

A Review on the Matrix Toughness of Thermoplastic Materials

Enes Akca

Department of Mechanical Engineering, Faculty of Engineering and Natural Sciences, International University of Sarajevo, Hrasnicka cesta 15, 71210 Sarajevo, Bosnia and Herzegovina

eakca@ius.edu.ba

Ali Gursel

Department of Mechanical Engineering, Faculty of Engineering and Natural Sciences, International University of Sarajevo, Hrasnicka cesta 15, 71210 Sarajevo, Bosnia and Herzegovina

Department of Mechanical Engineering, Faculty of Engineering, Duzce University, Duzce, Turkey

agursel@ius.edu.ba

Abstract

Composite material has attracted increasingly remarked interest over the last few decades and set it apart in its own class due to its distinct properties. This paper is a review on the matrix toughness of thermoplastic polymer composites. Toughness of thermoplastics has been actively studied since the 1980s. The main advantage in using thermoplastics to toughen resins is that their incorporation need not result in important decreases in desirable properties such as modules and yield strengths. However, the predominant criteria for achieving optimum toughness enhancement in the thermoplastic toughening of epoxy resins are still not all that clear from the literature. Epoxy and polyester resins are commonly modified by introducing carboxyl-terminated butadiene-acrylonitrile copolymers (ctbn). A tough elastomeric phase, for example, a silicone rubber with good thermal resistance in a polyimide resin, produced a tough matrix material. It summarizes what the authors believe are the important requirements for good thermoplastic toughening.

Keywords: toughness; ctbn; polymer; thermoplastic; epoxy

1. Introduction

In recent years considerable attention has been focused on the use of tough, high-temperature, solvent-resistant thermoplastic polymers as matrix materials for fiber-reinforced composites. Thermoplastic resin systems have shown potential for reducing manufacturing costs and improving the damage tolerance of composite structures. In order to produce high-quality composite laminates from continuous fiber-reinforced thermoplastic prepregs the processing temperature and pressure must be selected so that intimate contact (coalescence) at the ply interfaces is achieved resulting in the formation of strong interfacial bonds (consolidation).

Thermoplastics [1] are polymers that require heat to make them processable. After cooling, such materials retain their shape. In addition, these polymers may be

reheated and reformed, often without significant changes in their properties.

This review has focused upon the importance of the thermoplastic materials and the matrix toughness of the thermoplastic.

The results of this study show that matrix toughness influences the long-term behavior of fiber composites. The transcendent criteria for accomplishing ideal toughness enhancement in the thermoplastic toughening of epoxy resins are still not too clear from the literature. Epoxy and polyester resins are ordinarily altered by presenting carboxyl-terminated butadiene-acrylonitrile copolymers (ctbn). However, a tough elastomeric stage, for instance, a silicone elastic with great thermal resistance in a polyimide resin, delivered a tough matrix material. It outlines what the authors accept are the critical prerequisites for good thermoplastic toughening.

2. Composite Materials

Engineering materials can be classified in different ways according to various criteria. The classification in Figure 1 is helpful in illustrating the fact that composite materials are basically combinations of the three conventional engineering materials; namely metals & alloys, polymers and ceramics & glasses.

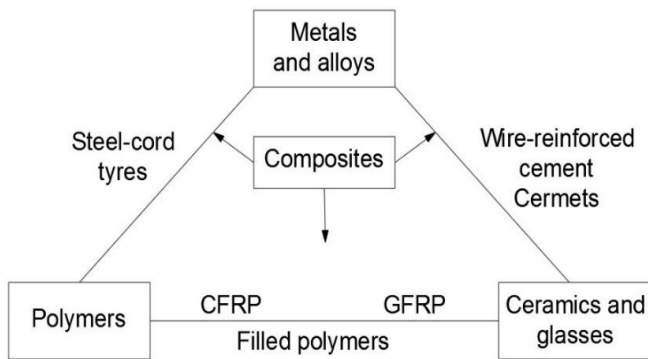


Figure 1: The classes of engineering materials from which articles are made

A composite material is composed of two main components/constituents/phases bound together: Matrix and reinforcement. Matrix is the phase that binds the reinforcement material, which is usually the stronger one. While matrix is a continuous phase, reinforcement is discontinuous and its arrangement within the matrix strongly affects overall performance of the final product; i.e. the composite.

