Polybutadiene and its Role in the Golf Ball Core

An Honors Thesis (HONRS 499)

by

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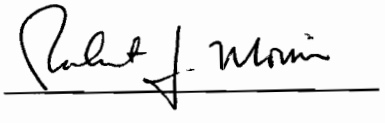

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Table of Contents

Abstract

As the race for distance off the tee continues, golf ball manufacturers are constantly seeking out any possible way to improve their product. The one area in the game of golf that has prospered the most from technology is in the golf ball. More specifically speaking, the greatest advances have taken place in the development of the core of the ball. Polybutadiene is a synthetic type of rubber that is produced after Butadiene, a petrochemical, undergoes a solidification process called emulsion polymerization. New materials are constantly being tested in hopes of finding the next product that everyone will want. In an effort to find out more about the golf ball core, I give a brief overview of the production and history of Polybutadiene, as well as where manufacturers are letting technology take them today.

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INTRODUCTION

Sergey Vasilyevich Lebedev was a Russian chemist who developed a method for industrial production of synthetic rubber. In 1910, while researching processes by which small molecules combine to form large ones, Lebedev made an elastic rubber by polymerizing butadiene ($CH_2CH\text{-}CHCH_2$), which he obtained from ethyl alcohol. Production of polybutadiene in the Soviet Union using Lebedev's process was begun in 1932-33, using potatoes and limestone as raw materials. By 1940 the Soviet Union had the largest synthetic rubber industry in the world, producing more than 50,000 tons per year. During WW II his process of obtaining butadiene from ethyl alcohol was also used by the German rubber industry.

Natural rubber is a natural polymer found just inside the bark of the rubber tree, Hevea brasilensis. The rubber tree grows naturally throughout the tropics and is also grown on plantations in Southeast Asia, Malaysia and Indonesia. The natural rubber monomer is 2-methyl-1,3-butadiene, with the monomers arranged as *cis*-isomers, which gives the rubber its elasticity. Natural rubber has been known for a long time, but was not widely used until Charles Goodyear's discovery of vulcanization, which consists of heating the rubber in the presence of sulfur to produce a more elastic substance by cross linking of the polymer chains.

As mentioned earlier, cores are made of polybutadiene, a petroleum-based synthetic rubber. This type of rubber is also used in car tires. It is very light and flexible. Approximately 20,000 metric tons of polybutadiene are used worldwide each year in golf ball cores due to its outstanding resiliency. This number is growing as wound ball technology is fading into the more diverse two-piece, solid core construction.

OVERVIEW

What is in the golf ball?

The driving for of the golf ball is its core. Its makeup is what affects the spin rate (control), velocity (distance), and compression (feel). The core of a golf ball takes on two forms, a wound core or a solid core. A wound core is a small solid or liquid filled rubber sphere that is wound with rubber thread. A solid wound center is simply a small, solid rubber ball. The liquid wound center is a small, hollow rubber ball that is filled with either a liquid or a paste. Regardless of the types, either of the centers is wound to a predetermined size to optimize velocity and spin and then a balata or durable cover is applied. The amount of thread used per golf ball will vary. Usually, about 35 yards of thread will be stretched to about 275 yards as it is wound. A wound core construction is known as a three-piece ball. A solid core in a two-piece ball is made up of a single piece of solid, elastic material. The solid core is typically made of a high resiliency rubber compound with a blend of additives to further enhance its performance. A cover is then applied.

JOURNEY TO THE CENTER OF THE BALL

What does it take to make a core?

Butadiene is a petrochemical. It is turned into a solid through a process called emulsion polymerization. The result is a synthetic rubber called polybutadiene. After being loaded into a milling machine the blocks of polybutadiene are flattened into sheet-

like structures. The sheets are then fed through an extruder which cuts the rubber into marshmallow shaped plugs that have the consistency of taffy. The plugs are loaded into a compression molding press. As they enter the molding press, the plugs are heated and pressed into shape. Once the spheres have been cured, an attendant working for the company will remove them from the press with a vacuum hose that picks them up to start the buffing process. Compressed cores come out of their molds with extra rubber attached, often around the seam. That excess is ground off to be used in other cores. The buffed cores are then removed from a storage bin and placed into an injection mold made of steel. A plastic called an ionomer is injected into the mold; the ionomer hardens, forming the mantle or the mid-layer around the core. The result of this injection molding process is a tree of golf balls that are connected by a series of runners and gates. Runners are rings and gates are small rods that attach the runners to the balls. The last structural step is placing the cover over the core. A machine that acts like an electric shaver snips the mantled core off of their trees. Then comes the cover made of another plastic, urethane, which is cast onto the mantled core. From there the last steps are purely cosmetic, paint jobs and logo stamps are all that awaits the ball before being packaged for shipment.

