



Volume 2, Number 2, Fall 2014

Polymer Modifiers & Additives News

A Publication of Polymer Modifiers and Additives Division of Society of Plastics Engineers

TABLE OF CONTENTS

Division News.....	2
Chairman's Message	3
2014 International Polyolefins Conference	4
PMAD Challenge 2015	5
Featured Paper - Using ZeMac® Copolymers To Upgrade Virgin Nylon Performance	6-11
PMAD Councilor Report.....	12
PMAD Membership	13

New PMAD Officers for 2014-15

PMAD board of directors held an election in April and the following volunteers have been elected for the positions announced. PMAD congratulates and thanks them for their continued support of our Division.

- Ms. Kim Crane as PMAD Chair
- Dr. Ray Pearson as PMAD Chair-elect
- Dr. Richard (Dick) Grossman as PMAD Treasurer
- David Schultz as PMAD Secretary
- Dr. Baris Yalcin Technical Program Chair
- Dr. Saied Kochesfahani, Past President/Membership Committee Chair
- Dr. Ashok Adur as Communication Committee Chair and Newsletter Editor
- Dr. Thoi Ho as PMAD Councilor to SPE
- Ms. Bridgette Budhlall as Education & PMAD Challenge Committee Chair
- Other directors elected were:
- Frank Cangelosi, Ronald Becker, Joseph Fay
- Hayder Zahalka, David Riley, Kasinath Nayak
- Tie Lan, Tariq Oweimreen, Wei Zhao and Ernie Coleman.


PMAD/Vinyl Division Wine and Cheese Reception at ANTEC

PMAD held a joint reception with Vinyl Division and Engineering Properties and Structure Division (EPSDIV) at ANTEC on Tuesday April 29 from 5:00 to 7:00 pm. The reception was held at the Rio Suites Hotel, Las Vegas, NV and was well attended. This reception is always a good opportunity to network with peers, meet board members and communicate your views and interests.

During the reception, PMAD introduced our new officers, PMAD challenge winners, and special recognition award winners. New Chair and Officers were introduced by the outgoing Chairman, Saied Kochesfahani. Ray Pearson announced the PMAD Challenge Award Winners. Special Recognition Award Winners were given their certificates and cash awards by Kim Crane, incoming Chairperson and Dr. Thoi Ho while the Polyolefin PMAD Scholarships were given to the winners by Dr. Ho.

Congratulations to Al Whitney, 100 and going strong

Our PMAD member Al Whitney was 100 years old on August 8th. While sitting with Al at an ANTEC awards dinner a few years ago, he confided that he is related to Eli Whitney, inventor of the cotton gin! Al is still an active member of the Society and we could not be more grateful for his dedication and service. Happy Birthday and Many Happy Returns, All!



IMERYS

- **Imerys talcs for improved plastics performance**
 - HAR[®]**
 - Maximum reinforcement, dimensional stability and barrier performance
 - Jetfine[®] / JetFil[®]**
 - Best stiffness, impact balance
 - Cimpact[®]**
 - High brightness, high performance
 - Mistron[®]**
 - Efficient and low-haze anti-blocking
 - NEW Engineered talcs**
 - Superior foam nucleation
- **Full range of muscovite/phlogopite micas and kaolin products**

www.imerystalc.com - www.imerys-perfmins.com

Polymer Modifiers & Additives News

Can be found on PMAD page on SPE website at: <http://www.4spe.org/technical-groups/newsletters>

Several months ago, a very dear friend of mine, Dr. Richard Grossman, was kind enough to send me the very first volume of the Polymer Modifiers and Additives Division Newsletter. It announced that our division had been formally chartered at ANTEC in 1984. So 2014 marks our 30th year as a division of SPE. Happy 30th birthday PMAD! When I think how our industry has progressed and changed over the last 30 years, I'm amazed. But thankfully there are some things that remain the same. The people I've come to know through PMAD, and the relationships I've been fortunate enough to build through my participation in Division activities are to my mind the very best part of being a member. What a wealth of collective knowledge and wisdom is available to us all. We need only take the opportunity to become involved and get to know our fellow PMAD members. Our purpose as a Division has not changed much. In the Chairman's message of that first newsletter, Guy Martinelli stated that PMAD's scope was "To stimulate and encourage a continuing interchange of information primarily relating to the role(s) of modifying agents and additives in polymeric compositions." That continues to be our primary focus today. How we accomplish that goal and foster better communication within our membership may need updating as the years go by, but our purpose remains the same.



I am very excited about our plans for the next two years. We will continue our participation in ANTEC and the Polyolefins RETEC in Houston, and we are looking for other ways to effectively exchange information and fulfill our purpose. The PMAD Challenge is in progress and we look forward to honoring our winners again at ANTEC. This year, our Communications Committee is working to activate and improve our LinkedIn page. This is a critical step so we can take advantage of social media outlets. We invite all our members to please "link us in." It is an honor and a privilege to serve this term as Chairman of the Division. PMAD appreciates the support of all its members and we invite you to get involved and make connections that will endure throughout your working life and perhaps beyond.