Figure 2 clearly illustrates benefit of reinforcement, which, in this particular composite, is discontinuous fiber, can stop crack propagation, enhancing overall strength of the composite [2].

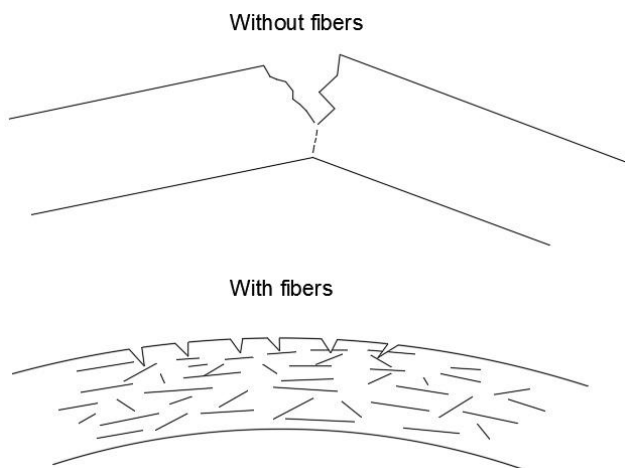


Figure 2: Demonstration of how cracks are prevented from running in a brittle material because of fibers in their path.

Composite materials have been increasingly used in manufacturing a large variety of products, ranging from sports equipments to cutting tools used in machinery, from automotive to medical products. For example, the Boeing 787 Dreamliner consists of 50% composite material by weight [3]. Figure 3 shows application areas of composites.

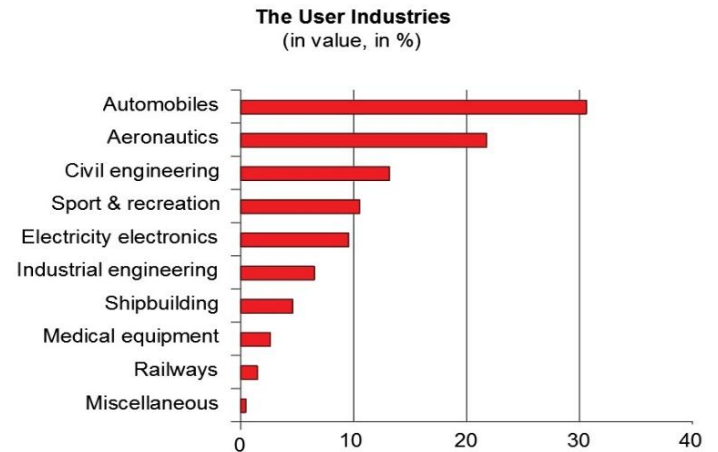


Figure 3: Application of Composite Materials [4]

Polymers are structurally much more complex than metals or ceramics. They are cheap and can be easily processed. On the other hand, polymers have lower strength and modulus and lower use temperature limits. Prolonged exposure to ultraviolet light and some solvents can cause the degradation of polymer properties. Because of predominantly covalent bonding, polymers are generally poor conductors of heat and electricity. Polymers, however, are generally more resistant to chemicals than are metals. Structurally, polymers are giant chainlike molecules (hence the name macromolecules) with covalently bonded carbon atoms forming the backbone of the chain. The process of forming large molecules from small ones is called polymerization; that is, polymerization is the process of joining many monomers, the basic building blocks, together to form polymers.

2.1. Composite Material Classification According To Reinforcement

Composites can be classified according to reinforcement materials. They can also be classified by the geometry of the reinforcement as follows: particulate, flake, fibers and nanocomposites.

a) **Particulate composites** consist of particles immersed in matrices such as alloys and ceramics. They are usually isotropic because the particles are added randomly. Particulate composites have advantages such as improved strength, increased operating temperature, oxidation resistance, etc. Typical examples include use of aluminum particles in rubber; silicon carbide

particles in aluminum; and gravel, sand, and cement to make concrete.

