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Poly-Paraphenylene Terephthalamide: A Life Saving Polymer

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Abstract

The revolutionary discovery of poly-paraphenylene terephthalamide which is commercially known as Kevlar, by Stephanie Kwolek and Herbert Blades in 1965 has positively impacted several industries. Prominent among this is the use of this polymer for bullet proof protection by military officers, para-military officers as well as civilians. As such this polymer has not only played a principal role in life preservation but has also improved different aspects of human life. This review highlights the discovery, synthesis, peculiarities and applications of poly-paraphenylene terephthalamide with the intent that a better understanding of this polymer will aid in harnessing its potentials as well as explore new opportunities for developing novel polymers especially from natural sources.

Keywords: Poly-paraphenylene terephthalamide; Polymer; Kevlar; Military; Fiber

Introduction

Poly-paraphenylene terephthalamide is a unique synthetic, highly crystalline aromatic polyamide polymer commercially known as Kevlar. It is a widely used polymer in stress bearing applications such as bullet-proof body armor, shielding for sports equipment, and fiber reinforced polymer composites in the aerospace industry [1-4]. Molecules of this polymer have a strong, ring-like structure identical to that of benzene. This ring-like aromatic molecules connect together to form long chains which run inside (and parallel to) the fibers similar to the steel bars ("rebar") in reinforced concrete.

Poly-paraphenylene terephthalamide is sold in several different grades, each of which is optimized to develop specific properties. For instance, Kevlar 129 has the highest strength, while Kevlar 119 is more ductile than the other grades such as Kevlar 49 [5,6].

Figure 1: Poly-paraphenylene terephthalamide [7].

Poly-paraphenylene terephthalamide was developed in 1965 by two research scientists, Stephanie Kwolek and Herbert Blades. The two scientists worked for the DuPont Company. Their product offered a number of benefits that led to its commercial introduction in the early 1970's.While working for DuPont in their Wilmington labs. In anticipation of a gas shortage, in 1964 the DuPont research group led by Kwolek began searching for a new lightweight but strong fiber to use for tyres [8]. One day in 1965, while trying to dissolve one of her polymers, something strange happened. Stephanie Kwolek reported: "Ordinarily a polymer solution sort of reminds you of molasses, although it may not be as thick. And it's generally transparent. This polymer solution poured almost like water, and it was cloudy. I thought, 'There's something different about this. This may be very useful. Normally such a "cloudy, opalescent, and low viscosity" solution would just be thrown away. However the technician, Charles Smullen, who ran the "spinneret" persuaded Kwolek to test her solution. When spun into a fiber, they were amazed to find that, unlike the other well-known fiber of the time, nylon, this new fiber did not break. Both her supervisor and laboratory director understood the significance of her discovery and new fields of aramid polymer chemistry were born [7]. The new polymer was named 'Kevlar.' It then took six years to produce Kevlar commercially, finally reaching the market in 1971.

In 1995, Kwolek became the fourth woman to be added to the National Inventor's Hall of Fame and she was awarded the National Medal of Technology in 1996 [9]. Kwolek was also awarded the 1997 Perkin Medal from the American Chemical Society, and she was a named inventor on 28 patents (the "Kevlar" patent is 71 pages long). She was elected to the National Academy of Engineering in 2001 [8].

The most famous use for Kevlar, though, is in bullet proof vests. Most police forces and military personnel now have body armour made of Kevlar as it is light and strong. There are thousands of people alive today because of the protection they got from Stephanie Kwolek's invention [10].

