

TMG News – February, 2013



Welcome to TMG News

Welcome to TMG News, the newsletter brought to you by The Madison Group. This is a quarterly newsletter that contains plastics-related articles and information regarding educational opportunities. This issue marks the beginning of the second year of publication. We enjoy working with our clients to help them solve their plastics problems. We also believe that it is our responsibility to help educate our clients.

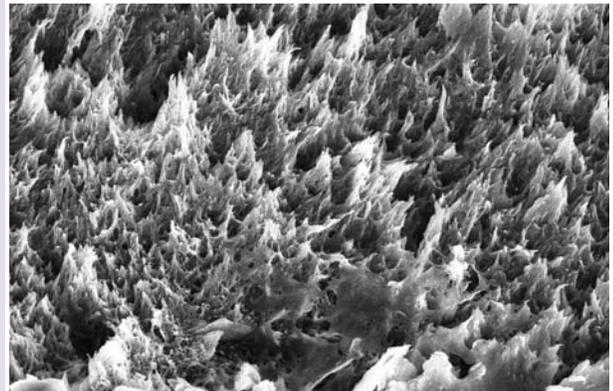
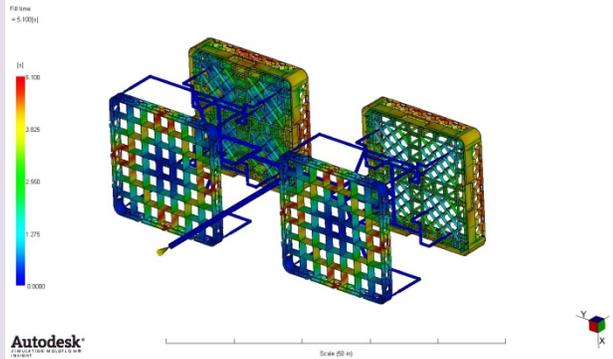
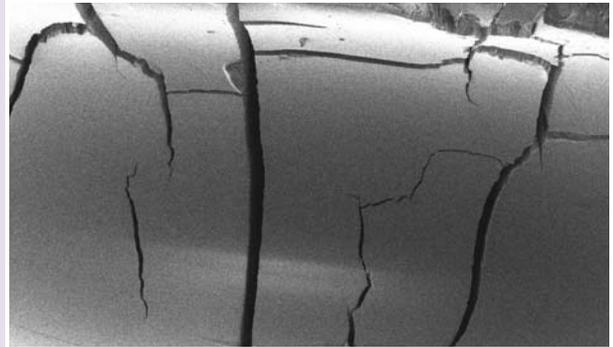
Working with plastic parts, whether in part design, manufacturing, or material or failure analysis, presents some unique challenges. The molecular structure and the resulting viscoelastic properties requires special knowledge.

This issue of the newsletter features the first of a multi-part article series that address an in-depth treatment of poly(vinyl chloride) (PVC). PVC is an important plastic material that finds wide utility across in a number of diverse applications. The second article looks at environmental stress crack testing (ESC), and in particular at the importance of ESC testing. .

I hope that you find this issue interesting and helpful. I also encourage you to contact me if you have ideas for future issues.

Jeff Jansen

If you do not wish to receive TMG News you can opt out by contacting me at jeff@madisongroup.com.



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The Madison Group
 5510 Nobel Drive Suite 215
 Madison WI, 53711 USA
 Ph: (608) 231-1907
 Fx: (608) 231-2694
 email: info@madisongroup.com

PVC Part 1: It's All About Composition

Javier Cruz, Ph.D.

Poly(vinyl chloride) (PVC) is a very unique material when compared to most other plastics. Its unique qualities make PVC one of the most used plastics worldwide. PVC is currently manufactured into an extremely wide range of products using numerous processing techniques. It is amazing to think that you could be standing over a PVC (vinyl) floor, looking through a window with PVC frames, while you open a faucet that is draining water through PVC pipes. You could even be looking at the neighbors house which probably has PVC siding or a PVC fence. Most people do not realize it, but PVC is almost everywhere. PVC is abundant in construction materials like piping, siding, flooring, and wire; but it can also be found in a variety of other applications like packaging, household products, toys and medical devices. PVC can be formulated into

materials ranging from hard and tough to soft and flexible. As shown in Figure 1, the possible ranges for the mechanical properties of this material can be extremely large depending on the formulation.