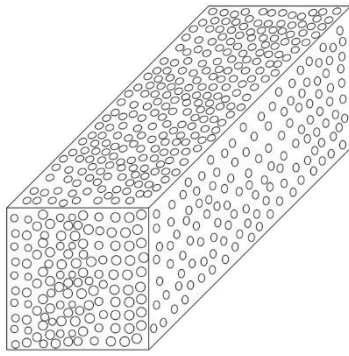


Figure 4: Particles as the reinforcement

b) **Flake composites** consist of flat reinforcements of matrices. Typical flake materials are glass, mica, aluminum, and silver. Flake composites provide advantages such as high out-of-plane flexural modulus, higher strength, and low cost. However, flakes cannot be oriented easily and only a limited number of materials are available for use.

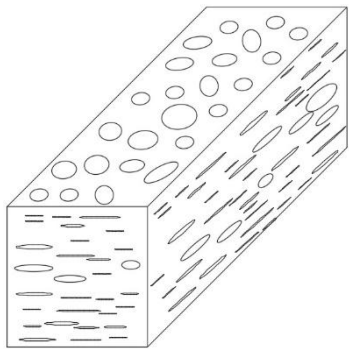


Figure 5: Flat flakes as the reinforcement

c) **Fiber composites** consist of matrices reinforced by short (discontinuous) or long (continuous) fibers. Fibers are generally anisotropic and examples include carbon and aramids. Examples of matrices are resins such as epoxy, metals such as aluminum, and ceramics such as calcium–aluminum silicate. Continuous fiber composites are emphasized in this book and are further discussed in this chapter by the types of matrices: polymer, metal, ceramic, and carbon. The fundamental units of continuous fiber matrix composite are unidirectional or woven fiber laminas. Laminas are stacked on top of each other at various angles to form a multidirectional laminate.

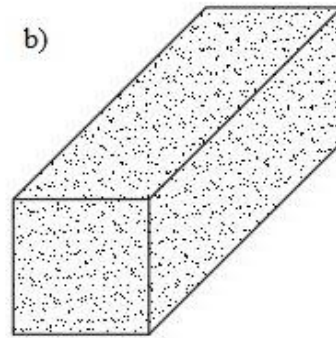
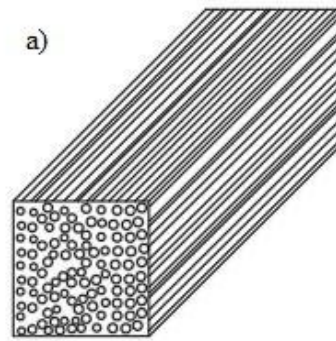


Figure 6: (a) Random fiber (short fiber) reinforced composites, (b) Continuous fiber (long fiber) reinforced composites

d) **Nanocomposites** consist of materials that are of the scale of nanometers (10^{-9} m). The accepted range to be classified as a nanocomposite is that one of the constituents is less than 100 nm. At this scale, the properties of materials are different from those of the bulk material. Generally, advanced composite materials have constituents on the microscale (10^{-6} m). By having materials at the nanometer scale, most of the properties of the resulting composite material are better than the ones at the microscale. Not all properties of nanocomposites are better; in some cases, toughness and impact strength can decrease. Applications of nanocomposites include packaging applications for the military in which nanocomposite films show improvement in properties such as elastic modulus, and transmission rates for water vapor, heat distortion, and oxygen. Body side molding of the 2004 Chevrolet Impala is made of olefin based nanocomposites. This reduced the weight of the molding by 7% and improved its surface quality. General Motors™ currently uses 540,000 lb of nanocomposite materials per year. Rubber containing just a few parts per million of metal conducts electricity in harsh conditions just like solid metal. Called Metal Rubber®, it is fabricated molecule by molecule by a process called electrostatic self-assembly. Awaiting applications of the Metal Rubber include artificial muscles, smart clothes, flexible wires, and circuits for portable electronics.