Kim Crane

PMAD Chair

PMAD OFFICERS and BOARD OF DIRECTORS

- Chair** – Kim Crane, kim.crane@boral.com
- Chair-elect** – Ray Pearson, rpo2@lehigh.edu
- Past Chair / Membership Chair** – Saied Kochesfahani, saied.kochesfahani@imerys.com
- Councilor** – Thoi Ho, thoi.ho@sbcglobal.net
- Secretary** – David Schultz, schultzd@harwickstandard.com
- Treasurer** – Dick Grossman, grole@verizon.net
- Technical Program Chair** – Baris Yalcin, byalcin2@mmm.com

- Director** – Ron Becker, ron.becker@verizon.net
- Director** – Frank Cangelosi, fcangelosi@unimin.com
- Director** – Ernie Coleman, eccpt@aol.com
- Director** – David Riley, drdavidwiley@msn.com
- Director** – Joseph Fay, joseph.fay@basf.com
- Director** – Tie Lan, tie.lan@nanocor.com
- Director** – Kasinath (Kas) Nayak, Kasinath.Nayak@siigroup.com

The 2014 International Polyolefins Conference was very successful with about 690 attendees. Attendance was up about 10%, which beat the record for attendance held for 16 years. PMAD sponsored the Polyolefins Material Science and Applications tutorials and 3 technical sessions on polyolefin stabilization and modifications. The tutorial sessions were very well attended with over 140 attendees. The feedback from the attendees on the quality of the presentations and the relevance of the topics was excellent. The tutorial sessions were video recorded and posted on the conference website. There were 14 leading additives suppliers worldwide who contributed papers and shared their latest developments of products and technologies in three PMAD technical sessions. PMAD also awarded two scholarships as a means to encourage students interested in polymer additives and modifier sciences. The scholarship winners are Melissa Hawkins and Peng Li, both PhD candidates from Texas A&M University.



Thoi Ho (right) and Melissa Hawkins (left)

We would like to thank Rajen Patel (Dow Chemical), Jeanine Smith (LyondellBasell), Pierre Donaldson (Flint Hills Resources), Sudhin Data (Exxon Mobile Chemical), and Seema Karande (Dow Chemical) who served as tutorial speakers, Rick King (BASF) and J. Osby (Dow Chemical) for moderating the technical sessions.



2015 SPE INTERNATIONAL POLYOLEFINS CONFERENCE

February 22-25, 2015
Hilton Houston North Hotel
Houston, Texas USA

FOUR DECADES OF ADVANCES IN POLYOLEFIN TECHNOLOGY

Join us as the 2015 SPE International Polyolefins Conference celebrates its 40th birthday!

Over 650 technical and business professionals will attend the 2015 conference, which features 65 exhibitors, 5 Keynote Plenary talks, 80 technical papers, a tutorial session on polyolefin technology, 2 networking socials and a student poster competition.

The technical program will cover:

- Current Trends in Markets, Technology and Investments
- Innovation (Strategies and Case Studies)
- Catalyst and Process Advances in Polyolefins
- Advances in Polyolefin Stabilization
- New Polyolefin Resin and Copolymer Development
- Polymer Testing and Characterization
- Advances in Equipment and Processing of Polyolefins
- Advances in Polymer Modification
- Additives for Polyolefins
- Polyolefins in Medical Applications
- Durable Applications

Did You Miss the 2013 or 2014 Conference?

Visit the conference website to purchase past conference proceeding and Plenary/Tutorial videos. Below are some of the free videos that are available to give you an idea of what the 2015 conference will be like.

ABC News report on the 2014 SPE International Polyolefins Conference

2013 Plenary Keynote talk by Tim Roberts (VP, LyondellBasell), "Feedstocks - North American Petrochemical Industry"

Information and registration:
<http://www.spe-stx.org/conference.php>

The PMAD CHALLENGE is a technical writing competition designed to encourage student members to participate in SPE activities as well as to promote scientific and engineering knowledge relating to plastics. Monetary prizes will be awarded to the winners (both undergraduate and graduate students) of the competition who demonstrate excellence in technical writing and scientific creativity. The PMAD Challenge is sponsored by the Polymer Modifiers and Additives Division (PMAD) of the Society of Plastics Engineers.

Awards: There will be three graduate student awards (\$2,000 for 1st Place, \$1,000 for 2nd Place, and \$500 for 3rd Place) and three undergraduate awards (\$2,000 for 1st Place, \$1,000 for 2nd Place, and \$500 for 3rd Place). If a winning undergraduate student wants to carry on the proposed research, an additional award of \$1000 will be granted to support the research.

Website: Will be activated soon.

Deadline: The complete write up must be completed and received by email by midnight, Monday, January 19, 2015.

EXTRUSION ENGINEERS

DAVID W. RILEY PLASTICS PROCESSING CONSULTANT
Fellow ASTM, SPE, AIC, AAAS

Polymer Melt Flow Corrective Actions, Extrusion Analysis, Polymer Analysis by Rheology, Detection of Gels & Non-uniform Flow Particles, ASTM Quality Method Development, "PVC Specialist". Molecular Structural Analysis.

858 Princeton Court, Branchburg, NJ 08853
Business & Fax (908) 369-7260 drdavidwiley@msn.com

Minbloc®

PLASTIC FILM ADDITIVES

The Advantage is Clear

www.PlasticFilmAdditives.com

©MINBLOC is a registered trademark. All rights reserved. unimin

Leistritz

169 Meister Avenue
Somerville, NJ 08876
Phone: (908) 685-2333
Email: sales@alec-usa.com
www.leistritz-extrusion.com

Twin Screw Extruders and Systems



Leistritz manufactures modular, high speed, energy input (HSEI) twin screw extruders for compounding, devolatilization, REX, foaming, and direct extrusion. Technical services include system engineering, workshops, and a complete process laboratory.



