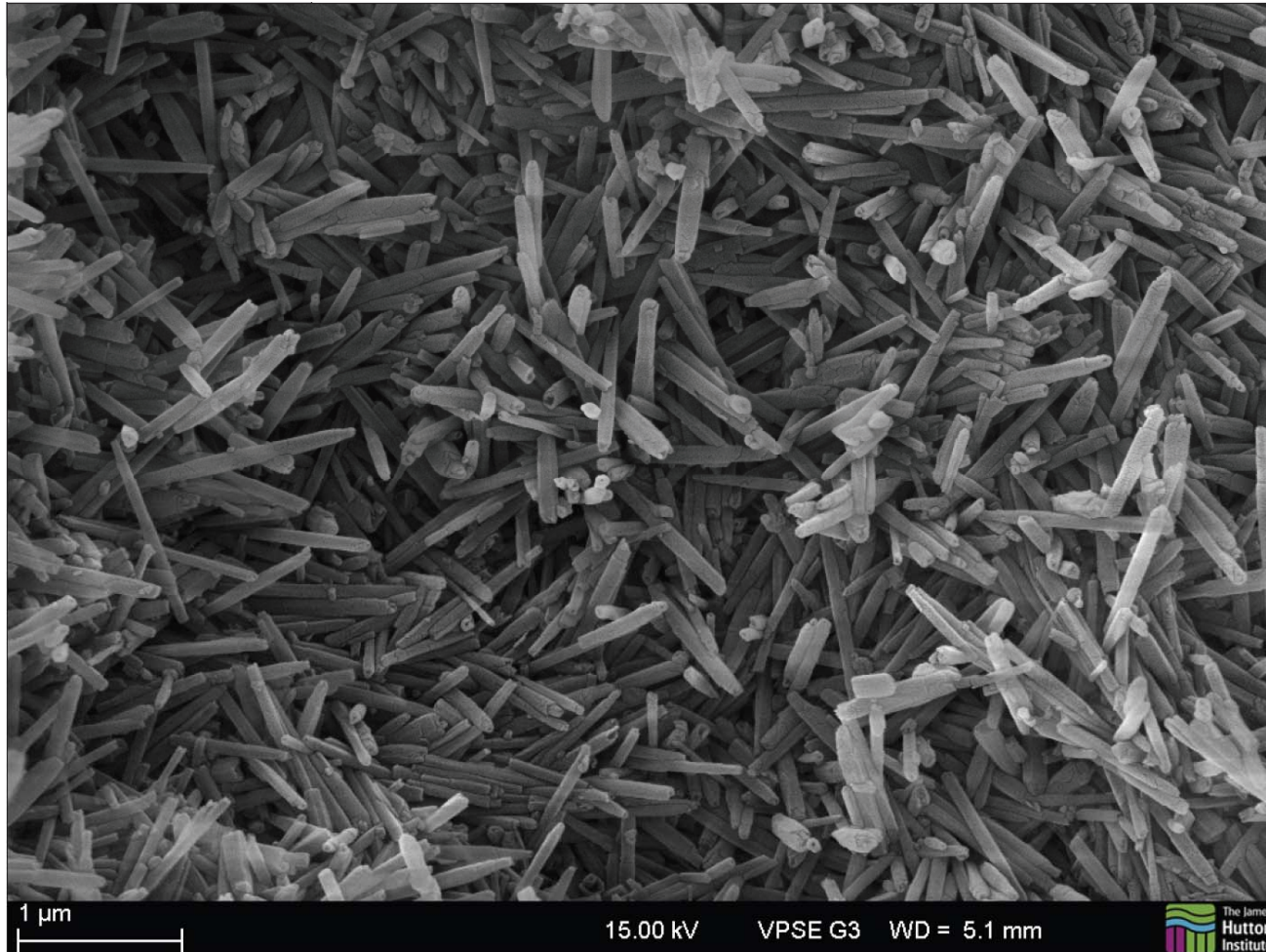
Technology Description - What is Halloysite?



- Halloysite is a natural aluminosilicate clay with a hollow tubular morphology
- Naturally exfoliated morphology means no need to chemically separate particles and makes for easy dispersion
- Halloysite nanotubes typically have diameter ~50nm with lengths ranging from 1 to 2 microns giving an aspect ratio of ~20
- Traditional uses include fine china, fillers in paints and paper, food extenders, catalysts and molecular sieves



Dragonite™ SEM



Halloysite Property Overview

- Aluminosilicate mineral: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$
- Molecular weight: 294.19
- CAS: 1332-58-7
- Density: $2.70 \pm 0.03 \text{ gcm}^{-3}$
- Refractive index at room temperature: 1.534, dried at 100°C 1.548
- Specific heat capacity: $0.92 \text{ kJkg}^{-1}\text{K}^{-1}$
- Thermal conductivity: $0.092 \text{ WK}^{-1}\text{m}^{-1}$
- Thermal diffusivity: $5.04 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$
- CTE: 10.0 ± 1.5 perpendicular to the layer, 6.0 ± 2.0 parallel
- Colorless and UV transparent
- pH in water 6.4-7.2
- Particle shape: 1-2 microns long, 50nm across, 15nm diameter hole
- Surface area: $65\text{-}120 \text{ m}^2\text{g}^{-1}$
- Dragonite™ purity: 95-100%



Dragonite™ Intrinsic Properties and Applications

High aspect ratio

- Reinforcement of plastics, elastomers, coatings etc.