2.2. Composite Material Classification According To Matrix

Composites can be classified by their geometry of the matrix as follows: polymer, metal, ceramic and carbon.

a) **Polymer Matrix Composites:** The most common advanced composites are polymer matrix composites (PMCs) consisting of a polymer (e.g., epoxy, polyester, urethane) reinforced by thin diameter fibers (e.g., graphite, aramids, boron). For example, graphite/epoxy composites are approximately five times stronger than steel on a weight - for - weight basis. The

reasons why they are the most common composites include their low cost, high strength, and simple manufacturing principles. The main drawbacks of PMCs include low operating temperatures, high coefficients of thermal and moisture expansion, and low elastic properties in certain directions. The most common fibers used are glass, graphite, and Kevlar. Typical properties of these fibers compared with bulk steel and aluminum are given in Table 1.

Table 1: Typical Mechanical Properties of Fibers Used in Polymer Matrix Composites [5].

Property	Units	Graphite	Aramid	Glass	Steel	Aluminum
<i>System of units: USCS</i>						
Specific gravity	-	1.8	1.4	2.5	7.8	2.6
Young's modulus	Msi	33.35	17.98	12.33	30	10.0
Ultimate tensile strength	ksi	299.8	200.0	224.8	94	40.0
Axial coefficient of thermal expansion	µin./in./°F	-0.722	-2.778	2.778	6.5	12.8
<i>System of units: SI</i>						
Specific gravity	-	1.8	1.4	2.5	7.8	2.6
Young's modulus	GPa	230	124	85	206.8	68.95
Ultimate tensile strength	MPa	2067	1379	1550	648.1	275.8
Axial coefficient of thermal expansion	µm/m/°C	-1.3	-5	5	11.7	23

Glass is the most common fiber used in polymer matrix composites. Its advantages include its high strength, low cost, high chemical resistance, and good insulating properties. The drawbacks include low elastic modulus, (reduces tensile strength), and low fatigue strength. The main types are E-glass (also called “fiberglass”) and S-glass. The “E” in E-glass stands for electrical because it was designed for electrical applications. However, it is used for many other purposes now, such as decorations and structural applications. The “S” in S-glass stands for higher content of silica. It retains its strength at high temperatures compared to E-glass and has higher fatigue strength. It is used mainly for aerospace applications. The difference in the properties is due to the compositions of E-glass and S-glass fibers.

b) **Metal Matrix Composites:** Metal matrix composites (MMCs), as the name implies, have a metal matrix. Examples of matrices in such composites include aluminum, magnesium, and titanium. Typical fibers include carbon and silicon carbide. Metals are mainly reinforced to increase or decrease their properties to suit the needs of design. For example, the elastic stiffness and strength of metals can be increased and large coefficients of thermal expansion and thermal and electrical conductivities of metals can be reduced,

by the addition of fibers such as silicon carbide. Metal matrix composites are mainly used to provide advantages over monolithic metals such as steel and aluminum. These advantages include higher specific strength and modulus by reinforcing low-density metals, such as aluminum and titanium; lower coefficients of thermal expansion by reinforcing with fibers with low coefficients of thermal expansion, such as graphite; and maintaining properties such as strength at high temperatures. MMCs have several advantages over polymer matrix composites. These include higher elastic properties; higher service temperature; insensitivity to moisture; higher electric and thermal conductivities; and better wear, fatigue, and flaw resistances. The drawbacks of MMCs over PMCs include higher processing temperatures and higher densities. Metal matrix composites applications are:

- Space: The space shuttle uses boron/aluminum tubes to support its fuselage frame. In addition to decreasing the mass of the space shuttle by more than 320 lb (145 kg), boron/aluminum also reduced the thermal insulation requirements because of its low thermal conductivity. The mast of the Hubble Telescope uses carbon-reinforced aluminum.
- Military: Precision components of missile guidance systems demand dimensional stability — that is, the

geometries of the components cannot change during use.²⁷ Metal matrix composites such as SiC/aluminum composites satisfy this requirement because they have high micro yield strength. In addition, the volume fraction of SiC can be varied to have a coefficient of thermal expansion compatible with other parts of the system assembly.