ADVANCED PERFORMANCE ADDITIVES

Organic Bentonite Plastic Additives



AMCOL MP™
Porous Micro-particles with controlled release of active ingredient



CHAREX™
Char promoter for better flame retardant plastics



IMPERM®
Resins for high performance barrier and eco packaging



NANOMER®
Improved physical properties for resins in light-weight auto parts and wood composite applications

www.amcol.com and www.nanocor.com
Contact: Sales@nanocor.com



Discover the
Harwick Standard Difference

www.HarwickStandard.com
Phone: 330.798.9300
Fax: 330.798.4089

Harwick Standard is a premier supplier to the rubber, plastics, and adhesives industries

Advertise in PMAD News

Contact
kim.crane@boral.com or
saied.kochesfahani@imerys.com

Using ZeMac[®] Copolymers To Upgrade Virgin Nylon Performance

Ashok M. Adur and Prasad Taranekar, Vertellus Specialties Inc., Parsippany, NJ

Abstract

Nylon is widely used in many applications. At the 2013 ANTEC, our paper covered the results obtained with compounding primarily recycled nylon with the addition of small quantities of alternating copolymers of ethylene and maleic anhydride and specific property improvements for applications in injection molded compounds. The resulting compounds have performance that can match or exceed prime virgin nylon at 30-50% cost savings. This current paper will cover the unique chemistry of alternating copolymers of ethylene and maleic anhydride to provide several advantages for upgrading prime or virgin nylon. For example, this paper will cover results of increasing relative viscosity and the advantages that brings to various applications. Another set of results will cover the unique improvements obtained in impact-modified nylon-6 and nylon-6,6 by reducing the negative impact of traditional impact modifiers by offering synergistic set of properties.

Introduction

Nylons are typically condensation copolymers formed by reaction of dicarboxylic acids with diamines or by ring opening of lactams. Various nylon polymers can be synthesized by adjusting the number of carbons. The most commercially common variant of nylon, Nylon 6-6, has six carbons from the diamine, and six carbons from the diacid, and Nylon 6-12 would have six carbons from the diamine and twelve carbons from the diacid. Distinct from nylon 6-6, nylon 6 is a homopolymer formed by a ring-opening polymerization. Because each variant has a differing chemical structure, the physical properties of nylons differ with regard to their impact resistance, tensile strength, elasticity, tear strength, melting point temperature, color fastness and other properties.

Nylons are one subset of polyamides. A polyamide is a polymer containing monomers of amides. These polymers can occur both naturally, like wool and silk and other proteins, and can be made artificially through step-growth polymerization, with examples being nylons, aramids, and sodium poly(aspartate). Currently, polyamides are commonly used in textiles, automobiles, carpets, food packaging, sportswear and a myriad of other applications due to their extreme durability, strength and excellent oil resistance. Globally about 6 million MT of nylon are produced annually and this figure is expected to grow at about 3-5% every year with most of the increased production coming from Asia.

When molten, most nylons exhibit Newtonian behavior, meaning at a fixed temperature, the viscosity is essentially flat as a function of shear rate. This limits its application especially for virgin nylon into applications where melt strength is not needed. Typically applications where melt strength is important are not usually run with conventional nylon.

It is well known that fiber grade nylon typically has lower molecular weight with relative viscosity (RV) in the range of 1.6 to 2.4 (measured in sulfuric acid) and lower properties than injection molded grades with RV in the range of 2.3 to 2.8. For some specialized applications such as wear-resistant injection molding materials, high performance pipe, lower weight automotive air bags, and high strength tire cord, the viscosity of conventional nylon in the usual range of relative viscosity in the range of 2.3 to 2.8 (when measured in sulfuric acid) need to be improved all the way to the 3.5 to 5.0 RV range by a process of solid state polymerization, which is slow and expensive. An alternative method to achieve higher viscosity is by compounding with chain extenders¹.

Previous work has been based on chain extenders for nylon which are generally bi-functional compounds that are easily incorporated, thermally stable, nonvolatile and capable of fast reaction with polymer chain ends.² Inata and Matsumura³⁻⁵ identified that the maximum increase in molecular weight depends on the content of the end groups that react with the chain extender. Further studies by Yan *et al.*⁶ demonstrated that a diffusion effect can retard the progress of chain extension reaction. Simulated results of a statistical model indicated that impaired mobility in the melt can lead to wider molecular weight distributions, and lower average molecular weights⁷. However such α - Ω chain extenders result in a long linear polymer chain with resulting high viscosity, which is difficult to process. The use of styrene-maleic anhydride copolymers has also been demonstrated to provide some improvement¹.

Our previous work in this area has shown that compounding in a small amount of this 1:1 alternating copolymer of ethylene and maleic anhydride increases many of the performance properties and allows a compounder to increase melt and solution viscosity. At the 2013 ANTEC, our paper covered the results obtained by upgrading recycled nylon to match or exceed the performance and quality of prime nylon. The unique chemistry of this copolymer allows rapid increase of viscosity and the resultant polymer exhibits non-Newtonian behavior, which opens up new applications for this upgraded nylon that were not possible even with

prime quality nylon. This paper will describe the work carried out with virgin nylon and some of the results obtained.

Experimental

Materials:

Nylon 6 (grade Ultramid[®] B3S) and nylon 6,6 (grade Ultramid[®] A34) both prime quality from BASF were used. Care was taken to ensure that all grades stayed dry. A 1:1 ethylene-maleic anhydride alternating copolymer grade ZeMac[®] E60P in powder form from Vertellus Specialties Inc. with a weight average molecular weight (M_w) of 60,000 was used. A stabilizer package, consisting of 0.09% potassium iodide (KI), 0.01% cuprous iodide (CuI), 0.04% Irgafos[®] 168 (phosphite stabilizer), and Irganox[®] 1098 (hindered phenol antioxidant), was used with all compounded samples. In some cases master batch grades based on the same E60 such as ZeMac[®] Extend grades M600 and M650 containing a stabilizer package and in pellet form were also used. Some of the impact modifiers used included Fusabond[®] N493 and Royaltuf[®] 485.

Compound preparation:

Composite pellets were prepared in a counter-rotating inter-meshing twin screw extruder (Berstroff 25 mm. 32D). Some of the compounding was carried out on a 40 mm. Coperion twin screw extruder. Nylon-6 samples were run using the temperature settings of 235, 245, 255, 245, 240, 240, 240, 240°C, while nylon-6,6 samples were compounded using temperature settings of 250, 265, 275, 270, 270, 270, 270, 280°C. For the glass fiber-reinforced runs the glass fiber was fed downstream with a side feeder.