Chemical Structure of Poly-paraphenylene Terephthalamide Similar to Nomex, Kevlar is a distant relative of nylon, the first commercially successful "super polyamide", developed by in the 1930s [11]. It is an aramid consisting of long polymeric chains with a parallel orientation deriving its strength from inter-molecular hydrogen bonds and aromatic stacking interactions between aromatic groups in neighboring strands. These interactions are much stronger than the Van Der Waals interaction found in other synthetic polymers and fibers like Dyneema. The presence of salts and certain other impurities, especially calcium, would interfere with the strand interactions and has to be avoided in the production process. Kevlar consists of relatively rigid molecules, which form a planar sheet-like structure similar to silk protein. These properties result in its high mechanical strength and its remarkable heat resistance. Because it is highly unsaturated, as the ratio of carbon to hydrogen atoms is quite high, it has a low flammability. Kevlar molecules have polar groups accessible for hydrogen bonding [10].

The hydrogen bonds also strengthen the bonds. The large phenyl groups separating the amides cause the polymer of Kevlar to nearly always form the trans-conformation, where the phenyl groups arrange themselves so that they are on opposite sides of the rigid amide bond. This is caused by the phenyl groups to be too large to fit on the same side of the bond, as there would be great steric hindrance between the hydrogen atoms. This situation where all the monomers connect in a trans-conformation, means that very long straight chains are formed, making an almost ideal fiber, and allowing it such a wide range of uses [10].

Water that enters the interior of the fiber can take the place of bonding between molecules and reduce the material's strength, while the available groups at the surface lead to good wetting properties. This is important for bonding the fibers to other types of polymer, forming a fiber reinforced plastic. This same property also makes the fibers feel more natural and "sticky" compared to non-polar polymers like polyethylene [12].

The inherent bond strength of the molecules is exploited within aramid fibers, due to the prevalent orientation of molecules along the fiber axis. The initial preparation of the polymer is generally achieved by a chemical reaction between amine group and a carboxylic acid halide group. Once the polymer has been produced, the aramid fiber is then created by spinning. In structural applications, Kevlar fibers can be bonded to one another or to other materials to form a composite [11].

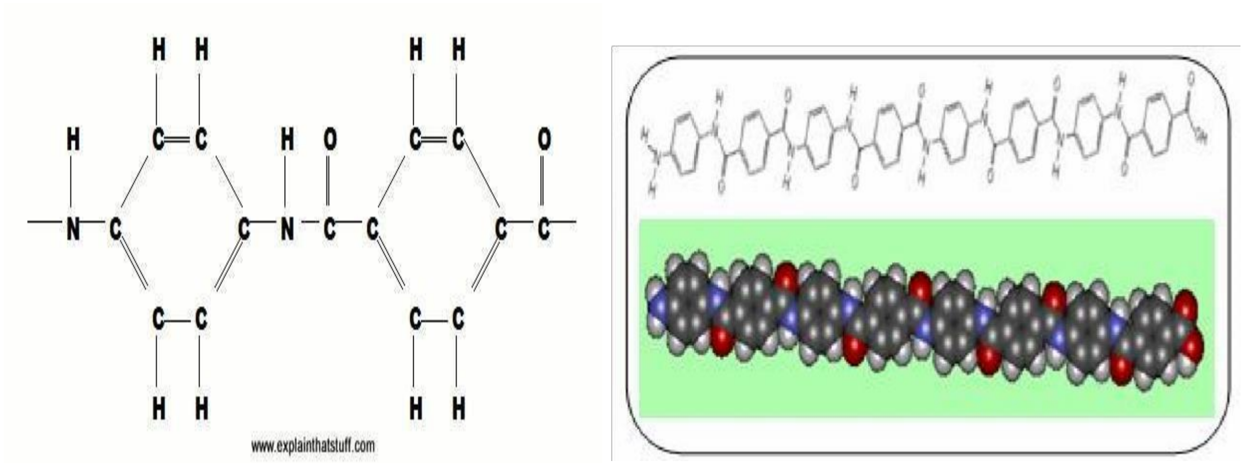

Figure 2: A section of an individual Kevlar chain [12].