Manufacturers use additives like zinc oxide and calcium carbonate to add weight and hardness which varies compression. Each core compound has a unique formulation for desired compression and resilience. Ball makers will vary the core color by adding pigment to the rubber. This helps manufacturers in making sure different balls don't get mixed up in the manufacturing process. For quality control, manufacturers X-ray

finished balls or cut open samples to make sure the cores are centered. If they're not, that batch of balls doesn't make it to the market.

HISTORY AND RESEARCH

According to legend, the first golf balls were made of wood. Later on came the featherie, a pouch stuffed with goose feathers, then the gutta-percha ball which was a smooth hunk of sap. For most of the 20th century, the best balls were wound balls, packed full of rubber yarn looped around a liquid-filled core. The turn of the new century brought a revolution to the industry: three-piece balls that outperformed any wound ball.

Evolution

Ten years ago there were only two types of golf balls. A hard, two-piece distance ball for high handicappers, and wound three-piece golf balls for better players seeking more spin. Now there are multi-core golf balls, soft distance balls, just about any type of golf ball imaginable. Many of the performance benefits can be traced to advanced core designs and their materials. Golf ball designers tried to make cores larger and softer, but the materials they used based on availability ten years ago caused them to be slow, not producing much velocity at impact with the club head. In recent years new formulations and materials have allowed the designers and companies to make much larger, lower compression cores that do not suffer a loss of velocity. This combination creates golf balls that feel soft, but create tremendous speed and velocity at impact. The latest development in this field is multi-layered cores that consist of polybutadiene. (Gorss)

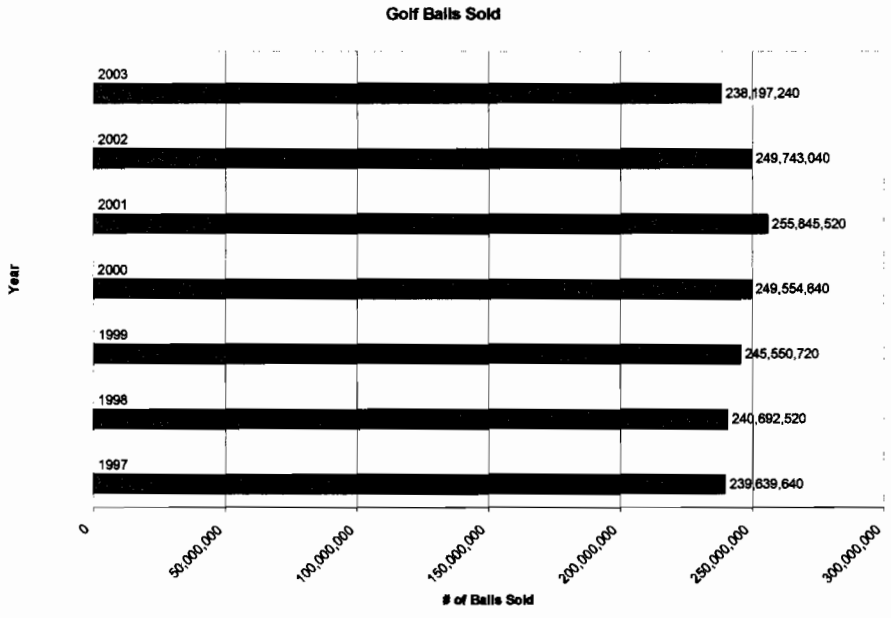
Two-piece balls don't have to be considered "rocks" anymore. With softer cores and covers, many now deliver good feel and spin as well as distance. Solid-core three-piece ball seemed far fetched a half dozen years ago. Now they're the industry leaders with a lively core and mantle fueling tremendous distance off the driver. The mantle and cover work together more on iron shots, with the cover providing spin and feel on low-clubhead-speed wedge shots, chips and putts.