High surface area

- Catalysts, adsorbents, carrier, elastomers, immobilization, nucleation of crystal growth and foam cell formation

Hollow

- Controlled release, thermal insulation, light-weighting, wicking, membranes, reverse osmosis

Bound water

- Fire retardance, temperature indicator, foaming agent

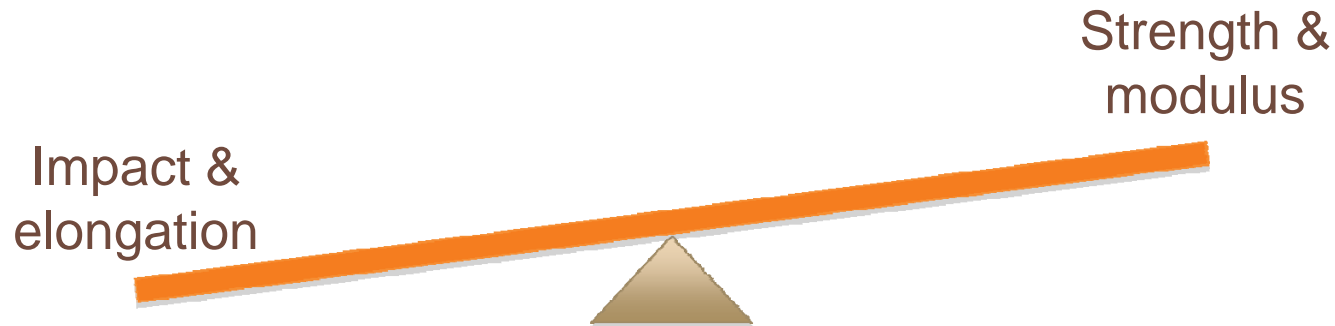


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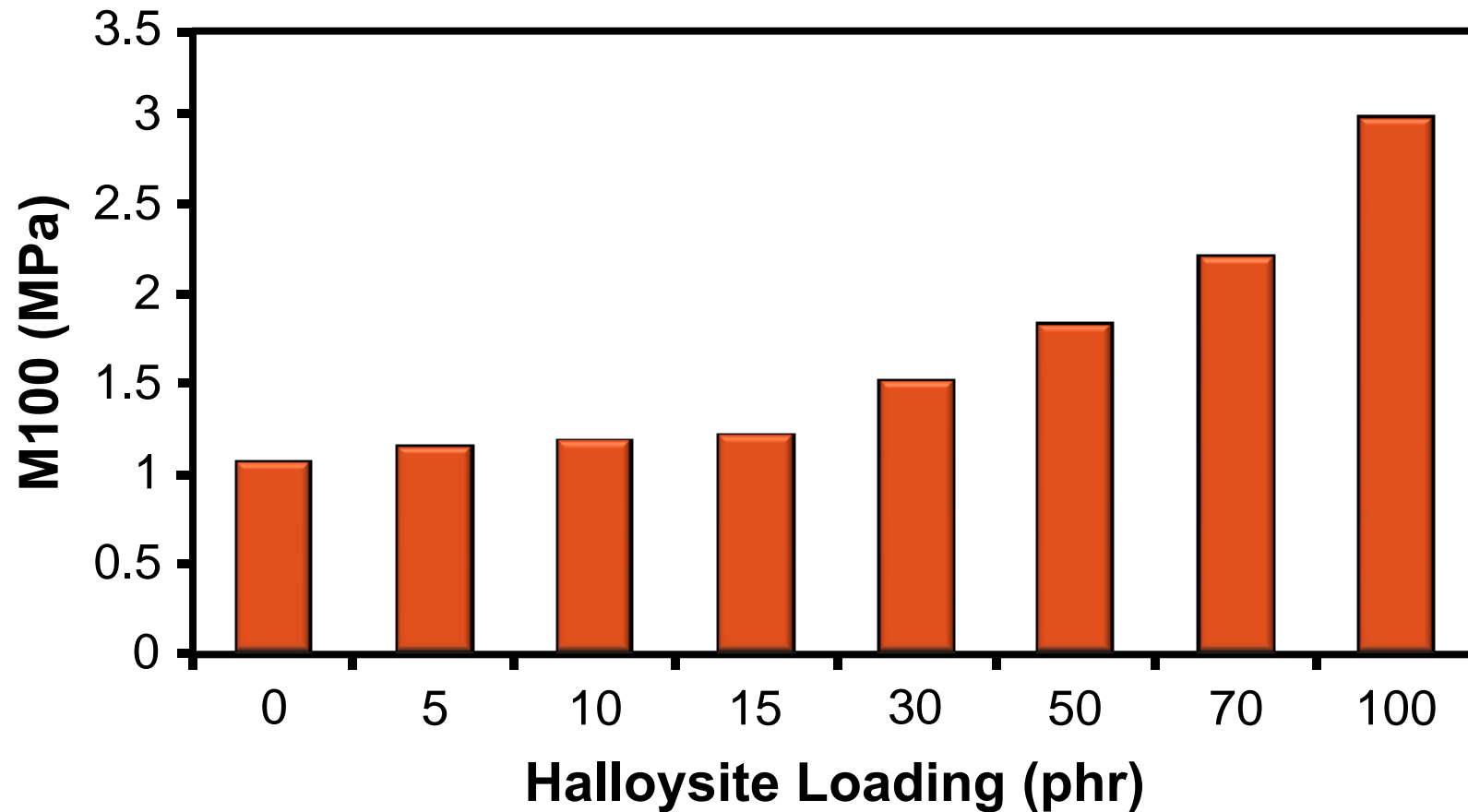
Property See-Saw