- Transportation: Metal matrix composites are finding use now in automotive engines that are lighter than their metal counterparts. Also, because of their high strength and low weight, metal matrix composites are the material of choice for gas turbine engines.

c) **Ceramic Matrix Composites:** Ceramic matrix composites (CMCs) have a ceramic matrix such as alumina calcium alumino silicate reinforced by fibers such as carbon or silicon carbide. Advantages of CMCs include high strength, hardness, high service temperature limits for ceramics, chemical inertness, and low density. However, ceramics by themselves have low fracture toughness. Under tensile or impact loading, they fail catastrophically. Reinforcing ceramics with fibers, such as silicon carbide or carbon, increases their fracture toughness because it causes gradual failure of the composite. This combination of a fiber and ceramic matrix makes CMCs more attractive for applications in which high mechanical properties and extreme service temperatures are desired. Ceramic matrix composites are finding increased application in high-temperature areas in which metal and polymer matrix composites cannot be used. This is not to say that CMCs are not attractive otherwise, especially considering their high strength and modulus, and low density. Typical applications include cutting tool inserts in oxidizing and high-temperature environments.

d) **Carbon–Carbon Composites:** Carbon–carbon composites use carbon fibers in a carbon matrix. These composites are used in very high-temperature environments of up to 6000°F (3315°C), and are 20 times stronger and 30% lighter than graphite fibers. Carbon is brittle and flaw sensitive like ceramics. Reinforcement of a carbon matrix allows the composite to fail gradually and also gives advantages such as ability to withstand high temperatures, low creep at high temperatures, low density, good tensile and compressive strengths, high fatigue resistance, high thermal conductivity, and high coefficient of friction. Drawbacks include high cost, low shear strength, and susceptibility to oxidations at high temperatures. The main uses of carbon–carbon composites are the following:

- Space shuttle nose cones: As the shuttle enters Earth’s atmosphere, temperatures as high as 3092°F (1700°C) are experienced. Carbon– carbon composite is a material of choice for the nose cone

because it has the lowest overall weight of all ablative materials; high thermal conductivity to prevent surface cracking; high specific heat to absorb large heat flux; and high thermal shock resistance to low temperatures in space of –238°F (–150°C) to 3092°F (1700°C) due to re-entry. Also, the carbon–carbon nose remains undamaged and can be reused many times.

- Mechanical fasteners: Fasteners needed for high temperature applications are made of carbon–carbon composites because they lose little strength at high temperatures [5].

2.3. Common Thermoplastic Matrix Materials

Thermoplastics are characterized by linear chain molecules and can be repeatedly melted or reprocessed. It is important to note that in this regard the cool-down time affects the degree of crystallinity of the thermoplastic. This is because the polymer chains need time to get organized in the orderly pattern of the crystalline state; too quick a cooling rate will not allow crystallization to occur. Although repeated melting and processing are possible with thermoplastics, it should be recognized that thermal exposure (too high a temperature or too long a dwell time at a given temperature) can degrade the polymer properties such as, especially, impact properties.

Common thermoplastic resins used as matrix materials in composites include some conventional thermoplastics such as polypropylene, nylon, thermoplastic polyesters (PET, PBT), and polycarbonates. Some of the new thermoplastic matrix materials include polyamide imide, polyphenylene sulfide (PPS), polyarylsulfone, and polyetherether ketone (PEEK). Figure 7 shows the chemical structure of some of these thermoplastics. PEEK is an attractive matrix material because of its toughness and impact properties, which are a function of its crystalline content and morphology. It should be pointed out that crystallization kinetics of a thermoplastic matrix can vary substantially because of the presence of fibers [6]. In order to make a thermoplastic matrix flow, heating must be done to a temperature above the melting point of the matrix. In the case of PEEK, the melting point of the crystalline component is 343 °C. In general, most thermoplastics are harder to flow in relation to thermosets such as epoxy! Their viscosity decreases with increasing temperature, but at higher temperatures the danger is decomposition of resin.

Thermoplastic resins have the advantage that, to some extent, they can be recycled. Heat and pressure are applied to form and shape them. More often than not, short fibers are used with thermoplastic resins but in the

late 1970's continuous fiber reinforced thermoplastics began to be produced. The disadvantages of thermoplastics include their rather large expansion and high viscosity characteristics [7].