So what gives PVC the ability to have such a vast range of properties? In order to understand this, one must understand the basics of PVC.

PVC is manufactured from vinyl chloride monomer via a free radical reaction to produce a polymer with a simple backbone structure as shown in Figure 2. The structure looks much like a polyethylene except a chlorine atom replaces hydrogen resulting in a chlorine content of approximately 55% by mass. The chlorine atom is much larger than a hydrogen atom which will greatly affect the stiffness of the backbone. Additionally, a halogen atom on the backbone will also provide a unique set of chemical resistance properties.

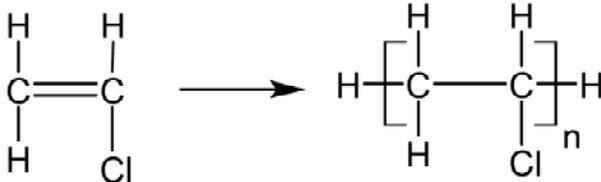
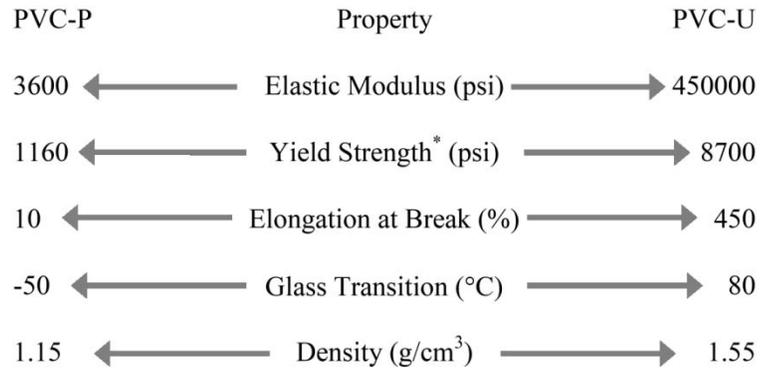


Figure 2 – Chemical structural of PVC polymerization.

Like all plastics, PVC properties can be modified by changes in the chemical structure. Molecular weight (MW) is one of the important elements directly related to the molecular structure that will have an immense effect on the mechanical properties and processing behavior. Molecular weight values are controlled at the material synthesis level, but these are also affected during processing and while parts are in service. A reduction in molecular weight due to aggressive processing or chemical attack can lead to a brittle material behavior. Other changes that can be done directly to the PVC's molecular structure include controlling the position of the chlorine atom or increasing the chlorine content. The latter results in another popular material, CPVC. However, this is a topic for another article.

Specific changes in the polymer's chemical structure can be a means of affecting the properties of the material. However, it is usually not the preferred technique for controlling most properties of PVC. The use of additives is the preferred way to obtain PVC material with the best processing and performance characteristics. In general, modifying the polymer structure



* refers to break for PVC-P

Figure 1 - Schematic showing the vast property ranges for PVC.



itself will only enhance certain properties but not all the necessary ones to make reliable products. The use of additives however, can enhance most of the properties of interest and usually at a fraction of the cost.



The truth is, that a lot of people do not know is that *PVC on its own is of little use*. Raw polymerized PVC is a material that is extremely difficult to process. It has poor heat stability and a high coefficient of friction that causes sticking of the polymer to metal surfaces of the processing equipment. If you were to process 100% PVC you would end up with overly brittle parts with very poor mechanical performance. So what makes PVC plastic such a versatile material? It is the combination of the numerous additives that make up a PVC compound.