History

The golf ball core has undergone many facelifts over the past 500 or so years since the invention of the game of golf. In 1452, the first recorded golf ball sold for 10 Scottish schillings, around $5 today. It was made of leather with a feather stuffed core. In 1845, a man named Robert Paterson of St. Andrews, the birthplace of the game of golf, received a statue in a crate packed with gutta-percha, the sap from the Southeast Asian gutta tree. He proceeded to melt the sap into the first gutta-percha golf ball. It flew 25 yards further than a featherie. It lasted longer and cost less. In 1898, two gentlemen named Coburn Haskell and Bertram Work designed the Haskell ball. It was the first rubber-cored golf ball. Haskell tried to wind the rubber string around the core by hand while Work, who was a B.F. Goodrich employee, had company engineers build a machine to perform the task.

The turn of the 20th century brought about the liquid core technology. Although in 1906, Goodrich rolled out a pneumatic ball that used a core made of compressed air rather than rubber. The ball proved to be a "bust." In 1930, Spalding introduced the first ball with a liquid center called the Kro-Flite and it was a comprehensively modern ball

for the times. Spalding called it "the ball that will last till it's lost." The liquid centers then had the same construction of many golf balls as recent as the year 2000. Their ingredients: corn syrup and salt water. In 1935, the L.A. Young Golf Company released the Hagen ball, a ball having a core made of pure honey that the company claimed would never evaporate. MacGregor, one of the largest golf equipment companies today, countered the move with the Pace-Maker ball, whose dry-ice center is said to make the ball more resilient. In 1974, hall of fame golfer Lee Trevino recorded the first PGA Tour victory for a two piece non-wound ball. Spalding re-entered the golf ball technology scene by introducing the Strata, the first multi-layered, non-wound ball. The Precept golf company introduced a ball called the MC Tour, the first urethane covered, three-piece non-wound ball. In 2000, Tiger Woods switched from a wound liquid-centered Titleist made golf ball, to a multi-layer, solid-core Nike golf ball and won 4 straight major tournaments, a feat accomplished only one other time in the history of golf. The year 2004 marked the official end of the wound core golf ball. Less than four years after the wound, liquid-center Titleist Tour Distance



Tiger Woods' effect on the golf ball industry. In the year 2001, Woods captured his 4th straight major championship.

Source: Golf Datatech

was the market leader, not one U.S. Manufacturer would make another wound ball for sale. (Golf Digest Feb 2006)

Chemistry of Polybutadiene

When polybutadiene is used for golf ball cores, it commonly is crosslinked with an unsaturated carboxylic acid crosslinking agent. The unsaturated carboxylic acid component of the core composition typically is the reaction product of the selected carboxylic acid or acids and an oxide or carbonate of a metal such as zinc, magnesium, barium, calcium, lithium, sodium, potassium, cadmium, lead, tin, and other similar metals. Preferably, the oxides of polyvalent metals such as zinc, magnesium and cadmium are used, and most preferably, the oxide is zinc oxide. Examples of the unsaturated carboxylic acids which find value in the core compositions include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, sorbic acid, and other similar acids or mixtures thereof. Preferably, the acid component is either acrylic or methacrylic acid. Usually the carboxylic acid cross-linking agent is included in the core composition in an amount from about 5 to about 40, and preferably from about 15 to about 30 parts by weight of the core composition. Zinc diacrylate (ZDA) is a preferred form of the carboxylic acid cross-linking agent. The unsaturated carboxylic acids and metal salts thereof are generally soluble in the elastomeric base, or are readily dispersible therein. (Rogers)

Why Polybutadiene?