Testing:

Tensile, flexural, notched Izod impact strength and melt flow index measurements were carried out using standard ASTM methods D-638, D-790, D-256 and D-1238 respectively all at 23 °C, while Charpy impact strength was measured using the ISO-179-2/2 method at room temperature of 23 °C and at -30 °C. Heat deflection/distortion temperature was measured using ASTM method D-648. All these mechanical and thermal tests were carried out without any additional drying as molded but after conditioning test specimen as per ASTM protocol. Water absorption tests were carried after drying to equilibration to ensure that all the absorbed water has been removed and all the samples are dry. The percent increases in the amount of water absorbed were determined after 24, 48 and 72 hours. Capillary rheometry was carried out using standard capillary rheometers.

Results and Discussion

Reaction of Alternating Ethylene-Maleic Anhydride Copolymer with Nylon:

When polyamides with amine end groups are compounded with alternating ethylene-maleic anhydride copolymer a chain extension reaction even at low loadings occurs. The end-group amines of nylon react with multiple groups in 1:1 alternating ethylene-maleic anhydride (EMAh) copolymer chain as shown in Figure 1.

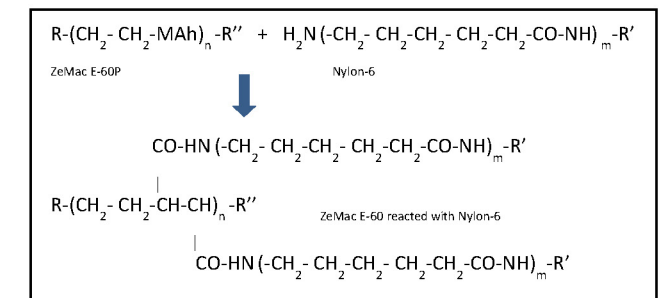


Figure 1. Reaction of nylon-6 amine end groups with multiple anhydride groups of ZeMac[®] E60P copolymer

The weight molecular weight of this ZeMac[®] copolymer grade is 60,000 while the number average molecular weight is around 27,000. This works out to approximately 216 maleic anhydride groups per molecule. These multiple anhydride groups on the ZeMac[®] E60P react with amine end groups. The resultant structure of the reactive extrusion is one where there are multiple nylon chains linked to most of the maleic anhydride groups on the EMAh molecule with a highly branched structure, as shown in Figure 2.

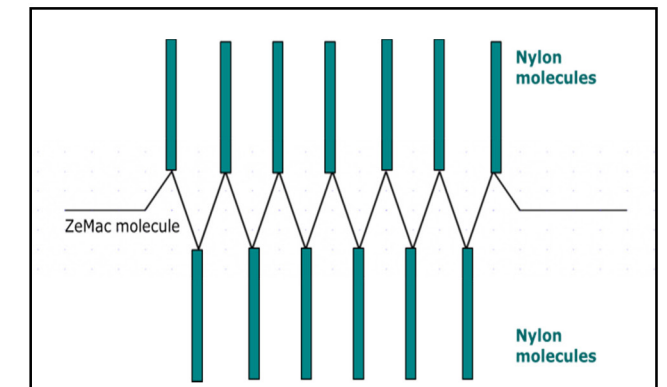


Figure 2. Shape of EMAh reacted nylon

Shear Thinning Behavior:

This change in structure from the linear nylon molecule without the reaction of the EMAh copolymer to the transformed branched structure results in the phenomenon of shear thinning. This difference is similar

to the difference between linear low density polyethylene (LLDPE), which exhibits a flatter viscosity curve than the branched low density polyethylene (LDPE), which shows tremendous shear thinning by comparison to the rheological behavior of LLDPE.

The proof of this rheological modification is demonstrated in Figure 3, where the data was generated by capillary rheometry. The increase in viscosity at low shear and hence the decrease in melt flow rate is due to chain extension. Due to the branching, at high shear the melt rheology is dramatically transformed from the almost Newtonian flat response of apparent melt viscosity as a function of shear rate to confirmed non-Newtonian shear thinning phenomenon as shown in this figure.

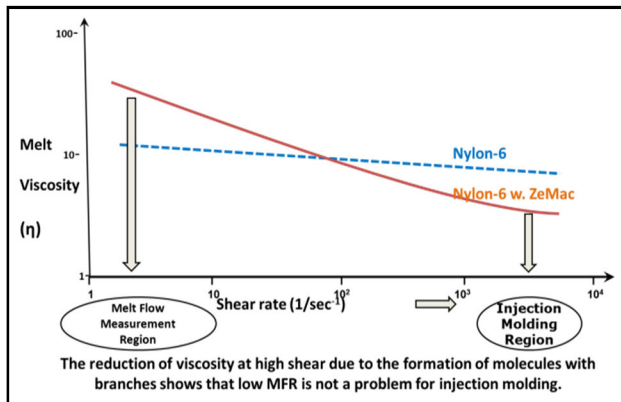


Figure 3. Shear thinning of Nylon-6 due to ZeMac® reaction

This chemically modified nylon exhibits non-Newtonian shear thinning rheology rather than the typical flatter viscosity of conventional nylon as a function of shear rate which is called Newtonian behaviour. This enables excellent injection molding in spite of the fractional melt flow rates obtained when ASTM test specimen were molded or when large parts are molded with the modified nylon. This is true irrespective of whether the polyamide is nylon-6 or nylon-6,6.

The higher melt strength that results from this shear thinning behavior allows the modified nylon to have higher relative viscosity and can open up new applications like sheet, pipe and profile extrusion, foaming, blow molding & thermoforming all of which are difficult to carry out with conventional nylon. Another advantage is the wider widths now possible after compounding with EMAh reduces overall cost of extrusion processing compared to the narrower widths without using EMAh.