PVC is truly a recipe of numerous additives such as fillers, stabilizers, lubricants and processing aids that are compounded together to create a plastic with unique processing and performance characteristics. The ability to use numerous individual additives provides the benefit of tailoring the material for a specific processing technique and application. In this article we will discuss several of the most commonly used additives for improving the mechanical performance of the final product. Additives specifically intended for affecting the processing of the material as well as processing effects will be discussed in the next article.

Common additives designed to improve multiple properties in the final product include plasticizers, UV stabilizers, impact modifiers, reinforcing agents and flame retardants. As evident from the chemical structure (Figure 2), PVC is a polymer with high polarity which will make it compatible with multiple other high-performance polymers. Therefore, mixing other polymers into the PVC blend is a common technique for improving an otherwise poor material performance. Impact modifiers are an example of this.

Impact modifiers as expected, will increase the toughness and prevent a brittle fracture response. Common examples of these modifiers include polymers such as ABS, CPE, EVA, and MBS. When mixing polymers such as these, other properties can also be improved. For instance, ABS will also improve the heat resistance while CPE, EVA, and MBS the processability. Many other polymers can also be added to the blend to improve other properties. For example, TPU can be mixed into PVC to increase resistance to abrasion and material elasticity. All these polymers need to be properly compounded within the PVC to result in a homogenous blend in order to optimize the material performance.

Many fillers and reinforcing agents are currently used with PVC. These may not only reduce cost but can increase the stiffness and enhance the shrinkage properties of the material. Common fillers include minerals such as calcium carbonate, kaolin and talc. Reinforcing agents can range from natural fibers to more complex reinforcements such as glass microspheres. In general, these agents can improve mechanical properties such as tensile strength, flexural modulus, and deflection temperatures.

Plasticizers are a unique set of additives that provide a whole new range of applications for PVC. We could write an entire thesis on the complexities of these additives and their interactions with the polymer. Different theories are used to explain the interaction between the plasticizer and the polymer. Whichever is more accurate, the end result is the same. Plasticizers interact with the polymer resulting in a softening effect. Plasticizers are chemicals that show good affinity with the polymer. When PVC is plasticized, the molecular weight should not be affected. Plasticizers result in chemical effects that do not cause chemical attack (i.e. chain scission) but the affinity with the chemical used as plasticizer increases mobility.



Plasticization can be undesirable if the chemical has too much affinity (too aggressive) or in certain applications where the plasticizing chemical is unintentionally absorbed by the polymer resulting in a significant reduction

in mechanical properties. The key characteristic of a plasticizer is that it needs to interact with the polymer-to-polymer molecular forces so that it reduces them, thus softening the material. However, it cannot be too aggressive or it will otherwise solvate the polymer. Furthermore, the best plasticizers are those that can interact enough with the polymer chains so that they are not readily and easily diffused (leached) out of a part while in service.



Plasticizers are added to the polymer under certain specific conditions of heat and stress. Therefore, exposure to these conditions, as well as contact with unplasticized materials of similar affinity, can allow for the plasticizer to be diffused out of the part. Currently, polymeric-based plasticizers are commonly used when there is interest in limiting plasticizer diffusion since it is more difficult for the larger molecules to freely move. For example, for medical devices, certain phthalate free alternative plasticizers have been developed due to the increasing concerns on the possibility of plasticizers leaching out of the plastic and into the human body.

For PVC, the most common types of plasticizers used worldwide are phthalates. The most common types of phthalates used include DEHP (also known DOP), DINP, and DIDP. Stronger plasticizers that cause a solvation effect on PVC show high polarity and/or aromatic rings. When a plasticizer is absorbed by the polymer, the interaction with the polymer that leads to softening effects can be observed as reduction in the glass transition (T_g), modulus, and material density. This allows for an otherwise stiff and brittle material to behave in a flexible and moldable manner which brings an altogether new set of applications for PVC material. Very common applications for flexible PVC include cable and wire, medical devices, tubing, and soft toys. One of the great benefits of most of these plasticizers is that they possess a whitish color which does not significantly affect the color of the material allowing for transparent components to be manufactured.



