213

Composite Particles, Inc.

2330 26th Street S.W. • Allentown, PA 18103
phone: 610-791-9900 • fax: 610-791-2486

SURFACE-MODIFIED RUBBER PARTICLES IN POLYURETHANE

Bernard D. Bauman

COMPOSITE PARTICLES, INC.
2330 26th Street, S.W.
Allentown, PA 18103

(610)791-9900

Presented at the Polyurethane Manufacturers Spring Meeting
Wesley Chapel, Florida
April 9 - 13, 1994

SURFACE-MODIFIED RUBBER PARTICLES IN POLYURETHANE

Bernard D. Bauman

COMPOSITE PARTICLES, INC.

INTRODUCTION

A new type of material, surface-modified rubber particles, is a novel reinforcing, *elastomeric filler*. The combination of these particles with polyurethane represents a very important development for the polyurethane industry. Rubber and polyurethane are both recognized as families of materials having desirable and unique physical properties. For many applications, such as industrial wheels, the two materials compete with each other. Surface-modification of the rubber particles enables one to effectively combine polyurethane and rubber. This results in formation of composites in which rubber particles are dispersed in a continuous phase of polyurethane. The resulting new class of polyurethane/rubber composites are lower in cost than pure polyurethane formulations, and frequently have performance benefits as well. Surface-modified rubber particles hold promise to significantly expand the markets for polyurethanes by altering its performance/cost ratio and make it more competitive with other materials.

This paper describes the technology of surface-modification of rubber particles, discusses molding techniques, characterizes properties of some rubber/polyurethane composites, and reviews applications that have been developed to date.

SURFACE-MODIFIED RUBBER PARTICLES

Rubber and polyurethane are generally incompatible and can not be combined to give homogeneous material with good physical properties. With rubber particles being non-polar and polyurethane precursors being fairly polar, trying to combine the two is like mixing oil and water. Even if one does force them together, there is generally very little bonding at the interface between the two materials. Hence, the combination of non-treated rubber particles with polyurethane generally gives materials with poor physical properties, and which have relatively little commercial usage, primarily in applications having low performance requirements.

With a patented, proprietary surface-modification, rubber particles are rendered compatible with polyurethanes. The surface-modification is a controlled oxidation of the outermost molecules on each rubber particle. The treatment chemistry is the reaction of halogen and oxygen gases with the rubber backbone to form pendant polar functional groups. In fact, the rubber surface becomes so hydrophilic that the treated particles are readily wetted by water.

Surface-modification also enables excellent interfacial bonding between the rubber particles and the polyurethane. The effectiveness of this surface-modification in facilitating adhesion is demonstrated by comparing the bond strength of strips of rubber with polyurethane cast on them. In T-peel tests, it was found that where polyurethane was cast onto non-treated strips of rubber, the bond strength was 3 lb./inch. In analogous tests with strips of surface-treated rubber, the bond strength exceeded 150 lb./inch; the rubber tore before the adhesion bond failed.

Because the modification involves a chemical change to the backbone, the treatment is permanent.

These surface-modified rubber particles are now commercially available from Composite Particles, Inc. under the VISTAMER™R trade name. The various product grades differ in particle size, ranging from diameters of 1.5 mm (10 mesh) down to less than 175 μ (80 mesh).

The quality of our treated rubber products conforms to the highest standards. At this time, all of our rubber starting material is derived from truck tire treads. This is a high performance rubber material that is widely available and is essentially free of metal and fiber. Tire buffings, generated during the tire retreading process, represents a uniform source of rubber. There are several well established companies that are in the business of performing fine grinding on such rubber materials. The ground rubber that we purchase is certified to be within defined specifications in terms of particle size distribution, types of rubber, filler content, and extraneous materials. In addition, we perform analyses on in-coming raw materials and out-going products.

HYGROSCOPIC NATURE

The moisture content of treated rubber particles has been found to be an important variable. We have developed grades of super-dry rubber particles that circumvent this complication.

It has been discovered that surface-modification causes the rubber particles to become very hygroscopic. The polar surface readily absorbs moisture from the atmosphere. Laboratory studies have shown that treated rubber particles can absorb as much as 1.4% moisture by weight, and that the particles can absorb moisture at a rate greater than 0.15% in 15 minutes when exposed to the atmosphere.