Synthesis and Production of Poly paraphenylene Terephthalamide

The production of Poly paraphenylene terephthalamide is a very expensive process as there arises several challenges from the use of concentrated sulphuric acid in sustaining the water-insoluble polymer in solution during its synthesis and spinning [13]. There are two main stages involved in making this polymer. The primary stage involves the production of the basic plastic from which it is made (a chemical known as poly-para-phenylene terephthalamide-which gives rise to its name) the secondary stage involves converting it into strong fibers. During the process of polymerization, the coils of the molecules become tangled, causing it to hardly stretch.

Inside a bulletproof vest are many strips and layers of this polymer thus making it difficult for bullets to push the fibers apart and penetrate it [13].

Primary production step (Chemical synthesis)

Poly paraphenylene terephthalamide is synthesized in solution from the monomers 1,4phenylene- diamine (paraphenylenediamine) and terephthaloyl chloride in a condensation reaction yielding hydrochloric acid as a by-product [8].

Secondary production step (Wet spinning)

The chemical obtained is turned into fibers by a process called wet spinning, which involves forcing a hot, concentrated, and very viscous solution of poly-para-phenylene terephthalamide through a spinneret (a metal former a bit like a sieve) to make long, thin, strong, and stiff fibers that are wound onto drums. The fibers are then cut to length and woven into a tough mat to make the super-strong, super-stiff finished material we know as poly paraphenylene terephthalamide. Thereafter, this fiber is woven into sheets [14].

Types of poly paraphenylene terephthalamide

Although Kevlar is the main product, there are various grades of Kevlars produced [14] such as Kevlar K-29which is commonly used in industrial applications, such as cables, asbestos replacement, brake linings, and body/vehicle armour. Kevlar K49 with high modulus is used in cable and rope products. Kevlar K100 is the coloured version of Kevlar. Kevlar K119 is unique for its higher-elongation, flexible and more fatigue resistant. Kevlar K129 possesses higher tenacity for ballistic applications while Kevlar AP has 15% higher tensile strength than K29. In addition, Kevlar-super tough fiber 80 and Kevlar KM2 possess enhanced ballistic resistance properties for armour applications.

Peculiarities of poly-paraphenylene terephthalamide

Poly-paraphenylene terephthalamide has a number of beneficial properties that make it such an important material in different fields. Prominent among this include it being very strong but relatively light with specific tensile strength being over eight times greater than that of steel wire. Unlike most plastics it does not melt and is reasonably resistant to high temperatures decomposing only at about 450°C (850°F). In addition although it can be ignited, burning usually stops when the heat source is removed. On the other hand, extremely low temperatures have no effect on it no embrittlement or degradation" was found down to −196°C [12].

Kevlar has also been reported to be resistant to attacks from many different chemicals, though prolonged exposures degrade it over time. In a test carried out by DuPont's, this unique polymer remained virtually unchanged after exposure to hot water for more than 200 days and its super strong properties were unaffected by moisture [12]. Other peculiarities of this poly include its high impact resistance; negative co-efficient of thermal expansion, exceptional resistance to abrasion, high modulus, and compressive strength comparable to E-glass fibers. It is however worthy to note that despite all this unique features, poly paraphenylene terephthalamide also has its drawbacks. One of which it being susceptible to degradation by the ultraviolet rays of sunlight (UV degradation). As such, it is rarely used outdoors without protection against sunlight [15]. In particular, although it has very high tensile strength, it has a very poor compressive ability making steel more as a primary construction material for houses, bridges, and other structures where compressive forces are commonly required [12].

Application and Uses of Poly paraphenylene Terephthalamide

Military body armor and jackets

Soldiers serving in every branch of the armed forces since the 1970s have depended upon body armour and flak jackets made with poly paraphenylene terephthalamide (Kevlar®) to help protect them from combat hazards, such as ballistic projectiles and explosive fragmentation. Military body armour and flak jackets made with this fabric is extremely lightweight and comfortable enough to improve mobility and reduce fatigue for soldiers in the field [8]. Yet Kevlar® fiber is five times stronger than steel on an equal weight basis, offering superior protection against fragmentation and ballistic threats in military body armour and flak jackets [16-18].