High RV Nylon:

This reactive compounding can also increase in relative viscosity from the conventional nylon-6 or 6,6 range of 2.3 to 2.8 (measured in sulfuric acid) or 30 to 55

(measured in formic acid) to the range of 3.5 to 5 (measured in sulfuric acid) or 90 to 240 (measured in formic acid). The conventional process to produce such high relative viscosity is with solid state polymerization, which is relatively expensive and slow. Such high RV nylons are used in applications such as wear-resistant injection molding materials, high performance pipe, lower weight thinner gauge automotive air bags, and high strength tire cord.

The exact dosage needed to achieve a specific RV value is dependent upon the RV and amine end group levels of the starting polyamide, as well as the screw speed and output rate. The results generated with virgin nylon-6 on a 40 mm. Coperion twin screw extruder are shown in Figure 4 using two screw speeds of 185 (marked in the table as VN-6-1) and 370 RPM (marked in the table as VN-6-2) at the same output rate of 100 lb./hr. or 45.5 kg./hr. The lower screw speed of 185 RPM gives higher RV values. Also as expected the higher the dosage of the EMAh the higher is the RV of the modified nylon-6 obtained.

Experiment #	Virgin Nylon-6 %	ZeMac E60P %	RV (Formic acid)	RV (Sulfuric acid)	Output (kg./hr.) / Screw RPM
VN6-1	100.00%	0.00%	46	2.4	45.5 / 185
VN6-1 #1	99.75%	0.25%	88	3.4	45.5 / 185
VN6-1 #2	99.50%	0.50%	130	3.9	45.5 / 185
VN6-1 #3	99.00%	1.00%	144	4.0	45.5 / 185
VN6-2	100.00%	0.00%	45	2.4	45.5 / 370
VN6-2 #1	99.75%	0.25%	71	3.1	45.5 / 370
VN6-2 #2	99.50%	0.50%	98	3.5	45.5 / 370
VN6-2 #3	99.00%	1.00%	104	3.6	45.5 / 370

Figure 4. Effect of % ZeMac® E60P on RV of Nylon-6

The results generated with virgin nylon-6,6 are shown in Figure 5, where comparison is made using the same screw speed but at two different output rates with sets VN66-1 and VN66-2 compounded at 45.5 and 22.8 kg./hr. respectively and screw speed of 370 RPM.

Experiment #	Virgin Nylon-6,6 %	ZeMac E60P %	RV (Formic acid)	RV (Sulfuric acid)	Output (kg./hr.) / Screw RPM
VN66-1	100.00%	0.00%	57	2.8	45.5 / 370
VN66-1 #1	99.85%	0.15%	78	3.2	45.5 / 370
VN66-1 #2	99.70%	0.30%	83	3.3	45.5 / 370
VN66-1 #3	99.40%	0.60%	745	>5	45.5 / 370
VN66-2	100.00%	0.00%	40	2.4	22.8 / 370
VN66-2 #1	99.85%	0.15%	47	2.6	22.8 / 370
VN66-2 #2	99.70%	0.30%	54	2.8	22.8 / 370
VN66-2 #3	99.40%	0.60%	81	3.3	22.8 / 370
VN66-2 #4	99.10%	0.90%	108	3.6	22.8 / 370

Figure 5. Effect of % EMAh on RV of Nylon-6,6

In this case, much higher RV values are obtained at the higher screw output rate of 100 lb./hr. or 45.5 kg./hr. Another critical variable to evaluate is the number of amine end groups of the starting virgin nylon-6 and 6,6. We are continually developing data on the effect of this critical variable as well. Our preliminary data indicates

that the higher the amine level, the higher is the RV of the modified nylon, as you would expect. This data is being developed to enable customers to precisely choose the dose needed for each nylon grade depending upon whether it is a nylon-6, 6,6, 11 or other polyamide, the starting RV and amine value of the nylon as well as process parameters such as temperature, screw speed and output rate, which control the shear rate and residence time.

General Property Improvement:

Similar to the data presented at the 2013 SPE ANTEC, when off-spec nylon is compounded with alternating ethylene-maleic anhydride copolymer powder, general improvement in almost all properties are obtained as shown in Figure 6.

Property	Test method	Off-spec Nylon-6	Off-spec Nylon-6 + 0.75% ZeMac E60P	Virgin Nylon-6	Units
Tensile Strength @ Yield	ASTM D-638	61.1	80.8	83.6	MPa
Elongation @ Break		9.5	21	12.4	%
Tensile Modulus		2419	2541	2705	MPa
Flexural Modulus	ASTM D-790	2385	2942	2795	MPa
Flex. Strength @ Break		77.24	115.9	113.8	MPa
Izod Impact Strength @ 23°C	ASTM D-256	0.52	1	1.33	ft-lb/in
Izod Impact Strength @ -30°C		0.42	0.9	0.46	ft-lb/in
Charpy Impact Strength @ 23°C	ISO	33.8	38	33.2	KJ/m²
Charpy Impact Strength @ -30°C	ISO	14.7	29.6	22.3	KJ/m²
Melt Flow Rate @ 235°C 1 kg	ASTM D-1238	13.03	0.48	9.65	g/10 min.

Figure 6. Effect of 0.75 % ZeMac® E60P on various properties of off-spec Nylon-6

The results show that general property improvement is obtained in tensile strength, elongation and elastic modulus, flexural strength and modulus, impact strength whether measured by the Izod or the Charpy method at room temperature and at -30°C. As expected all these properties increase to approach or exceed those of prime virgin nylon-6. We have also since run and obtained similar improvements in mechanical properties of recycled nylon sourced from fishnets, carpet scrap, and post-industrial post-consumer nylon, as well as PBT, PET and other polyesters with hydroxy end groups. This data will be presented in the future.