Analysis techniques are available for examining composition and molecular changes in PVC. These techniques can provide valuable insight into the processing characteristics and final properties of the polymer.

As discussed in this article the composition of a PVC formulation is critical to obtain the best performance for a given application. Part II of this series we will delve into processing which is another critical aspect that directly affects the performance of PVC.

If you would like more information regarding PVC or other plastic materials, please contact The Madison Group at 608-231-1907, or email at javier@madisongroup.com.

5 Educational Seminars

The Madison Group together with the University of Wisconsin - Stout will be offering a seminar entitled **“Understanding Viscoelasticity in Plastic Part Design, Processing, and Performance - What you Really Need to Know”**. This half-day seminar will highlight the importance of accounting for the time and temperature-dependent material properties of plastics to ensure product success. Often referred to as viscoelasticity, engineers and designers need to account for these unique material properties during each phase of the product life-cycle, including design, material selection, manufacturing, and service. Three separate presentations will focus on the practical aspects of viscoelasticity and will show real life examples to highlight the concepts. The attendees will come away from the presentation having a better understanding of creep, stress relaxation, life-time prediction and how simulation and material testing can be used to address these design issues during the design and processing stages.”

The same seminar will be conducted at two separate locations:

Location 1

University of Wisconsin Stout; Menomonie, Wisconsin
Tuesday, May 14, 2013
9:00 to 12:20 Presentation
12:30 to 1:30 Tour of UW Stout Plastics Lab

Location 2

Waukesha County Technical College; Waukesha, Wisconsin
Monday, June 10, 2013
9:00 to 12:20 Presentation
12:30 to 1:30 Tour of WCTC Plastics Facilities

Cost: **Free of Charge**

The seminars are being presented as an educational outreach between The Madison Group, the UW - Stout SPE Student Chapter and Waukesha County Technical College. To register or obtain more information, contact Jeff Jansen of The Madison Group at 608-231-1907 or jeff@madisongroup.com.

6 Environmental Stress Crack Testing

Jake Nemec

When plastic parts are designed and manufactured, great effort is placed into producing a part with optimal mechanical, physical, and aesthetic properties. Additionally, considerations are made to ensure that the part will be able to adequately perform in the intended environment for its anticipated lifetime without a dramatic reduction in these properties. In almost all applications, plastic parts are exposed to some form of external or internal chemical agent. This could range from hand lotion to fuel to water to numerous other substances. For a plastic part to properly function and perform for an extended period of time it must have the ability to withstand these agents. Many chemical agents can be harmful to plastic through a variety of mechanisms, including molecular degradation and environmental stress cracking. During the design and material selection phase it is critical to understand how a material will respond to the substances it will be exposed to over its useful life.

One of the difficulties in obtaining this understanding is identifying what type of chemicals the part will be exposed to during use. Once the substances are identified the question becomes, "how do I know how they will interact with my material"? The common place to look is chemical resistance tables for the plastic. These will provide information on whether cracking develops and/or the mechanical properties decrease when soaked in a variety of chemicals. These tables typically give values of 1 to 5 or "Good" or "Poor". While this is useful information, many plastic parts will fail from substances listed as "Good" or "Excellent" on these charts. It is simply not enough only to consider if a material will crack or lose strength when soaked in a substance.

Plastic parts will often behave in a porous manner with certain substances. If you've ever used an inexpensive plastic storage container that had spaghetti sauce or salad dressing in it and you forgot to wash it for a week, you've likely seen this behavior. You can scrub and scrub, but it will remain discolored. That's because the sauce or dressing has permeated between the individual molecules of the plastic and into the plastic container. If this can happen with spaghetti sauce or salad dressing, imagine how many substances might do this to your material?

Environmental stress cracking (ESC) in plastics is a phenomenon based on the simple example above. It is caused by an external substance permeating into the molecular structure of the plastic that interferes with intermolecular forces, making it easier for the individual molecules to slip and slide past each other while the part is in a stressed state. This slow disentanglement can eventually result in crack development and failure. This mechanism is not degradation and does not attack or break down the individual molecular chains. The information in chemical resistance tables is generally based on the evaluation of the effects of molecular degradation. With ESC, the molecules simply disentangle and slide apart in the presence of stress while in contact with the chemical agent. Compatibility tables may not adequately convey this effect on the plastic.