Not all of the moisture in treated rubber particles is available for interference with the polyurethane chemistry. Some of the moisture is located deeper within each particle, which takes longer time to permeate to the surface. The particle size of the rubber is an important variable in determining the available moisture, since surface area is a function of particle size.

Different types of polyurethanes have various degrees of moisture sensitivity. Some formulations require super-dry rubber particles (< 0.05% H_2O) to prevent foam formation. Other formulations seem to work equally well with less dry particles. It should be noted that even if foaming is not experienced or if it does not pose a problem, it still might be that the water will alter the stoichiometry and inadvertently diminish the polyurethane properties. This in turn would reduce the overall properties of the composite.

A process has been developed for the manufacture of super-dry rubber particles. This material is sold under the trade name of VISTAMER™RD. The hygroscopic property of the treated rubber particles means that this material must be stored in moisture barrier packaging, and that it should not be left exposed to atmospheric moisture any more than necessary.

ECONOMICS

The current price for treated rubber particles is in the range of $0.53 to 0.95/lb., depending primarily on the particle size. For super-dried versions, there is an additional cost of about $0.50/lb. This pricing is based on production in our current 5 million lb./year pilot, and using a relatively inefficient drying system. As commercial demand for these materials builds, production capacity will be increased. Economy of scale will result in further cost reductions, particularly for the super-dry materials (VISTAMER™RD). In the future, treated rubber, including super-dry material, is projected to be in the range of $0.30/lb. to 0.75/lb.

The most obvious incentive for using treated rubber in polyurethanes is cost reduction. With polyurethane resins priced in the range of $1.00 to over $4.00/lb., there is significant raw material cost savings with incorporation of treated rubber particles. For example, a molded part made in 25% treated rubber costing $0.65/lb. and 75% polyurethane costing $3.50/lb. will have raw material costs 20% lower than if it were molded in pure polyurethane.

PROPERTIES OF RUBBER/PU COMPOSITES

The physical properties of composites made with treated rubber particles in polyurethanes are similar to those of the pure polyurethane. This is exemplified in TABLE I., where the properties of a composite consisting of 15% treated rubber particles/85% polyurethane are nearly indistinguishable from those of the base polyurethane. The modest reduction in ultimate tensile strength is not considered of importance since few applications for elastomeric urethanes involve elongation greater than 100%. Composites comprising as much as 40% treated rubber particles have been shown to have good engineering properties.

For many applications, 20% to 25% treated rubber particles can be used to make specific end products with little or no change in the polyurethane formulation.
This amount of rubber will make the part gray to black, depending on the particle size of the rubber particles. With the use of color pigments, colors are made darker by the rubber particles. When fine particle sized treated rubber is used, it is almost impossible to see the rubber particles in the end products with the naked eye.

Treated rubber is the only known reinforcing, elastomeric filler. The use of VISTAMER™R, in general, does not make the formulation harder and less flexible. Most other fillers are inorganic minerals, which reduce the elastomeric properties of a polyurethane formulation. Oils are used as fillers for some polyurethanes and increase the flexibility. However, they certainly are not reinforcing fillers, and they significantly reduce overall properties.

TABLE 1

PHYSICAL PROPERTY COMPARISON
(HIGH PERFORMANCE PU)