- Isotropic fillers retain impact but do not reinforce
- Reinforcing fillers ruin impact resistance and elongation to break
- Halloysite reinforces and retains or improves impact and elongation
- This is possible due to shape, surface area and easy dispersibility



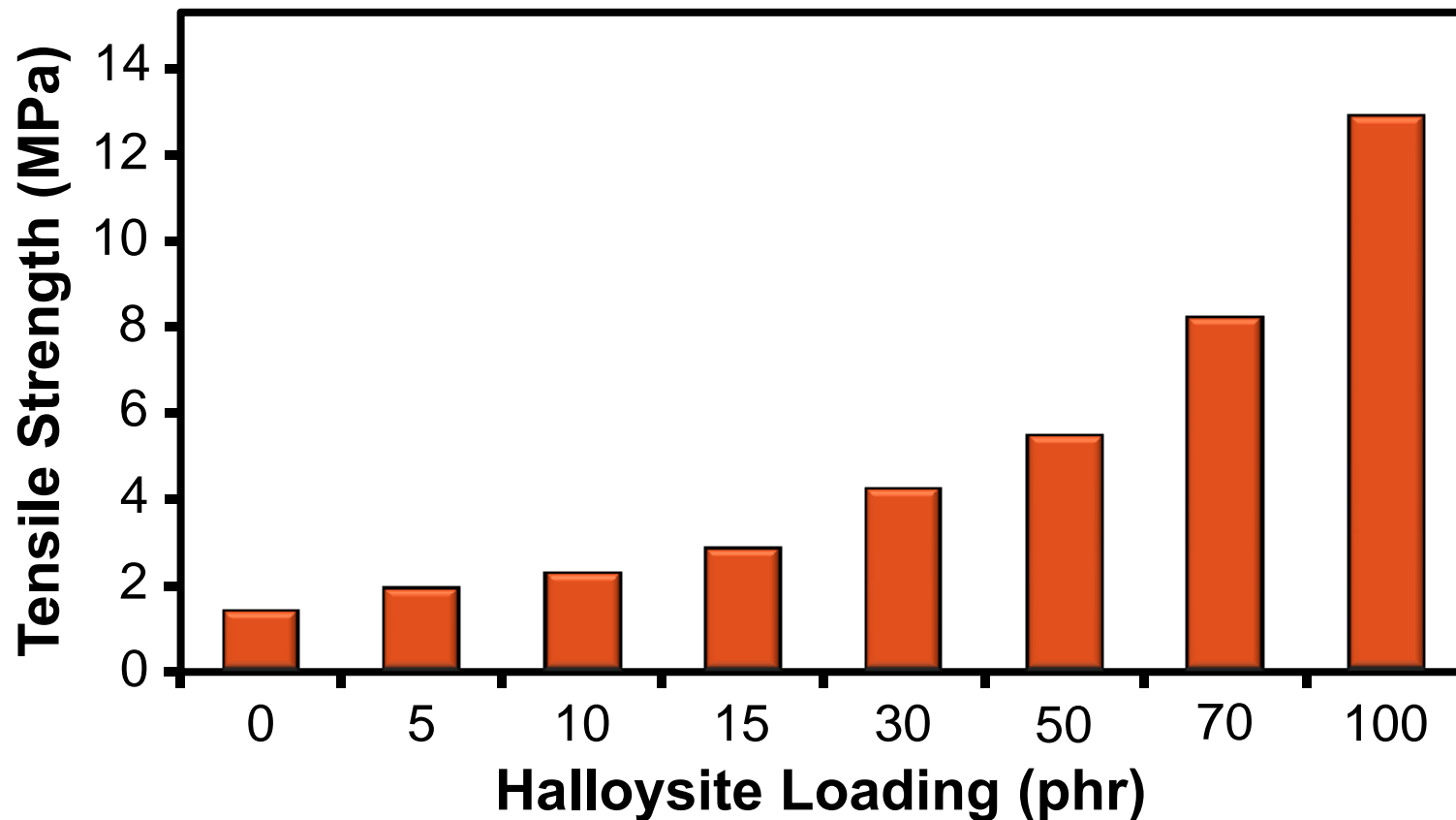
Halloysite in EPDM Rubber



Morphological, thermal and tensile properties of halloysite nanotubes filled ethylene propylene diene monomer (EPDM) nanocomposites, H. Ismail, Pooria Pasbakhsh, M.N. Ahmad Fauzi, A. Abu Bakar, *Polymer Testing* 27: 841-850 (2008).