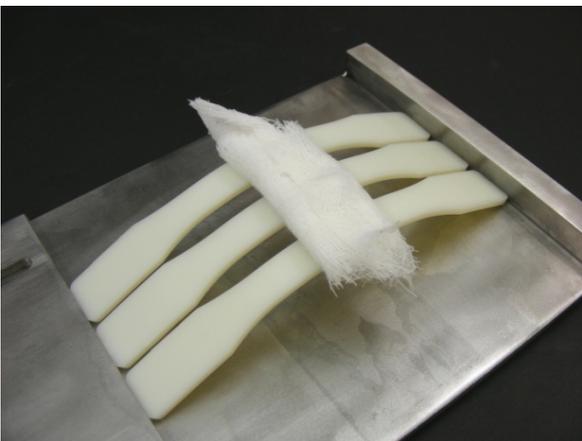


Figure 1 – ESC bend fixture.

Testing conducted to simulate ESC is based on ASTM D543 "Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents - Practice B. This test method essentially places a sample, usually a tensile or flex bar, in a continuously stressed state using controlled strain levels. There are several test fixtures that can be used for ESC testing, one such setup is shown in Figure A. The setup shown in Figure 1 bends or flexes the specimen which creates elevated tensile stresses on the outer edge/apex of the bend. The chemical agent is then locally applied to the surface of the specimen at the apex of the bend. This locally exposed area of the sample is periodically inspected for crack development during the lifetime of the test. An example of typical cracking is shown in Figure 2. By using a sample of known dimensions the strain level can be calculated and the test fixture can be set to generate the calculated strain value.

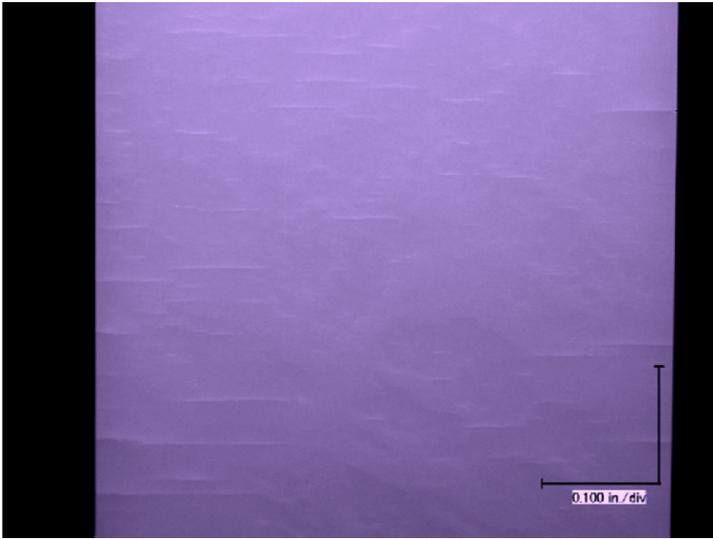


Figure 2 – Photomicrograph showing ESC cracking on a test specimen.

Furthermore, with a known modulus for the material the stress level can also be calculated. This can provide a stress at which ESC will occur when the plastic is exposed to certain chemical agents. When coupled with stress levels predicted in a finite element analysis (FEA) of the part, predictions can be made on whether a part will fail from ESC when in contact with chemicals that it anticipated to be exposed to during use.

It should be noted that ESC can occur even when external loads are not applied to the part. Molded-in residual stresses and thermal stresses in the presence of an ESC agent can also be sufficient to produce cracking. Whether you're hoping to avoid future failures or you're already experiencing failures, ESC testing can be a crucial test during failure analysis of plastic parts and the material selection/design process.

If you would like more information regarding ESC testing please contact The Madison Group at 608-231-1907, or email at jake@madisongroup.com.