Polybutadiene has been found to be a particularly useful core material because it imparts to the golf balls a relatively high coefficient of restitution. The coefficient of restitution refers to its ability to rebound back to its normal shape. It is also known as the "trampoline effect." As a base elastomer for the core composition, cis-1-4-polybutadiene is preferably employed. Optionally, a blend of cis-1-4-polybutadiene with other elastomers may also be utilized as the base elastomer. Polybutadiene can be cured using a free radical initiator such as peroxide. The free radical initiator included in the core composition is any known polymerization initiator (a co-crosslinking agent) which decomposes during the cure cycle. The term "free radical initiator" as used here refers to a chemical which, when added to a mixture of the elastomeric blend and a metal salt of an unsaturated, carboxylic acid, promotes crosslinking of the elastomers by the metal salt of the unsaturated carboxylic acid. (Voorheis)

Recent research has revealed a negative effect of the use of polybutadiene or other polymeric materials in the core and cover. When the ball is struck it creates micro-cracks on the surface allowing for increased passage of humidity and water. The core, polybutadiene, is mixed with fillers which are generally inorganic materials. The fillers are used to increase the overall weight and strength of the polybutadiene. Although the polybutadiene is hydrophobic, the water or humidity will channel through the polymer and be attracted to the filler-polybutadiene interface. The reduction in coupling between the filler and the rubber will decrease the golf ball's coefficient of restitution translating in a loss of distance. (Kim)

Where's the future going?

Future research regarding the core composition of golf balls and polybutadiene will probably take a turn towards how they can make the core firmer to reduce sidespin without sacrificing feel and playability. Making the core of polybutadiene firmer will raise the compression of the golf ball which in turn will alter its coefficient of restitution. There is current research experimenting with adding other compounds to the core such as Nickel and Tungsten to alter the weight of the innermost core, making for a ball that will increase in the amount of backspin it can produce. (Gorss).

The USGA just recently approved the NDMX golf ball for tournament play. The ball is produced by NanoDynamics. The unusual feature of the ball is that it contains a hollow steel core and is surrounded by a special casing that aides the ball to correct its shot shape in mid-flight so that it stays on the intended line of the golfer. Redistribution of the weight of the ball allows the new phenomenon to take place and that can be attributed to its chemical and physical properties. (Kanellos)

What's in it for the Pro's and Am's?

Professional golfers' golf balls are soft on the outside and harder on the inside. That is because a pro can deliver enough force to deform the outer layers of the ball and compress a hard core. The transfer of this amount of energy from the club to the core makes the ball rocket off of the clubface. From a June 2005 Golf Magazine interview, Dean Snell of Maxfli golf says, "The speed is on the inside of a Tour pro's ball. Most amateurs don't swing hard enough to get to it."

Swing speed has a directly proportional effect on the performance of the golf ball. An amateur's 80 to 90 mph swing cannot deform a hard core as much. Instead of creating a springlike effect as it would from the impact of Tiger Woods hitting a driver shot, an amateur's shot would fly and die. Many amateurs would be better served by playing a ball that has a softer core. With swing speeds of 80 mph or below, softer-cored, lower-compression balls will "squish" and rebound, giving junior, female and senior players more distance. Why don't pros hit a soft ball like the Maxfli Noodle? The answer is two reasons. First, two-piece soft-core balls don't spin enough on shorter shots. Secondly, pros would over compress their cores, sacrificing distance. A good analogy would be imagining trying to hit a marshmallow.

There is much speculation about the future or golf ball performance. Dr. Tetsuo Yamaguchi of Srixon Co. is the mastermind of a phenomenon called "nonlinearity." In Dr. Yamaguchi's vision of the near future, the core might be able to store more energy when hit at 130 mph. Nanotechnology could create rubber compounds that would "know" how to react. According to Dr. Yamaguchi, "a high-COR ball could be designed for low swing speeds by putting high-resilient material where there's low deformation and make the same ball work for high swing speeds by putting low-resilient material where there's high deformation." (Golf Digest. July 2004)

With all of the advances technology of the golf ball, the United States Golf Association has considered rolling the golf ball back. In other words, they plan to limit further gains of distance that the golf ball can travel. Their proposal reflects their desire to prevent an over-reliance on technological advances rather than skill. They have considered using a "Tournament Ball" that every player in the field of PGA Tour

tournaments would use. Every player would play the same ball with the same specifications. The ball would not travel as far as the current manufactured balls. In the July 2006 issue of *Golf Digest*, the world's number one player, Tiger Woods, offered his opinion on the possibility of a uniform tournament ball:

> "I don't think it is realistic at all. With all the competing companies out there, do you realize the impact that would have on the golf ball industry? That's billions of dollars we are talking about. We're playing such a different sport. I guess the only other sport where players have their own ball would be bowling. It's an individual sport, though. It's similar to ours. Each player chooses equipment that fits with his or her own game. But I think if you are going to do anything you go back to a shorter ball. You wouldn't make it uniform."