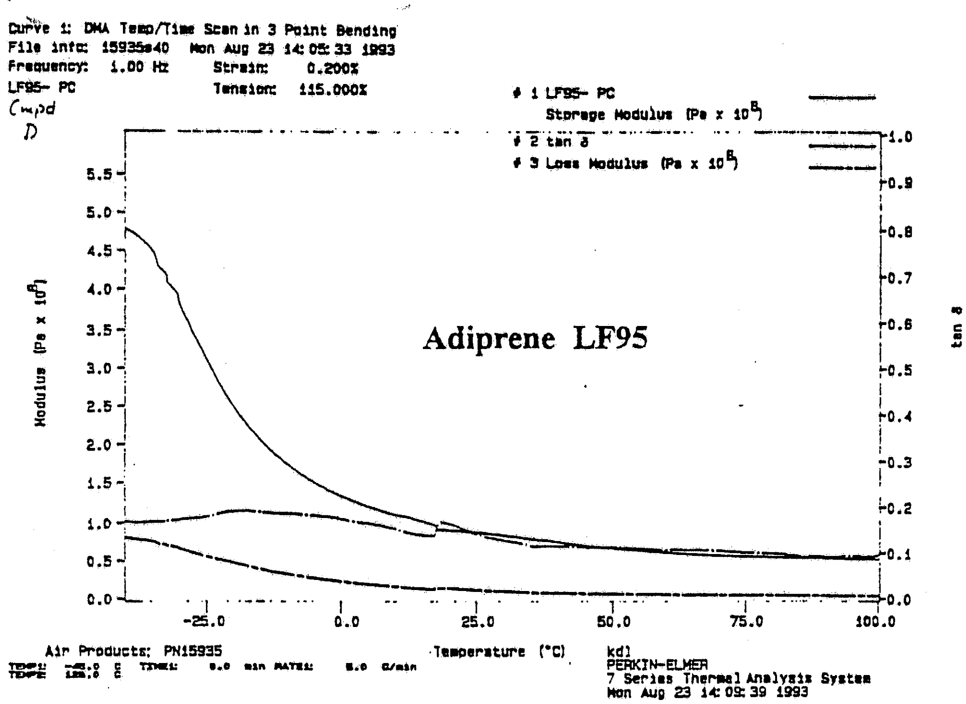
Property	Unfilled PU*	15% VISTAMER™R/85% PU*
Tensile Strength (psi)	4100	3500
% Elongation	278	275
Tear Resistance (Die C)	593	522
Tear Resistance (Trouser)	113	104
% Rebound	49	48
Hardness (Shore D)	50	50

* Polyurethane is AIRTHANE®PET 95A cured with ETHACURE®300.

The dynamic properties of PU composites made with treated rubber particles are very similar to those of the unfilled PU. FIGURE 1 shows dynamic mechanical analysis (DMA) curves for a composite composed of 20% treated rubber particles/80% polyurethane and for the unfilled polyurethane. The polyurethane used was ADIPRENE® LF95. The analysis was performed in accordance with ASTM D2231-87. This similarity in dynamic properties is consistent with findings that end products made with treated rubber particles perform almost identically to unfilled polyurethanes in dynamic applications.

ENHANCED PROPERTIES
The incorporation of treated rubber particles in polyurethane formulations can give beneficial property enhancements. Examples include higher coefficient of friction (especially on wet surfaces), greater thermal stability, higher modulus, and reduced moisture absorption. Data illustrating the benefits to coefficient of friction are in TABLE 2.

FIGURE 1


Curve 1: DMA Temp/Time Scan in 3 Point Bending
File info: 15935e40 Mon Aug 23 14:05:33 1993
Frequency: 1.00 Hz Strain: 0.200%
LF95- PC Tension: 115.000%
Cmpd D
1 LF95- PC Storage Modulus (Pa x 10^8)
2 tan δ
3 Loss Modulus (Pa x 10^8)
Adiprene LF95
Modulus (Pa x 10^8)
tan δ
Temperature (°C)
Air Products: PN15935
kdl
PERKIN-ELMER
7 Series Thermal Analysis System
Mon Aug 23 14:09:39 1993