Upcoming Society of Plastics Engineers Webinars

Educational Opportunities - SPE Webinars

Webinars provide a cost effective way to expand knowledge of plastics. The Society of Plastics Engineers (SPE) offers a wide selection of high quality webinars, many of which are taught by experts within The Madison Group. Below is a list of the upcoming webinars:

An Introduction to Plastics Wednesday, March 6, 2013 10:00 AM Central Time	Jeffrey A. Jansen
Weldlines: the Good, the Bad and the Ugly Thursday, April 4 th , 2013.	Erik Foltz
The Effects of Impact and Other Rapid Loading Mechanisms on Plastics Wednesday, May 1, 2013 10:00 AM Central Time	Jeffrey A. Jansen
Basic Rubber Technology Tuesday, July 16, 2013 10:00 AM Central Time	Jeffrey A. Jansen
Thermal Analysis in Failure and Compositional Analysis Thursday, September 12, 2013 10:00 AM Central Time	Jeffrey A. Jansen
Multi-factor Failure of Plastics Wednesday, November 6, 2013 10:00 AM Central Time	Jeffrey A. Jansen

For more information on the courses or to register, contact SPE's Barbara Spain at 203-740-5418 or bspain@4SPE.ORG.

TMG Tidbits

Article on Benefits of Integration of Moldflow Analysis on Plastic Part Design

Erik Foltz of The Madison Group is featured in the February 2013 issue of *Appliance Design Magazine*. His article, "Early Design Simulation Saves Cost and Time", highlights how the use of injection molding simulation early in the design process can benefit Original Equipment Manufacturers (OEMs) and design engineers in the optimization of plastic part design. While such analysis has traditionally been reserved for injection molders and toolmakers, the integration of this tool can help part designers identify potential problems earlier in the design stage, saving money and reducing time-to-market. Read the full article on appliance-design.com at <http://digital.bnppmedia.com/publication/?i=143490&p=16>.

TMG Simulation Adds Another Autodesk Moldflow Certified Analyst

The Madison Group is pleased to announce that Ross Jones has achieved his Associate certification from Autodesk Moldflow. As an analyst, Jones helps OEMs, molders and toolmakers optimize and troubleshoot injection molding processes and plastic part designs. He can assist clients with gate location selection, material selection, mold filling optimization, cooling optimization, and warpage troubleshooting. In addition to his certification, Jones is a degreed composite materials engineer from Winona State. For more information about The Madison Groups Moldflow services please visit our website.

(<http://madisongroup.com/engineering/moldflow.html>)

SPE Milwaukee Section Presentation "Analysis of Plastic Parts Using CT Imaging"

The Madison Group's Dr. Paul Gramann will give a presentation entitled "Analysis of Plastic Parts Using CT Imaging" at the upcoming Milwaukee Section meeting of the Society of Plastics Engineers

Abstract:

Analyzing the inside of an enclosed assembled plastic part is a formidable task without the use of invasive or destructive methods, e.g. sectioning the part. Invasive and destructive analysis can alter the part by deforming walls or seals and may not reveal the true state of the part prior to sectioning. Computed Tomography (CT) imaging has been used in the medical field for many years to analyze the fine details of the internal structure of the human body. This same technique, now being applied to analyze plastic parts, uses high resolution and accuracy without special preparation or modification of the part. CT imaging delivers a full 3D image of the part that can be electronically sliced and oriented at any location. This extremely powerful technique allows one to detect voids, view the actual assembled state of the part, perform metrology, reverse engineer a part, and help determine cause and origin of failure. This presentation will review the advantages and limitations of CT imaging as well as how it can be used in the plastics industry. Several case studies will be given throughout the presentation.

Date: Tuesday, February 19, 2013

Time: 5:30 PM - Networking

6:15 PM - Dinner

6:45 to 7:30 PM - Presentation

Where: Wildwood Lodge

N14 W24121 Tower Place

Pewaukee, WI 53072

For more information and registration visit <http://www.milwaukee-spe.org/>.