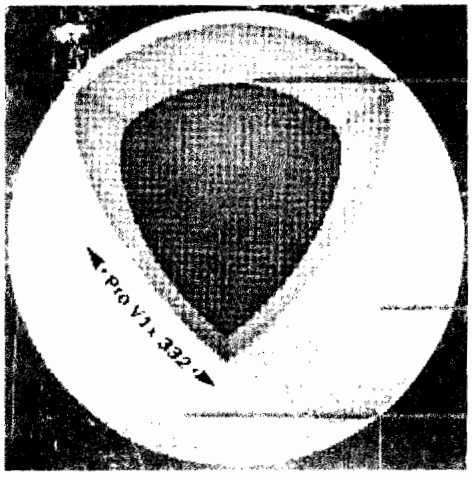
The Ohio Golf Association has already implemented the tournament ball and the Executive Committee at Augusta National Golf Club, home of the most prestigious major championship tournament in many people's opinion, The Masters, has also considered the idea. (Statchura)

SECRET RECIPES

What the different manufacturers have going on

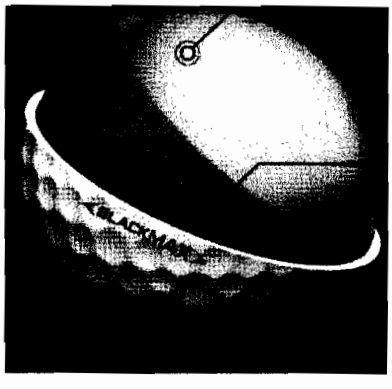
It is fair to say that Acushnet Co., who manufactures Titleist and Pinnacle golf products, dominates the golf ball market. Through March of 2004, 18.4% of all golf balls sold in golf shops across the country were the Titleist ProV1 and ProV1x models. This does not include the rest of their golf ball line that is aimed to help weekend and mid-handicap golfers play better. The main reason they are the industry leader is that the

company has updated the two balls every year. The ProV1 features a single, large, high velocity core that provides longer distance while maintaining a soft feel with added spin rate. The ProV1x contains a high velocity dual core to produce less spin and lower trajectory than the ProV1. The "x" is designed for better players who are looking to spin the ball at a lesser amount. The Titleist NXT model has a larger core than the two tour-model balls. This larger core leads to more distance but less spin around the greens.



Titleist's Pro V1x dual core. Inner core shown in blue, outer core shown in darker orange.

The Maxfli Black Max features a Neodymium Reactor Core that stores and releases wide-ranging energy at impact. The new core pushes the limit for maximum allowable velocity that equals noticeably longer shots. The Neodymium composition combines high COR with low compression, leading to more distance and feel. Tiger Woods plays a Nike golf ball, the Nike One Platinum. The Nike One Platinum is a four-piece ball and has a reformulated core that gets progressively firmer towards the outer edges of the core. The theory is this will reduce spin on tee shots while increasing the trajectory. Wilson Staff introduced a new ball called the Tx4 that features a core that is infused with particles aimed at increasing the resiliency of the core. The Bridgestone e6 golf ball utilizes a new core design to offer golfers straighter shots, and thus more distance. The Soft Kinetic Energy Core is



Maxfli's Neodymium Reactor Core shown in yellow.

designed to deliver consistently better feel on all shots and an optimum launch angle off of the tee for maximum carry. The Srixon Z-UR features a rare, membrane-thin urethane elastomer cover, which surrounds the largest, fastest energetic gradient growth core that the company has developed to date. A proprietary compound called bis (pentabromophenyl) disulfide or PBDS is added to the core to deliver amazing resilience and initial ball velocity with low spin.

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