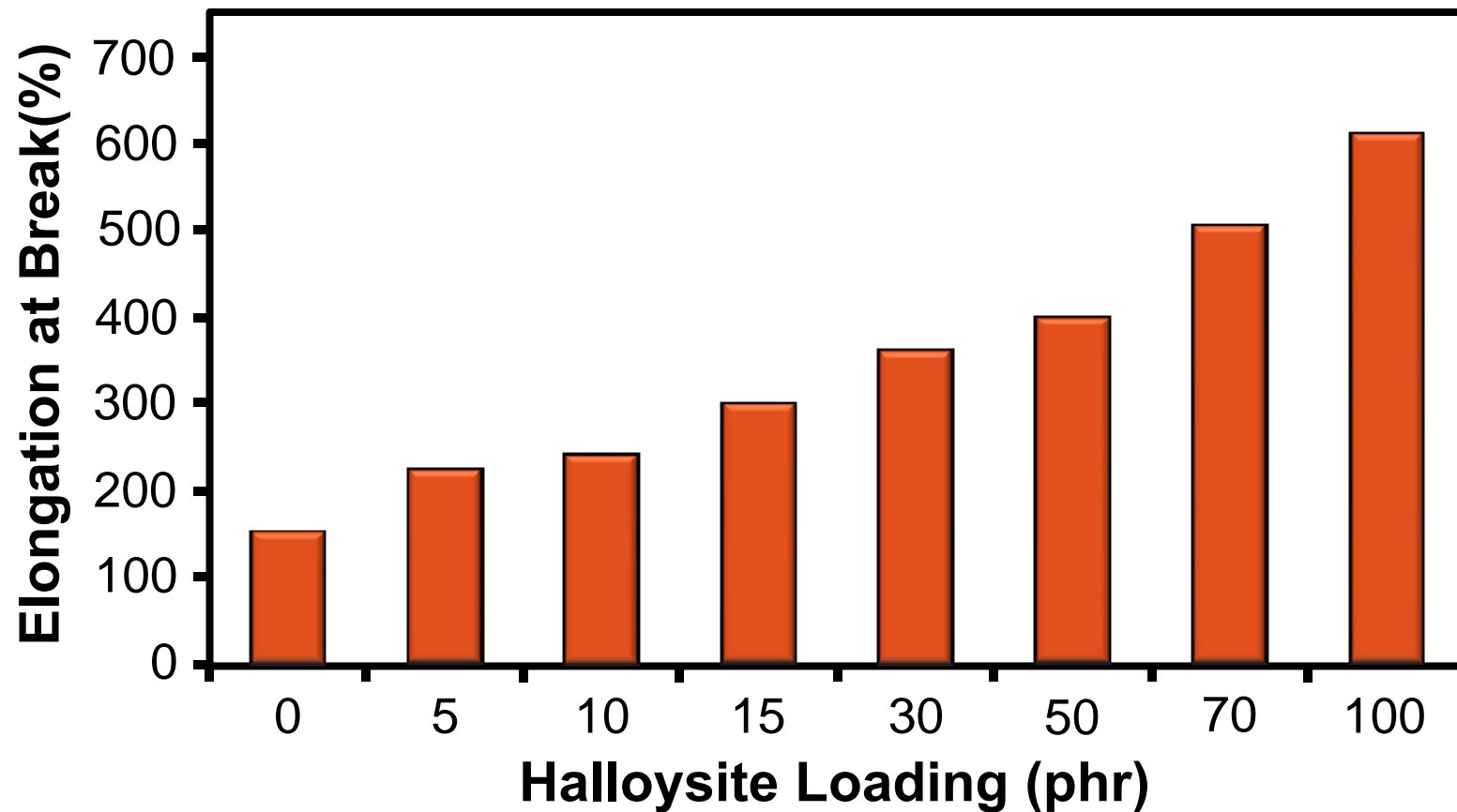
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Halloysite in EPDM Rubber

Material	M100 Modulus (MPa)	Tensile Yield Strength (MPa)	Elongation to Break (%)	UL 94 Classification
EPDM Unfilled	1.07	1.32	151	Unclassified
+5 phr Halloysite	1.16	1.94	223	Unclassified
+10 phr Halloysite	1.21	2.21	241	Unclassified
+15 phr Halloysite	1.24	2.85	299	Unclassified
+30 phr Halloysite	1.52	4.19	361	V-2
+50 phr Halloysite	1.85	5.42	400	V-1
+70 phr Halloysite	2.22	8.15	506	V-1
+100 phr Halloysite	2.99	12.86	613	V-0

Morphological, thermal and tensile properties of halloysite nanotubes filled ethylene propylene diene monomer (EPDM) nanocomposites, H. Ismail, Pooria Pasbakhsh, M.N. Ahmad Fauzi, A. Abu Bakar, *Polymer Testing* 27: 841-850 (2008).