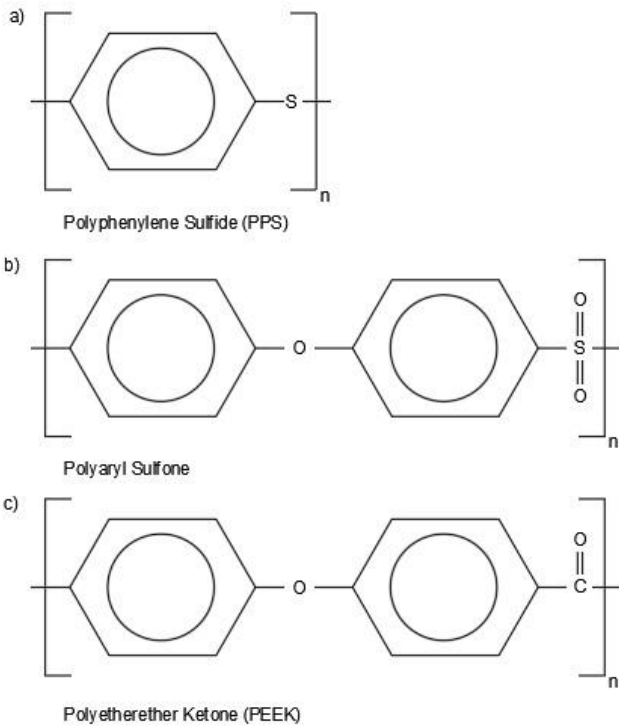


Figure 7: Chemical structure of (a) PPS, (b) polyarylsulfone, and (c) polyetherether ketone (PEEK)

An important problem with polymer matrices is associated with environmental effects. Polymers can degrade at moderately high temperatures and through moisture absorption. Absorption of moisture from the environment causes swelling in the polymer as well as a reduction in its T_g . In the presence of fibers bonded to the matrix, these hygrothermal effects can lead to severe internal stresses in the composite. The presence of thermal stresses resulting from thermal mismatch between matrix and fiber is, of course, a general problem in all kinds of composite materials; it is much more so in polymer matrix composites because polymers have high thermal expansivities.

2.4. Matrix Toughness

Thermosetting resins (e.g., polyesters, epoxies, and polyimides) are highly crosslinked and provide adequate modulus, strength, and creep resistance, but the same cross-linking of molecular chains causes extreme brittleness, that is, very low fracture toughness. By *fracture toughness*, it is meant resistance to crack propagation. It came to be realized in the 1970's that matrix fracture characteristics (strain to failure, work of fracture, or fracture toughness) are as important as

lightness, stiffness, and strength properties. Figure 8 (note the log scale) compares some common materials in terms of their fracture toughness as measured by the fracture energy in J/m^2 [8]. Note that thermosetting resins have values that are only slightly higher than those of inorganic glasses. Thermoplastic resins such as PMMA have fracture energies of about $1 kJ/m^2$, while polysulfone thermoplastics have fracture energies of several kJ/m^2 , almost approaching those of the 7075-T6 aluminum alloy. Amorphous thermoplastic polymers show higher fracture energy values because they have a large free volume available that absorbs the energy associated with crack propagation. Among the well-known modified thermoplastics are the acrylonitrile-butadiene-styrene (ABS) copolymer and high-impact polystyrene (HIPS). One class of thermosetting resins that comes close to polysulfones is the elastomer-modified epoxies. Elastomer-modified or rubber-modified thermosetting epoxies form multiphase systems, a kind of composite in their own right. Small (a few micrometers or less), soft, rubbery inclusions distributed in a hard, brittle epoxy matrix enhance its toughness by several orders of magnitude [9-13].

Epoxy and polyester resins are commonly modified by introducing carboxyl-terminated butadiene-acrylonitrile copolymers (ctbn). The methods of manufacture can be simple mechanical blending of the soft, rubbery particles and the resin or copolymerization of a mixture of the two. Figure 9 shows the increase in fracture surface energy of an epoxy as a function of weight % of ctbn elastomer [13].