Synergy with Impact Modifiers:

Improvements in impact alone cannot justify use of ZeMac. This is because ZeMac® does not have an elastomeric component to be a true “impact modifier”. The improvement obtained is only 33 to 100% at 0.2-1.5% loading of the ethylene-maleic anhydride copolymer. With traditional impact modifiers like EPDM-g-MAh (~0.8% MAh), or plastomeric polyethylene grafted with maleic anhydride (~1% MAh), ethylene-acrylate copolymers w. MAh (~0.8 to 2% MAh), ionomer (such as DuPont's Surlyn®), polyamides show

improvement greater than 200% for (1.0 to 2.5 J/cm) unfilled nylon compounds⁹ and about 80% (1.5 to 3.0 J/cm) in glass fiber-reinforced compounds for notched Izod impact strength using a typical impact modifier used at a typical 20%. The level of addition and type used depend upon the specific target properties needed for each application but typically 5-30% is used. However such impact modifiers reduce tensile and flexural properties by over 50% and HDT by over 20°C. They also do not improve hydrolysis resistance & tear properties. Hence such impact modifiers are not “true competitors” to ZeMac but rather complimentary products.

By using a combination of ZeMac with an impact modifier, >200% in impact strength with retention of 70-80% of other properties can be obtained. One example of this is demonstrated by a set of experiments shown in Figure 7.

Formulation			Mechanical Properties			
Virgin Nylon-6 (%)	Fusabond N493 (%)	ZeMac Extend M600 (%)	T. S. @ Yield (MPa)	Strain @ Break (%)	Flexural Modulus (MPa)	Izod Impact @ 23°C (ft-lb/in)
100			79.12	4.08	2850	1.25
90	10		65.72	8.09	2315	8.83
90	8	2	68.93	12.38	2458	8.20

Figure 7. Effect of 2% ZeMac® Extend M600 on various properties of Virgin Nylon-6 impact modified with 10% Fusabond® N493

When 10% of a commonly used impact modifier like DuPont's Fusabond® N493 is used, tensile strength drops from 79.1 to 65.7 MPa, flexural modulus drops from 2850 to 2315 MPa while Izod Impact and elongation increase substantially. By replacing some of the impact modifier with 2% of ZeMac® Extend M600 master batch grade, which contains 25% ZeMac E60P, impact properties are more or less retained but all the other properties improve.

Formulation			Mechanical Properties					
Virgin Nylon-6 (%)	Fusabond N493 (%)	ZeMac E60P (%)	T. S. @ Yield (MPa)	Tens. Mod. (MPa)	Strain @ Break (%)	Flex. Mod. (MPa)	Flex. Strength @ Break (MPa)	Izod Impact @ 23°C (ft-lb/in)
100.00			84.9	3036	5.29	2794	112.1	0.76
85.00	15		54.5	1921	9.73	1924	13.7	9.51
84.36	15	0.64	58.8	1988	25.69	1951	75.5	12.6
75.00	25		41.9	1457	13.13	1551	56.2	10.8
74.44	25	0.56	45.1	1558	19.47	1583	58.0	13.6

Figure 8. Effect of EMAh on Nylon-6 impact modified with 15 and 25% Fusabond® N493

When the same impact modifier is used at 15 and 25% the impact improvement is even more significant but the negative effect is the other properties drop even further, as can be seen from the results shown in Figure 8.

But the addition of a small amount of ethylene-maleic anhydride alternating copolymer brings most of the properties back and, in fact further improves the Izod impact strength at both 15% and 25% addition level of the

impact modifier. Similar results are obtained with another classical impact modifier that is based on an EPDM rubber called Royaltuf® 485 from Addivant. These results are shown in Figure 9.

Formulation			Mechanical Properties				
Virgin Nylon-6 (%)	Royaltuf 485 (%)	ZeMac E60P (%)	T. S. @ Yield (MPa)	Tens. Mod. (MPa)	Strain @ Break (%)	Flex. Modulus (MPa)	Izod Impact @ 23°C (ft-lb/in)
100.00			84.9	3036	5.29	2794	0.76
85.00	15		56.7	1993	13.94	2054	12.8
84.36	15	0.64	56.8	2025	28.42	2059	16.6
75.00	25		43.9	1560	13.21	1532	18.7
74.44	25	0.56	42	1516	29.57	1580	21.0

Figure 9. Effect of ZeMac® E60P on Nylon-6 impact modified with 15 and 25% Royaltuf® 485

Once again, when this impact modifier is added to the nylon the impact properties increase but all the other properties go down. However the addition of our EMAH additive remedies the negative effect of the impact modifier by recovering the tensile strength at yield, tensile modulus and flex modulus while at the same time increasing the Izod impact strength.

Another set of experiments were carried out using the same Fusabond® N493 impact modifier but in a polyamide-6,6 matrix. The results obtained at various levels of 7.5% of this impact modifier and two lower levels of 4.5% with small levels of ZeMac® E60P and ZeMac Extend M650 are shown in the Figure 10.

Formulation			Mechanical Properties			
Virgin Nylon-6,6 (%)	Fusabond N493 (%)	ZeMac E60P (%)	ZeMac Extend 650 (%)	Tensile Strength @ Yield (MPa)	Flex. Modulus (MPa)	Izod Impact Strength @ 23°C (ft-lb/in)
100.00				76.2	3259	0.7
92.50	7.5			65.8	2297	3.7
91.90	7.5	0.60		68.5	2390	3.5
94.75	4.5	0.75		76.1	2815	2.2
92.50	4.5		3.0	74.0	2456	2.2

Figure 10. Effect of ZeMac® E60P and ZeMac® Extend M650 on Nylon-6,6 impact modified with 7.5% Fusabond® N493

The results in Figure 10 show that the addition of the E60P grade powder recovers some of the tensile and flex modulus properties while not decreasing Izod impact strength significantly. When the amount of Fusabond is reduced and substituted with one of the master batch grades called ZeMac® Extend M650 or the same dosage of net ZeMac® E60P powder used, almost two-thirds of the impact strength is retained but the other properties improve.