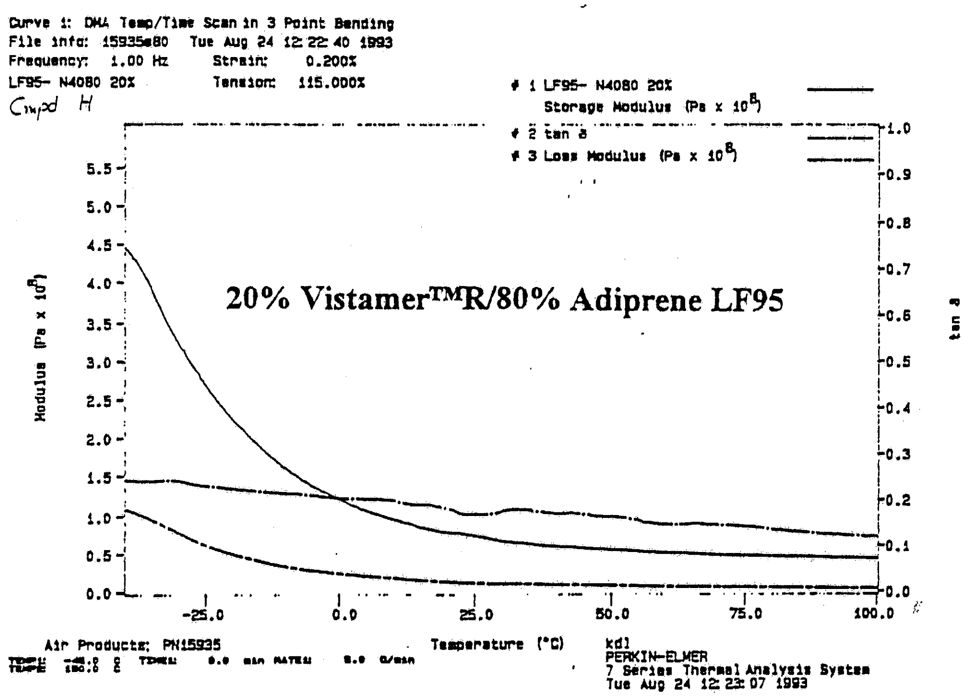

Curve 1: DMA Temp/Time Scan in 3 Point Bending
File info: 15935e80 Tue Aug 24 12:22:40 1993
Frequency: 1.00 Hz Strain: 0.200%
LF95- N4080 20% Tension: 115.000%
Cmpd H
1 LF95- N4080 20% Storage Modulus (Pa x 10^8)
2 tan δ
3 Loss Modulus (Pa x 10^8)
20% Vistamer™R/80% Adiprene LF95
Modulus (Pa x 10^8)
tan δ
Temperature (°C)
Air Products: PN15935
kdl
PERKIN-ELMER
7 Series Thermal Analysis System
Tue Aug 24 12:23:07 1993

TABLE 2

WET COEFFICIENT OF FRICTION*

	Static (lb.)	Dynamic (lb.)
Unfilled PU **	0.57	0.55
20% Treated rubber particles/PU **	0.58	0.69

* Tested via ASTM D1894-90 (Modified)
** Polyurethane is Uniroyal Adiprene® LF95 cured with ETHACURE®300

Incorporation of treated rubber particles in lower modulus polyurethane formulations has been shown to upgrade physical properties. This is illustrated in TABLE 3. With some systems, treated rubber particles have been demonstrated to give enhanced tensile strength and tear resistance. In applications where these properties are important, treated rubber particles can be classified as performance additives!

Examples of applications that have been developed that take advantage of the enhanced properties associated with the use of treated rubber particles are discussed below in the section "*END PRODUCTS MOLDED IN TREATED RUBBER/PU*".

It has also been discovered that surface-treatment can change the flexural modulus or elasticity of the rubber. Thus, when the treated rubber is combined with a polyurethane, a different modulus contribution occurs. The significance of this unexpected benefit is that treated rubber particles provide an additional degree of control over the properties of a composite. This is illustrated by comparing the stress-strain curves for four identical composites which differ only in the degree of treatment of the rubber particles, FIGURE 2.

TABLE 3

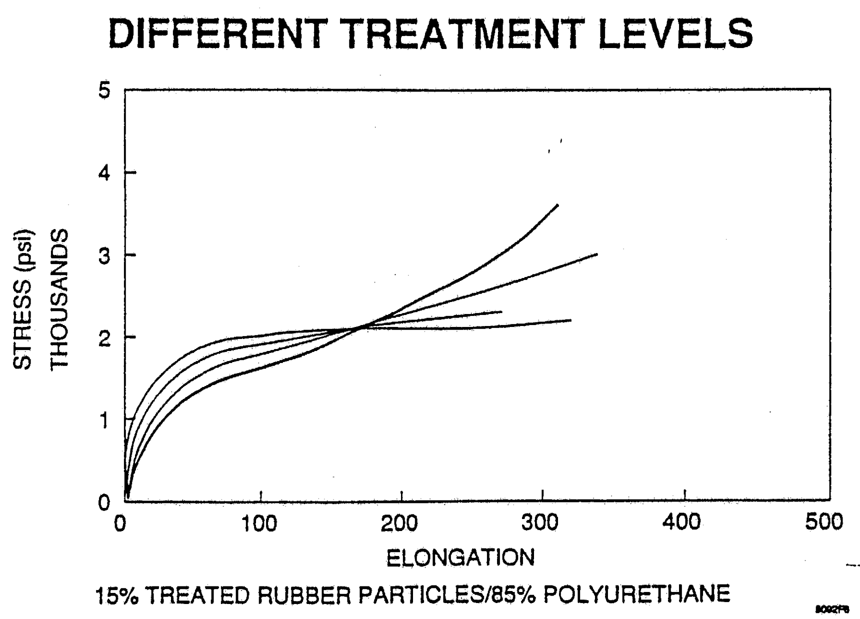
PHYSICAL PROPERTY COMPARISON

(LOWER MODULUS PU)