Halloysite with Natural Rubber

Material	200% Modulus (MPa)	300% Modulus (MPa)	Tensile Strength (MPa)	Elongation to Break (%)
Natural Rubber	0.83	1.12	14	1496
+10 phr Silica	1.03	1.03	12	996
+10 phr Halloysite	1.12	1.54	18	1270
+10 phr Halloysite + silane	1.24	2.18	15	1050

Preparation and properties of natural nanocomposites based on natural rubber and naturally occurring halloysite nanotubes, S. Rooj, A. Das, V. Thakur, R.N. Mahaling, A. K. Bhowmick, G. Heinrich, *Materials and Design* 31: 2151-2156 (2010).



Halloysite with SBR

Material	300% Modulus (MPa)	Tensile Strength (MPa)	Elongation to Break (%)	Permanent Set (%)
SBR	1.33	2.4	610	4
+10 phr Halloysite	2.27	3.4	580	6
+20 phr Halloysite	3.02	4.7	590	8
+30 phr Halloysite	3.57	6.6	600	16
+40 phr Halloysite	5.09	8.4	580	20
+50 phr Halloysite	4.81	9.3	600	30

Morphology, interfacial interaction and properties of styrene-butadiene rubber/modified Halloysite nanotube nanocomposites

Z.-X. Jia, Y.-F. Luo, S.-Y. Yang, B.-C. Guo, M.-L. Du, D.-M. Jia , *Chin. J. Polym. Sci* 27(6): 857-864 (2009).

1:1 molar mixture of hexamethylenetriamine and resorcinol as coupling agent



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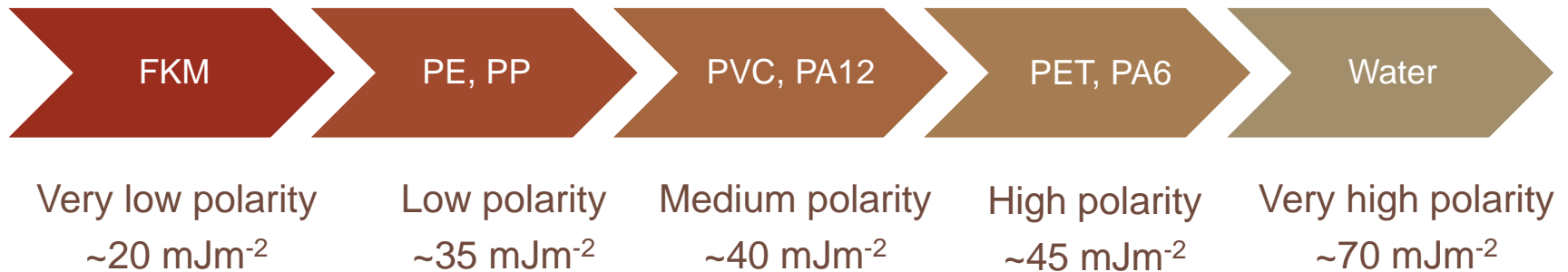
Halloysite with FKM Fluoroelastomer

Material	100% Modulus (MPa)	(E'_{∞} - E'_0) Modulus (MPa)	Tensile Strength (MPa)	Elongation to Break (%)
FKM gum	2.5	7.45	4.5	197
+5 phr Halloysite	3.0	8.50	6.2	217
+10 phr Halloysite	3.4	13.91	6.8	205
+20 phr Halloysite	3.6	15.48	7.3	200
+30 phr Halloysite	2.6	11.97	5.6	254

Tube-like natural halloysite/fluoroelastomer nanocomposites with simultaneous enhanced mechanical, dynamic mechanical and thermal properties, S. Rooj, A. Das, G. Heinrich, *European Polymer Journal* doi:10.1016/j.eurpolymj.2011.06.007.