Kevlar® is inherently flame resistant, providing thermal protection from and fire [7].

Military helmets

Military helmets made with poly paraphenylene terephthalamide meet demanding requirements for protection against a wide range of threats, includ ing bullets, shrapnel and fragmentation.

State-of-the-art military helmets made with this polymer like the U.S. Army Advanced Combat Helmet, absorb 20% more kinetic energy than the Personnel Armour System for Ground Troops

(PASGT) military helmets they are replacing, and offer protection from submachine gun bullets [7].

Innovative off-shore safety

Danger is ever present on offshore rigs. The weather, equipment breakage, risk of fire and explosion, personnel movement, supply failures and their inherent isolation combine to create a uniquely hazardous environment. Equipment must be of the highest quality and reliability. Often there is no second chance. Poly paraphenylene terephthalamide is already specified for the undersea and surface ropes and cables, but numerous ideas for innovative applications are at various stages of development. These include: deck and mud mats, lightweight honeycomb composites structures for use in platform accommodation modules and helicopter landing platforms, safe refuge and blast curtains. If things do go wrong, count on the strength and performance of Poly paraphenylene terephthalamide in critical life-saving applications, such as protective apparel and escape chutes [19].

Personal safety equipment

Kevlar is used in production of various personal protection gear such as firefighting apparel, because it is highly unsaturated, as the ratio of carbon to hydrogen atoms is quite high, it has a low flammability [20].

Protective apparel

Protective apparels such as gloves, motorcycle protective clothing and hunting gaitors, chaps, pants, riding shoe, helmets, industrial gloves, vests, body armors and body pads are made of this polymer [7]. Sports equipment Kevlar is used in making of various sports equipment due to light weight and strength. These include Kanoe hulls, race car parts and body, sport shoe, snow boards, skate boards, surf boards, gloves, racquets, motor sport helmets.

Industrial applications Kevlar is used to make industrial equipment such as hoses, belts, reinforcement materials. It is used to make parts of aircrafts, ship hulls, and reinforce tires. Belts and hosing for industrial and automotive applications. Other applications include construction of fiber optic and electromechanical cables, friction linings such as clutch plates and brake pads, gaskets for high temperature and pressure applications, adhesives and sealants [20].

Automotive Uses

DuPont™ Kevlar® brand fiber of poly paraphenylene terephthalamide help improve the safety, performance and durability of automotive components for a wide variety of vehicles, from passenger cars and light trucks to professional race cars. It is not uncommon for a new vehicle to have several crucial parts that employ products made of Kevlar® brand fiber. Kevlar® is available in several different product forms making it useful for a wide range of automotive applications: Poly paraphenylene terephthalamide fiber is a continuous filament yarn available in a broad range of deniers [21].

Poly paraphenylene terephthalamide as a composite

Poly paraphenylene terephthalamide is replacing fiber glass-reinforced plastic in NASCAR™ race car bodies and air dams because it doesn't shatter or leave hazardous debris on the track after a crash. In the HANS Device-the life-saving restraining linkage that supports the driver's head and neck- Poly paraphenylene terephthalamide absorbs impact forces that are strong enough to pulverize neck vertebrae [21].

Future Prospects

The development of strong materials still continues, both for new fibers and for ways to use them. Originally poly paraphenylene terephthalamide was designed for use as a replacement for steel in radial tyres but now has seemingly unlimited uses, from chord on the airbags of the mars pathfinder; to shrapnel resistant shielding in jet aircraft to protect passengers in the event of an explosion; to lightweight, small diameter ropes used to moor large naval ship and supertankers; to lighter stronger sports equipment like tennis racquets and skis. And undoubtedly the range of uses will continue to expand as new pursuits and the need for lightweight materials increases. However as strong and light Kevlar is it still has some disadvantages, in its most famous application as a bulletproof material Kevlar is not ideal as it is very stiff and so consequently the wearer suffers a great loss of movement, a great disadvantage when used by police who often need to react quickly. Poly paraphenylene terephthalamide also absorbs water and is consequently more susceptible to environmental influences than some other strong materials such as graphite base materials. Despite it incredible tensile strength poly paraphenylene terephthalamide also has relatively poor compressive properties and so there are still improvements, which can be made. The cost also should be reduced to make it more affordable and usable by common public [22-24].