Property	Unfilled PU*	20% VISTAMER™R/80% PU*
Tensile Strength (psi)	4600	2330
% Elongation	625	617
Tear Resistance (Die C)	297	322
Stress at 100% (psi)	635	865
Stress at 300% (psi)	1040	1060
Hardness (Shore A)	80	87

* Polyurethane is AIRTHANE®PET 75A cured with ETHACURE®300.

FIGURE 2



Stress-strain curves for four composites consisting of 15% treated rubber/85% PU in which the rubber was given different levels of treatment.

PROCESSING CONSIDERATIONS

There are several ways that treated rubber particles can be handled in the molding process. The particles can be combined with the prepolymer (or polyol) stream prior to combination with cross linker (or diisocyanate). It is also possible to combine the particles with the polyurethane precursors in the mixhead.

Molding end products in treated rubber/polyurethane composite materials frequently requires modifications to the molding process and /or to meter-mix equipment. Generally it is found desirable to enhance the degassing process when particles are used. This is because the particles entrain air, which must be removed. Furthermore, the particles cause the viscosity to increase, which further hampers deaeration and pumping.

Composite Particles is working to ensure that the conversion to solids handling capability by molders is smooth. We are working with several manufacturers of meter-mix equipment. Some meter-mix molding equipment require no modifications. For example, units based on displacement pumps or pistons (Liquid Controls; Flying Wedge) often require no changes. However, since most molding equipment was not originally designed to handle particles, modifications are usually necessary. For example, in the case of equipment made by the Automatic Process Controls Co. (APC), particle handling requires a different pump be used for pumping the prepolymer/particle stream.

It is also possible to combine the treated rubber particles in a mix head where the polyurethane precursors are being combined or in a mixhead directly following the mixhead where the PU precursors are mixed. Max Machinery Company has developed a prototype particle handling ancillary which can be added to the existing mix head. Edge Sweets has developed equipment in which the particles are combined with the PU precursors in a single mix head. This equipment has proven to work very well.

END PRODUCTS MOLDED IN TREATED RUBBER/PU

A number of different types of end products, molded in treated rubber particles/polyurethane, have been successfully developed and qualified for commercialization. It is obvious that this is just the beginning and that a large number of additional uses will be developed in the future. These examples merely demonstrate the technical and commercial feasibility of using treated rubber particles.

Our *modus operandi* has been to support the development activities of molders in the marketplace, as opposed to performing applications development ourselves. This is because only molders and their customers really understand all of the performance requirements for specific applications. Hence, the examples summarized below have much credibility. It should also be noted that in many of these cases customers have not revealed to us all of the benefits they observe nor all of the techniques and formulations that they employed. In some cases we are under confidentiality agreements to maintain certain aspects of their applications secret.

Solid Cast PU Industrial Wheels & Forklift Tires

Two firms have developed treated rubber/polyurethane formulations for molding a variety of industrial tires, casters, and wheels. Prototypes have been made and tested with as much as 46.5% treated rubber particles. In general, these molding tests and the subsequent performance testing of the wheels were very successful. Several of these wheels are still being evaluated in field tests at customers' sites.

The primary incentive for these development efforts on wheels was to reduce raw material costs. However, there was at least one performance benefit bonus observed - better wet traction.

In one case, a 6 inch diameter, 2 inch wide caster wheel was molded in a composite consisting of 46.5% treated rubber/53.5% polyurethane. The wheel was tested by Faultless Caster Corporation. It passed the compression set test and the impact test, and it just barely failed the endurance test. The sample failed after 9,784 cycles, with passing being 10,000 cycles. The technician who performed the test reported that the composite wheel was flexing more than do wheels that pass. This indicates that the early failure was a result of heat buildup from this flexing. It is clear that a slight reformulation with a harder polyurethane or use of super-dried rubber would produce a wheel that would pass this test.