Dispersibility of Halloysite and Polarity



- Halloysite has been shown to disperse well in all types of system, from apolar to very polar
- Wetting through the tubes gives mechanical bonding even in cases where no specific chemical interaction takes place
- In thermosets, thermoplastics and elastomers, effective reinforcement is reported even without dispersants or coupling agents
- Dispersants and coupling agents may also be used

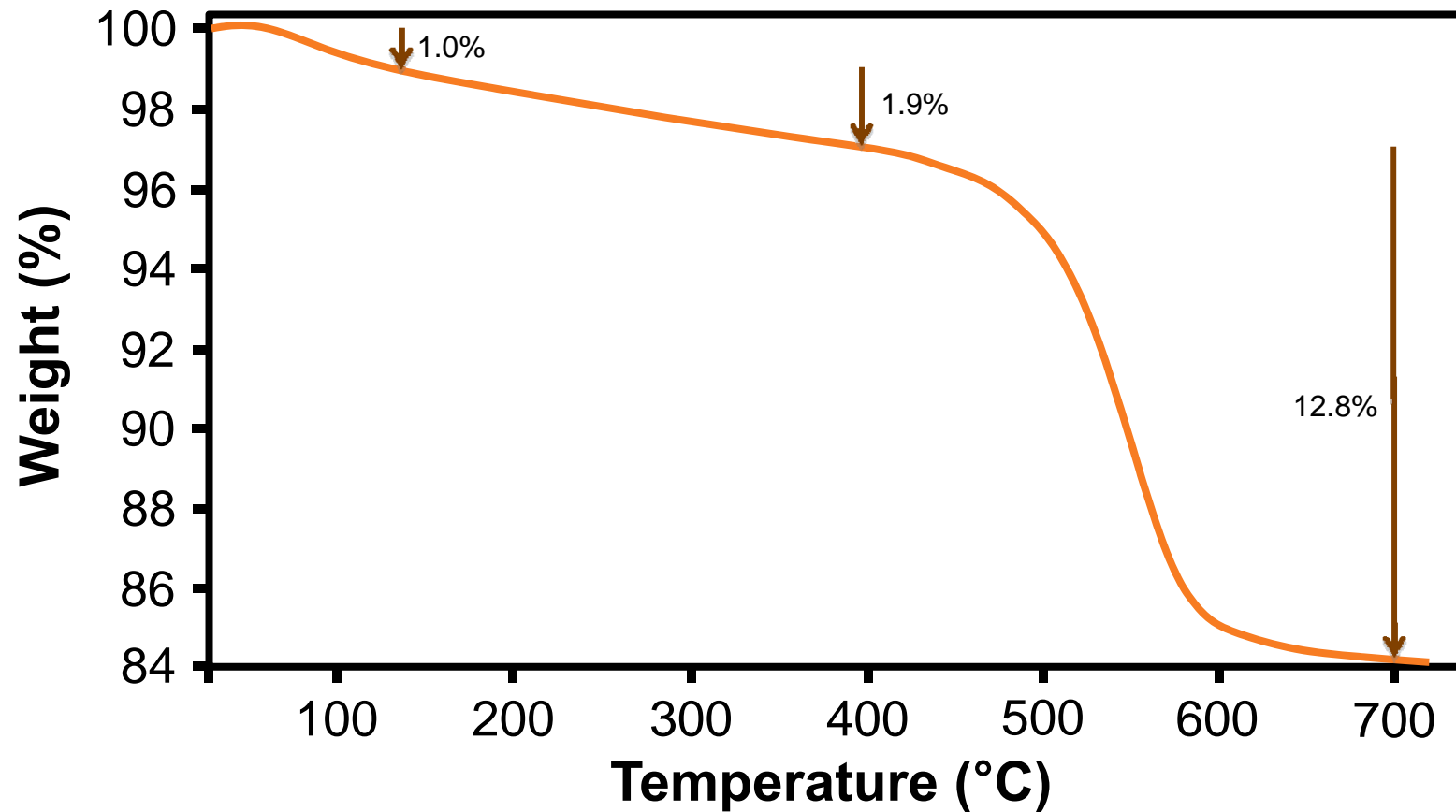


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Dragonite Thermal Stability by TGA



Flame Retardancy:

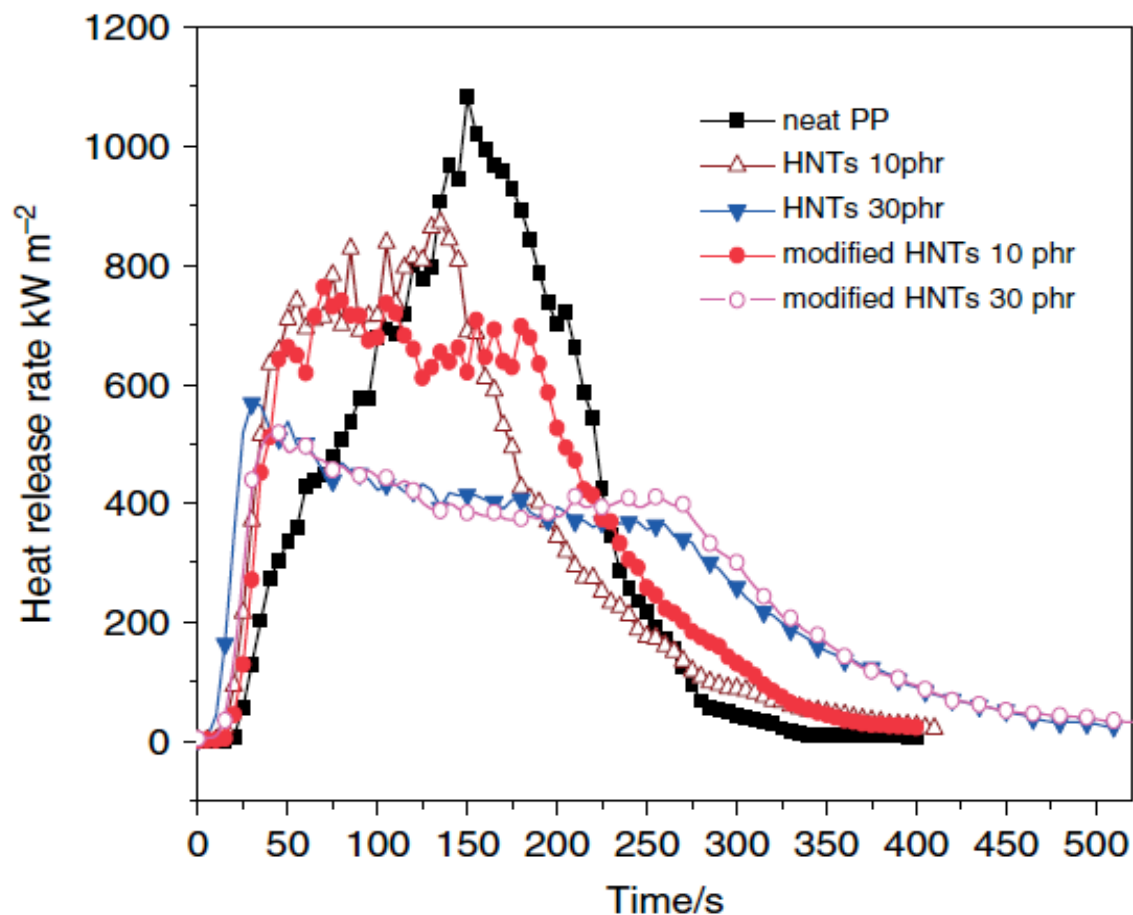
Dragonite XR vs. MDH - Magnesium Hydroxide

	Control	1	2	3	4	5
Dragonite XR	0	0	20	30	40	60
Magnesium Hydroxide (ST)	0	60	40	30	20	0
PP 20 MFI	100	40	40	40	40	40
Flexural Modulus tangent (Kpsi)	207	432	467	464	521	557
Flexural Modulus 1% (Kpsi)	212	373	391	392	440	461
Flexural Strength (psi)	6517	5131	5350	5347	5666	6200
Tensile Modulus (Kpsi)	150	277	275	285	300	294
Tensile Strength (psi)	5180	3242	3182	3189	3650	3818
Notched Izod Impact (ft-lb/in)	0.44	0.44	0.54	0.5	0.45	0.43
Smoke		low	low	very low	very low	low
UL 94 Rating		V2	V1	V1	V1	V1



Advantages of Dragonite-XR™

Reduced Flammability



Heat release rate of neat PP and PP/Halloysite composites

PET FR Development

- Reinforcing, halogen free flame retardant
- Good mechanicals in combination with glass fiber
- High water release temperature $>400^{\circ}\text{C}$ means Dragonite™ is ideally suited to polymers processed at high temperature
- Char strength boosted with Dragonite™ plus glass fiber
- Synergistic fluxing effect under investigation