At higher impact modifier dosages in the range of 15 to 25%, this effect is far more pronounced as the results in Table 11 show.

Formulation						Mechanical Properties		
Virgin Nylon-6,6 (%)	Fusabond N493 (%)	ZeMac E60P (%)	ZeMac Extend 650 (%)	ZeMac Extend 602 (%)	ZeMac Extend 600 (%)	T. S. @ Yield (MPa)	Flex. Mod. (MPa)	Izod Impact Strength @ 23°C (ft-lb/in)
85.0	15.0					53.0	1945	11.3
84.4	15.0	0.6				57.5	1956	13.0
85.1	12.5		2.4			60.9	2082	11.9
87.1	10.5		2.4			60.3	2148	12.6
87.5	6.5			6.0		62.2	2187	11.4
85.1	12.5				2.4	58.9	2145	14.8
87.1	10.5				2.4	61.7	2221	11.3
75.0	25.0					40.8	1390	19.7
74.5	25.0	0.5				44.9	1642	17.9
76.5	23.0	0.5				46.0	1697	17.6
75.0	23.0		2.0			46.8	1605	17.6

Figure 11. Effect of ZeMac® E60P and ZeMac® Extend grades M650, M602 and M600 on Nylon-6,6 impact modified with 15% and 25% Fusabond® N493

Once again the results show that the reduction of the tensile and flexural modulus properties by the addition of the impact modifier can be mitigated by the addition of ZeMac® E60P powder or one of the ZeMac® Extend master batch grades. In addition, by reducing the amount of impact modifier slightly and replacing it with one of the ZeMac® Extend master batch grades, all of which contain 25% of the E60P but have other differences in formulation, significant increases in tensile and flex properties can be obtained while retaining the impact strength. This approach allows the compounder to keep overall raw material costs about the same and yet obtain higher mechanical properties by taking advantage of the synergistic properties of ZeMac® copolymers and the master batch grades.

A few results on heat deflection/distortion temperature (HDT) show that EMAH can also ameliorate this reduction as well as the data in Figure 12 shows.

Formulation				Thermal Properties
Virgin Nylon-6 (%)	Royaltuf 485 (%)	ZeMac E60P (%)	ZeMac Extend 650 (%)	Heat Distortion Temperature (HDT) @ 66 p.s.i. / 0.455 MPa (°C)
100.000				188.5
85.000	15.000			145.9
87.875	12.500	0.625%		161.9
85.000	12.500		2.5%	157.7

Figure 12. Effect of EMAH on HDT in impact modified Nylon-6

What conventional impact modifiers do to the other properties of engineering plastics is well known but accepted by the compounding industry as something to live with. However the possibility that this negative effect can be reduced by using this additive has opened up new applications in automotive, appliance and other industrial markets, especially when the overall raw material costs can be kept about the same.

Future Work

Additional work is being carried out to optimize the level of the ZeMac® copolymer additives for maximum effect and to optimize the performance to cost ratio further. Also, results of low temperature (-30°C) impact strength of these compounds are being determined. type of experimental work is continuing and the results of the optimized work will be presented in the future. Work is continuing on determining the specific dosage needed for fine-tuning the relative viscosity increases of nylon-6 and nylon-6,6, especially with our master batch grades, which give more uniform incorporation. This is more critical for applications like fiber, sheet and profile extrusion. Some work for additional tests such as abrasion resistance and long term heat aging is also planned. Also testing to determine longer duration hydrolysis resistance to antifreeze will be carried out. This test is critical for automotive applications in the engine compartment. All this experimental work is also being carried out using ZeMac® E60 powder grade as well as our new master batch grades.

Conclusions

This work definitively demonstrates that such ethylene-maleic anhydride alternating copolymers are unique in improving mechanical properties and can provide value in:

- Upgrading off-spec and recycled nylon which has inferior properties,
- Increasing melt strength and relative viscosity and thus opening up new applications, and
- Reducing the negative effects of impact modifiers and in fact synergistically improving impact properties while increasing other properties such as tensile strength, flexural modulus and heat distortion temperature (HDT).

References

1. Austin, J.R. and Robb, B., paper presented at ANTEC 2010, *SPE-ANTEC Tech. Papers*, **53**, 2290 (2010).
2. Xanthos, M. Reaction Extrusion; Beijing Chemical Industry; Beijing, 1999.

3. Inata, H., Matsumara, S., *J. Appl. Polym. Sci*, **30**, 3325 (1985).
4. Inata, H., Matsumara, S., *J. Appl. Polym. Sci*, **32**, 5193 (1986).
5. Inata, H., Matsumara, S., *J. Appl. Polym. Sci*, **33**, 3069 (1987).
6. Yan, L-T., Guo, B-H., Xu, J., and Xie, X-M., *J. Polym. Sci: Part B: Polym. Phys*, **44(19)**, 2902 (2006).
7. Hargraves, M.K., Pritchard, J.G., and Dave, H.R., *Chem. Rev.*, **70**, 439 (1970).
8. Tsubouchi, H., Tsuji, K., and Ishikawa, H., *Synlett*, **63** (1994).
9. Epstein, Bennett N, U.S. Patent # 4174358 to DuPont, "Tough thermoplastic nylon compositions", November 13, 1979.