The significance of these results is the demonstration of the technical feasibility of these hybrid rubber/PU wheels. Historically, polyurethane and rubber have competed with each other for many industrial wheel applications. Often wheels made in rubber and in polyurethane have similar prices. This is because the lower raw material costs for rubber are offset by higher molding costs. Treated rubber offers the best of both worlds; a combination of lower material costs of a treated rubber/polyurethane formulation and the lower molding costs of the urethane casting process.

Much more field testing of these industrial wheels and tires in a broad range of applications is required before it is determined how much of the industrial wheel market can be served by this hybrid combination. Nevertheless, these initial efforts are very encouraging.

Polyurethane Industrial Enclosures

A family of proprietary commercial enclosures has been developed. These products, molded into 40% treated rubber particles/60% polyurethane, will replace various enclosures currently made in metal, wood, and concrete. The treated rubber is a critical component in this application because it improves the over-all physical properties, and because it reduces the raw material costs as compared to the use of unfilled polyurethane or polyurethane filled with other fillers. Non-treated rubber particles have insufficient dispersibility in this system, and do not form an acceptable product.

Microcellular Polyurethane Tires

Three firms have developed formulations for microcellular PU tires in formulations using treated rubber. The types of tires made were for wheel chairs, bicycles, and hand trucks. These developmental efforts employed loading levels of treated rubber particles as high as 30% by weight. There were few problems encountered in molding the prototype test tires. Performance testing of the various wheels revealed that the performance of the specimens made in unfilled polyurethane. Once again, a noteworthy difference was that inclusion of treated rubber improved the wet traction of the wheels--a big plus. The wheel chair tire is in final stages of testing. It is anticipated that the tire will be commercialized later this year.

Polyurethane Foam Product

A polyurethane flexible foam product using treated rubber particles has been developed. The initial incentive for using treated rubber was cost reduction. As development proceeded, it was discovered that incorporation of 20% treated rubber created a superior foam in terms of resiliency and uniformity. It is important to note that treated rubber particles, which are far larger than the cell dimensions, work very well. The company that developed this product termed the new foam a *rubber reinforced foam*. The company reported that they had absolutely no problems using the rubber particles in their existing plant equipment and molding process.

The development of this application is noteworthy in that it is in one of the largest current markets for polyurethanes. This presages a large use of treated rubber particles in polyurethane foam for property enhancements as well as for cost reduction.

PU RIM Automotive Components

A leading supplier of PU RIM resins is developing formulations which use treated rubber particles. The initial incentive for using treated rubber is cost reduction. Their results thus far are promising. Unlike other fillers commonly used in PU RIM (inorganic materials), the treated rubber particles do not reduce the elasticity of the end product. Thus, critical properties such as impact resistance and hardness are not compromised.

DOE SUPPORT

It is gratefully acknowledged that the development of this technology has been partly funded through a cost-share contract with the Office of Industrial Technologies, U. S. Department of Energy. The development and commercial implimentation of this technology promises to save a significant amount of energy on a national scale. It takes between 40,000 and 100,000 BTUs to manufacture a pound of virgin polymer, such as polyurethane precursors. It only requires about 2000 BTUs to manufacture a pound of surface-modified rubber particles. Hence, for each pound of virgin polymer substituted by a pound of treated rubber, significant quantities of energy are saved.

CONCLUSION

Surface-modified rubber particles is the only known reinforcing, elastomeric filler. VISTAMER™R can be readily combined with polyurethane to manufacture end products that have reduced raw material costs and, in some cases, better physical properties. This new class of materials promises to open significant new markets for polyurethanes by altering their performance/price ratio and making them more competitive with other materials.

Until now, surface-treated rubber particles were not available for commercial usage. Most of the work described above was done with material made expressly for research and development efforts. Now that Composite Particles, Inc. has acquired this technology and established a manufacturing facility, treated rubber particles are commercially available. This will make it reasonable for molders to begin developing uses for treated rubber in earnest--since they will be able to actually implement their new formulations.

Composite Particles' current capacity for manufacturing treated rubber particles is over 5 million lb./year from a prototype production line. In the next year, this capacity will be increased to approximately 20 million lb./year.