Conclusion

Poly paraphenylene terephthalamide is now being used in many principal end products, and has a wide usage having made very fast foray into a vast range of products. This is all due to the virtue of the properties it possesses. And in very near future poly paraphenylene terephthalamide is going to be used commonly in all walks of life. Most police forces and military personnel now have body armour made of poly paraphenylene terephthalamide as it is light and strong. There are thousands of people alive today because of the protection they got from Stephanie Kwolek's invention. Recent studies have also suggested the development of novel polymers from natural sources such as the thread-like filament of spider webs which will possess highly enhanced properties capable of transcending the shortcomings associated with poly-paraphenylene terephthalamide.

References

1. Audio speaker use. Audioholics.com (2009-07-23). Retrieved on 2012-05-26.
2. Body Armor Made with Kevlar (2005-0604) DuPont the Miracles of Science. Retrieved November 4, 2014.
3. Carbon fiber bows for violin, viola, cello and bass. CodaBow.
4. Chang A, Hung R, Lew K (2013) Function and Performance of Kevlar.
5. DuPont wins $900m Kevlar spy case
6. DuPont. Stephanie Louise Kwolek Biography..
7. Michael C Petty (2007) Molecular electronics: from principles to practice, John Wiley & Sons pp: 544.
8. Fink JK (2010) Handbook of Engineering and Specialty Thermoplastics: Polyolefin's and Styrene's, Willey Publishing, pp: 400.
9. Anthony Kelly (1989) Concise Encyclopedia of Composite Materials. MIT Press, Technology and Engeneering, pp. 317.
10. Frederick TW, Norman EW (2014) Natural fibers, Plastics and Composites. JWS Hearle (2016) High-performance Fibers. Journal of Chemical Engineering 20: 23-34.
11. Frederick T Wallenberger (2012) Advanced Fibers, Plastics, Laminates and Composites.

12. Iris G, Hale VI, Gold J (2017) Kevlar KM2 Technical Description. Dupont.com.

13. Lemelson-MIT program. Archived from the original on May 24, 2014. Retrieved March 24, 2017. Kevlar – DuPont Personal Protection. .dupont.com. Retrieved on 2012-05-26.

14. Krishan Kumar Chawla (2005) Fibrous Materials. Cambridge University Press, pp. 312.

15. Jones LI, Bishop HH (2014) Inventing Modern America: Insight-Stephanie Kwolek.

16. How Kevlar® works: a simple introduction. Explain that stuff.com.

17. KEVLAR Technical Guide. Dupont .com. pp. 24.

18. Kevlar 'Wallpaper' Could Protect Soldiers From RPG Blasts by Jordan Golson.

19. Quinn Jim (2009) I was able to be Creative and work as hard as I wanted". American Heritage Publishing. Archived from the original on May 24, 2009. Retrieved May 24, 2009.

20. Tanner D, Fitzgerald JA, Phillips BR (1999) "The Kevlar Story-an Advanced Materials Case Study". Angewandte Chemie International Edition 28(5): 649-654.

21. Welch WH (2015) What is Kevlar". DuPont. Retrieved 2016-03-22. Yang, H. H. (2013), Kevlar Aramid Fiber.

22. Richard PW, Xiuzhi Susan Sun (2015) Bio-based Polymers and Composites. Rubinstein M, Colby RH (Eds.), Polymer Physics, Oxford University Press, p: 337.

23. BBC News (2007) School uniforms made slash-proof: Could Kevlar protect children against knife crime?

24. Tribute to Inventive Women: BBC News, 27 November 2003. A short article about women inventors, including Stephanie Kwolek.