Key Words:

Impact-modified nylon, increasing relative viscosity, ethylene-maleic anhydride alternating copolymer, polyamide, nylon-6, nylon-6,6, impact modifier, chain extender, branching, branched nylon

Minutes of the SPE Council Meeting

Meeting was called to order at 1:10 PM EST
 Brian Landes presented on the following topics
 (Meeting Agenda)

1. Call to Order / Opening remarks (Brian, 5 min)
2. Discuss: combined meeting at council (All, 5 min).
3. Recommend: candidates for Vice President (Divisions, 5 min)
4. Communicate (Brian, 10 min):
 - D35 – Mold Making and Mold Design Division name and logo change
 - Applied Rheology SIG Petition to Move to Division-in-Formation
 - SIG Petition – Reaction Injection Molding Technology
5. Opportunities to partner with the Next Gen Advisory Board (Brian / All, 30 min).
6. Closing comments / Adjourn (All, 5 min)

The following were comments after the presentation:

1. Paul Browitt: Need to make existing Sections and Divisions stronger. Need to help student sections, especially in fundraising. Membership (especially international) wants to know more about getting involved and plugged in to the

resources and expertise that SPE has to offer.

2. Thoi Ho: Requested that the meeting presentation be sent out to everyone after the meeting.
3. Mark Corbett: Might prefer a 3 meeting structure where both the Divisions and Sections have their own short meeting (to take care of their specific responsibilities) and then have a combined meeting to discuss common goals and objectives. This might serve to better unify the society.
4. Mark Berard: Volunteered to be involved in Plastics 101. Will present this need to Vinyl Division and see if others are interested in participating as well.
5. Ron Markovich: There are unique activities and goals to the Divisions and Sections which might make combine meetings more challenging.
6. Jack Hill: Wanted to know how many were involved in the NGAB.
7. Jamie Gomez: Answered Jack Hill's question stating that since the formation of NGAB less than 2 years ago it has gone from 4 active members to 15.
8. Ron Markovich: Wanted to know the level of Student Activities Committee cooperation with university staff and industry.

Meeting was adjourned at 2:00 PM EST.

Our membership levels have remained fairly stable this year with some improvement over last year's figures. My report from January of 2013 listed 620 active members. We assumed there were problems with the data at that time and some of our membership was not being counted.

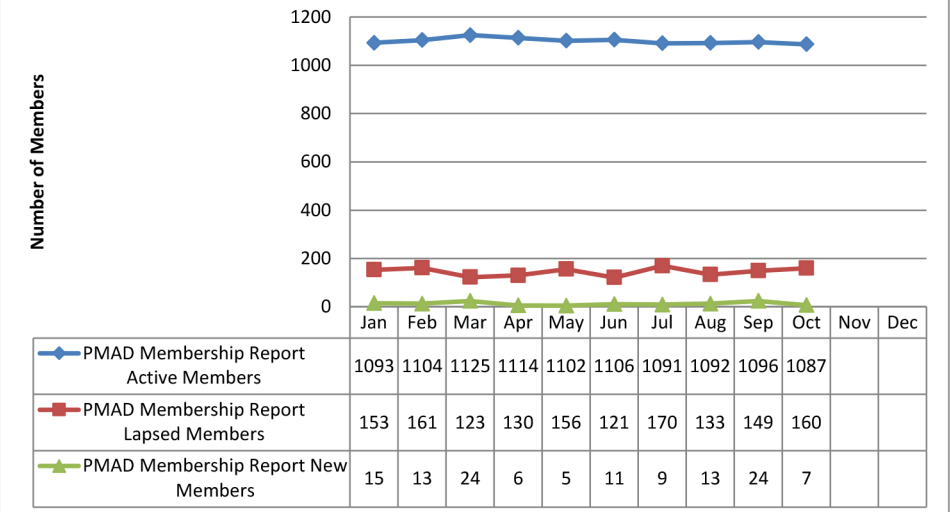

Visit Us on LinkedIn®

By Jim Botkin, Past-Chair and PMAD LinkedIn Group Moderator

The PMAD LinkedIn® Group provides a forum for our members and other professionals working in the field of polymer modifiers and additives to gather, network, discuss, and collaborate. We will also feature updates on upcoming conferences and events, our PMAD Challenge student initiative, job postings, and our latest newsletter. Please visit our group at <http://www.linkedin.com/groups/Polymer-Modifiers-Additives-Division-PMAD-3306225/about>.

Note: LinkedIn® is a trademark of LinkedIn Corp.

PMAD Membership Report - October 2014

Firebrake® ZB Multifunctional Fire Retardant

- Smoke Suppressant
- Afterglow Suppressant
- Anti-Arcing Agent
- Antimony Oxide Replacement

Rio Tinto Minerals, 8051 E. Maplewood Avenue, Greenwood Village, CO 80111
 +1 303.713.5000 • www.borax.com/markets/polymers



Expand your design possibilities – with 3M™ Glass Bubbles

New
3M™ Glass Bubbles iM16K

Featuring an ideal combination of high strength, small particle size and ultra-low density: 0.46 g/cc.

Order samples of 3M glass bubbles online at Shop3M.com

For injection molding, extrusion & more!

From utility grade fillers to high-strength additives for injection molding, 3M™ Glass Bubbles are re-shaping the way today's plastics are compounded – helping to reduce part weight and much, much more:

- Reduce part weight by 15% or more
- Make more parts per hour by improving cycle time 15–25%
- Reduce waste by improving dimensional stability
- Contribute to environmental sustainability and better fuel economy

For more information, or for help determining which 3M glass bubble is best for your application, [contact us](#).


Learn how you can **Do More** with 3M.

Visit our technical resource center for technical articles, application information, videos and more!
3M.com/engineeredadditives

©3M 2012. All rights reserved. 3M is a trademark of 3M. Photos courtesy of REHAU, Visteon and Hanil e-Hwa.

Celceram®: An excellent source of economical, recycled filler content for polymer applications!

For more information please contact
Kim Crane
kim.crane@boral.com
 C: (770) 331-3111



Submit Featured Technical Papers to PMAD Newsletter

Present your products, technologies and new developments in PMAD newsletter as long as they are related to polymer modifiers and additives and supported by strong technical content. Reach PMAD members, SPE members, and all professionals who attend PMAD sponsored events. If interested, please contact: kim.crane@boral.com