30% + 5% GF

30% + 10% GF

30% + 15% GF



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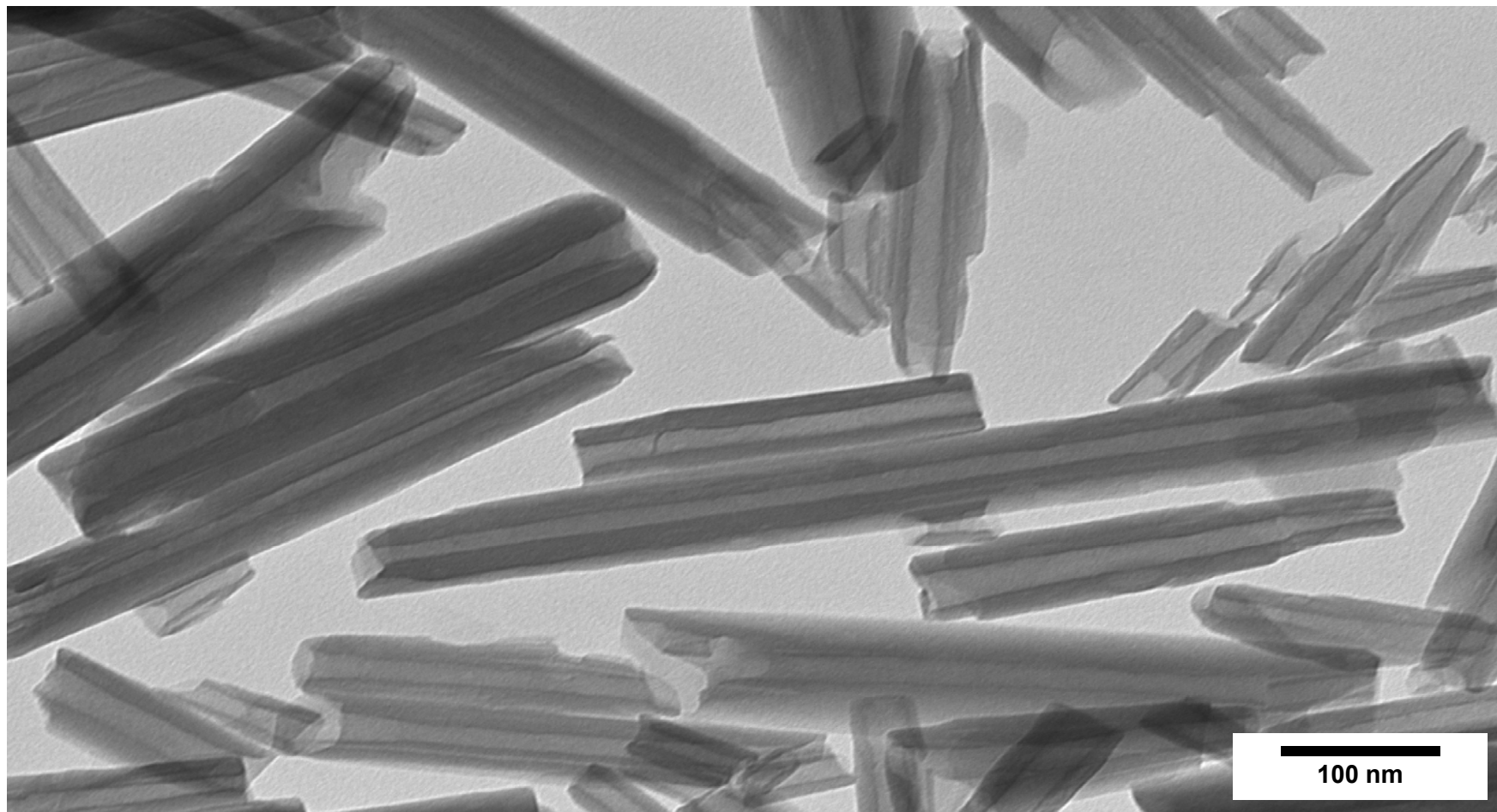
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Halloysite Tubules



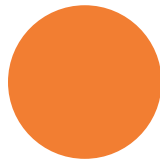
Controlled-Release

0.5 nm



Glucose
180 Da

7 nm



Hemoglobin Protein
60 kDa

15 nm



Dragonite™



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Loading the Tubes

Property	Density	Weight % Oil	Volume % Oil	Loading %*
Dragonite	2.666	0.0	0.0	0.0
1 Wintergreen	2.503	5.2	11	58
2 Wintergreen	2.583	2.7	5.9	31
3 Wintergreen	2.111	21	37	190
4 Winter & Cedar	2.479	5	12	63
5 Tinuvin 292	2.467	5.2	13	68
6 Tinuvin 292	2.448	5	13	68
7 Tinuvin 292	2.466	5.2	13	68
8 Mustard	2.620	1	2.6	14

*Based on Halloysite having 19% Lumen volume

Cedar Oil 0.95 gcm⁻³ Oil of Wintergreen 1.17 gcm⁻³ Tinuvin 292: 0.99 gcm⁻³
 50:50 Cedar + Wintergreen assumed 1.06 gcm⁻³ Mustard 1.00 gcm⁻³



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Nanotubes in Perspective

...the production capacity for all carbon nanotubes, nanofibers, graphenes, fullerenes and nanodiamonds was 4,065 tons in 2010, and is expected to exceed 12,300 tons in 2015. The actual production was less than 25% of the capacity in 2010 and about 50% of the capacity in 2015. Total production value is estimated at about \$435 million in 2010 and is expected reach a value of \$1.3 billion in 2015.

- Production capacity of the Dragon Mine exceeds the global capacity of all those materials combined
- Furthermore, Dragonite is safe, natural and is less than 1/100th the cost of even the cheapest carbon nanotubes

Availability and Pricing

- Dragonite™ brand high-purity Halloysite is commercially available from Applied Minerals
- Dragonite™ is shipped directly from the Dragon Mine in Utah, USA
- Masterbatch concentrates are available as well as neat powder
- Supply is plentiful (>30ktons) to support large-scale applications
- Pricing is in the \$1-3 / lb range
- Samples are available to interested parties
- Technical support is also available



Conclusions

- Nanotubular materials have long held great promise
- High cost, lack of availability and other factors have slowed progress until now
- Dragonite™ is 100% natural, safe, cost-effective and abundant enough to support large-scale commercial applications
- Due to high aspect ratio, surface area and easy dispersibility, Halloysite provides effective reinforcement to plastics and elastomers
- Water release at high temperature give a halogen-free FR alternative for high temperature and engineering polymers
- The hollow tubes provide a controlled release effect





Thank You For Your Time

Q&A

Contact Information

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