Toughening of glassy polymers by elastomeric additions involves different mechanisms for different polymers. Among the mechanisms proposed for explaining this enhanced toughness are triaxial dilation of rubber particles at the crack tip, particle elongation, and plastic flow of the epoxy. Ting [8] studied such a rubber-modified epoxy containing glass or carbon fibers. He observed that the mechanical properties of rubber-modified composite improved more in flexure than in tension. Scott and Phillips [13] obtained a large increase in matrix toughness by adding ctbn in unreinforced epoxy. But this large increase in toughness could be translated into only a modest increase in carbon fiber reinforced modified epoxy matrix composite. Introduction of a tough elastomeric phase, for example, a silicone rubber with good thermal resistance in a polyimide resin, produced a tough matrix material: a three- to fivefold gain in toughness, G_{Ic} without a reduction in T_g [12].

Continuous fiber reinforced thermoplastics show superior toughness values owing to superior matrix toughness. PEEK is a semicrystalline aromatic

thermoplastic [14, 15, 16] that is quite tough. PEEK can have 20–40 % crystalline phase. At 35 % crystallinity, the spherulite size is about 2 μm [15]. Its glass transition temperature T_g is about 150 $^\circ\text{C}$, and the crystalline phase melts at about 350 $^\circ\text{C}$. It has an elastic modulus of about 4 GPa, a yield stress of 100 MPa, and a relatively high fracture energy of about 500 J/m^2 . In addition to PEEK, other tough thermoplastic resins are available, for example, thermoplastic polyimides and PPS, which is a semicrystalline aromatic sulfide. PPS is the simplest member of a family of polyarylene sulfides [17]. PPS (trade name Ryton), a semicrystalline polymer, has been reinforced by chopped carbon fibers and prepregged with continuous carbon fibers [17].

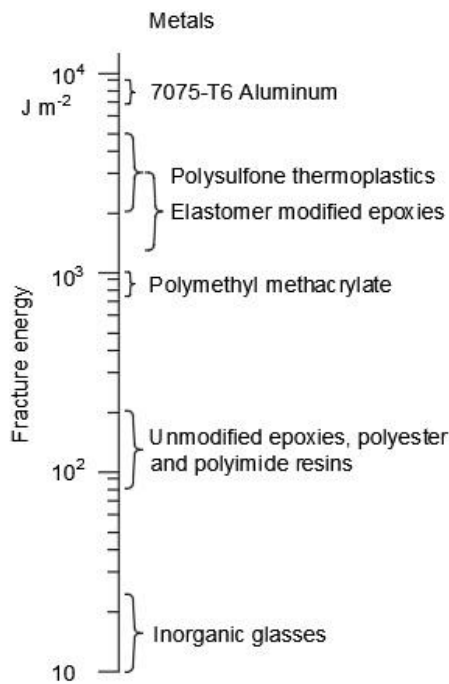


Figure 8: Fracture energy for some common materials

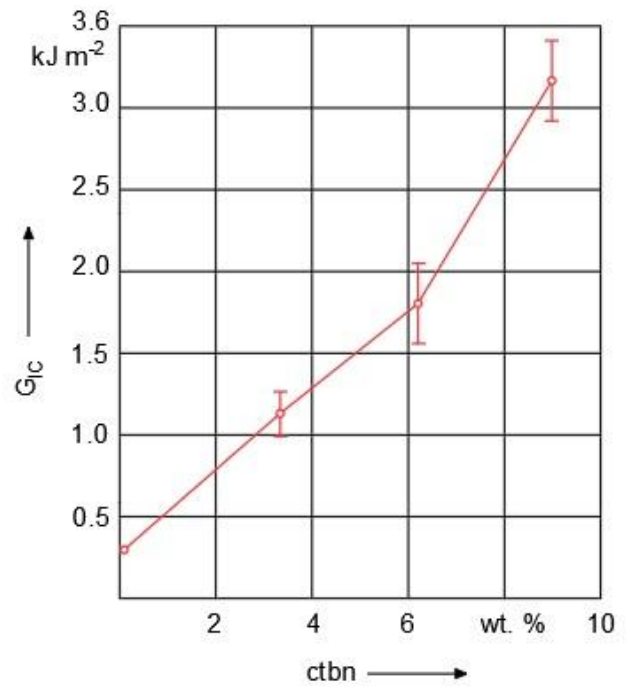


Figure 9: Fracture surface energy of an epoxy as a function of weight % of carboxyl-terminated butadiene-acrylonitrile (ctbn)

Conclusions

The purpose of this review article is to investigate about the matrix toughness of thermoplastic polymers. After the literature researches completed, some observations have been come up;

1. The mechanical properties of rubber-modified composite improved more in flexure than in tension.
2. It is obtained a large increase in matrix toughness by adding ctbn in unreinforced epoxy. But this large increase in toughness could be translated into only a modest increase in carbon fiber reinforced modified epoxy matrix composite.
3. A silicone rubber with good thermal resistance in a polyimide resin, produced a tough matrix material: a three- to fivefold gain in toughness, G_{Ic} without a reduction in T_g .
4. Thermoplastic polyimides and PPS, which is a semicrystalline aromatic sulfide, are available as tough thermoplastic resins. PPS is the simplest member of a family of polyarylene sulfides. PPS, a semicrystalline polymer, has been reinforced by chopped carbon fibers and prepregged with continuous carbon fibers.

References

1. R. Sinha, "Outlines of polymer technology," New Delhi: Prentice-Hall by India Private Limited, 2002.
2. A. Mortensen A, "Concise encyclopedia of composite materials," Second Edition. Amsterdam: Elsevier; 2007.
3. Cherrington R, Goodship V, Meredith J, Wood BM, Coles S, Vuillaume A, Feito-Boirac A, Spee F, Kirwan K. Producer responsibility: defining the incentive for recycling composite wind turbine blades in Europe. *Energy Policy* 2012; 47:13-21.
4. Yang Y. Recycling of composite materials. *Chemical Engineering and Processing: Process Intensification* 2012; 51:53-68.
5. Kaw K. *Mechanics of composite materials*. Second Edition. USA: CRC Press; 2006.
6. Waddon AJ, Hill MJ, Keller A, Blundell DJ. On the crystal texture of linear polyaryls (PEEK, PEK and PPS). *Journal of Materials Science* 1987; 22:1773-84.
7. Krishan KC. *Composite materials; science and engineering*. New York: Springer; 2013.
8. Ting RY. The role of polymeric matrix in the processing and structural properties of composite materials. Seferis JC, Nicolais L, editors. *Rubber Modified Matrices*, New York: Springer; 1983, p 171-188.
9. Sultan JN, McGarry FJ. Effect of rubber particle size on deformation mechanisms in glassy epoxy. *Polymer Engineering & Science* 1973; 13:29-34.
10. Riew CK, Rowe EH, Siehert AR. Toughness and brittleness of plastics Rudolph DD, Aldo MC, editors. *Rubber toughened Thermosets*. American Chemical Society, *Advances in Chemistry*; 1976, p 326-343.
11. Bascom WD, Cottingham RL. Effect of temperature on the adhesive fracture behavior of an elastomer-epoxy resin. *Journal of Adhesion* 1976; 7:333-346.
12. St. Clair AK, St. Clair TL. *International Journal of Adhesion and Adhesives* 1981; 1:249-255.
13. Scott JM, Phillips DC. Carbon fibre composites with rubber toughened matrices. *Journal of Materials Science* 1975; 10:551-562.
14. Blundell DJ, Chalmers JM, Mackenzie MW, Gaskin WF. Crystalline morphology of the matrix of PEEK-Carbon fibre aromatic polymer composites, Part 1: Assessment of crystallinity. *Sampe Quarterly* 1985; 16:22-30.
15. Cogswell FN. Microstructure and properties of thermoplastic aromatic polymer composites. 28th National Sampe Symposium 1983; 14:157-165.
16. Hartness JT. Polyether-etherketone matrix composites. 14th National Sampe Technical Conference 1982; 14:26-43.
17. O'Connor JE, Beever WR, Geibel JF. *Proc Sampe Materials Symp* 1986; 31:1313.