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Progress in Polymer Composite Materials for Cryogenic Applications

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Abstract
Polymers are excellent engineering materials and can serve as a substitute for metal in many applications. They are easy to be molded into any shape and have desired properties such as low thermal conductivity, electrical insulating properties, vacuum sealing effect, self-lubrication action, etc. A single polymer cannot meet all the requirements in advanced applications as its mechanical strength is low. Hence fillers are added selectively to the polymer matrix for reinforcement of its strength and other required properties resulting in polymer composites. Polymer composites are becoming more and more essential for such applications as superconductivity, space technology, cryogenic rocket engines, and storage of cryogenic liquids such as liquid nitrogen, liquid oxygen liquefied natural gas, etc. whose normal boiling point lies below -150 ^{0} C. One of the significant advantages of polymer composites is that various parts and vessels made of polymer composites are much lighter than their metallic counterparts for all cryogenic and allied applications.

The present paper attempts to present an overview of polymer and polymer composites and their characterization with particular reference to thermal and structural properties for the cryogenic application.

Keywords*-Cryogenic, polymer, composite, thermal properties, structural properties.*

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I.Introduction

Cryogenics, the science of low temperature, has emerged as a multidimensional subject for its application in the steel industry, fertilizer industry, petrochemical industry, metal fabrication, fuel, and energy science, space science, nuclear science, superconducting science, electronics, cryobiology, and environmental science and so on. Any temperature below(-150°C)is called Cryogenic temperature.

The gases having normal boiling points below -150°C(123K)are regarded as cryo-gases. Oxygen, nitrogen, hydrogen, helium, neon, argon, methane, carbon monoxide, etc. comes under the purviews of cryo gases. During cooling to cryogenic temperatures, polymers exhibit some peculiar characteristics that must be taken care of before undertaking any design of instruments or equipment to be operated in a cryogenic environment so that the finished device will serve the desired job.

The study of polymer materials at low temperatures has become a subject of much discussion with new developments in cryogenic liquid propulsion systems for space, superconducting magnets for diagnostic and motors, electronic and defense technologies, and also for large cryogenic engineering projects like International Thermonuclear Experimental Reactor (ITER), etc.

Hence, the present work begins with a brief description of methodologies of some important mechanical testing and then moves on to an overview of polymer composites and finally describes the change in properties like strength, modulus, toughness, brittleness, and thermal conductivity, etc. of polymer composite materials when they are exposed to a cryogenic temperature in comparison of their similar properties in relevance to the strength, modulus, toughness, brittleness, thermal conductivity, etc. Different characterization data on mechanical and thermal properties of polymer composites is also highlighted for assessing their suitability for cryogenic application which will serve as a comprehensive report on the effect of variation of temperature on modified polymer properties in the cryogenic temperature range so as to make one familiar with the properties and behavior of polymer composite materials at low temperature.

II.SIGNIFICANCE OF SOME IMPORTANT MECHANICAL TESTING TERMINOLOGIES

Impact testing is used to measure the impact toughness of the material used and is described as the toughness and the ability of the material to absorb energy due to sudden loading. The ductility and strength of the material are taken into account by toughness. Notched impact strength, as determined with a V-shaped notch, and the un-notched impact strength come under the purview of impact properties.

Fatigue is defined as the initiation and propagation of cracks in a material due to cyclic loading. Once a fatigue crack has initiated, it grows a small amount with each loading cycle until it reaches a critical size leading to a complete fracture of the structure. Macroscopic cracks resulting from cyclic thermal stresses and strains due to temperature changes, spatial temperature gradients, and high temperatures are known as **thermal fatigue** which may occur without mechanical loads

Fracture toughness is the critical stress intensity factor of a sharp crack where propagation of the crack suddenly becomes rapid and unlimited. A quantitative way of expressing a material's resistance to crack propagation is expressed by Fracture toughness.

The three-point bending flexural test provides values for the modulus of elasticity in bending, and flexural stress–strain response of the material and is performed in tensile testing machine testing. Results are sensitive to specimen and loading geometry and strain rate.

The tendency of a solid material to slowly move or deform permanently under constant stresses is regarded as **Creep** which measures the strain response due to constant stress.

III. OVERVIEW OF POLYMER AND POLYMER COMPOSITES

A polymer is a material consisting of very large molecules called macromolecules which are formed from repeating many small units called monomers through the polymerization process. Synthetic and natural polymers play essential roles in everyday life for their broad spectrum of properties[1, 2], Polymers range from synthetic plastics such as polyethylene and polystyrene to natural biopolymers like DNA and proteins that are fundamental to biological structure and function. Because of their large molecular mass, they possess unique physical properties such as toughness, high elasticity, viscoelasticity, and a tendency to form amorphous and semi-crystalline structures. The degree of polymerization greatly influences the properties of the derived plastics.

Plastics are a wide range of synthetic or semi-synthetic materials that use polymers as a main ingredient. Plastics can be moulded, extruded, or pressed into solid objects of various shapes due to their plasticity. This uniqueness coupled with other properties, such as being lightweight, durable, flexible, and low cost has led to its wide use in domestic and many industrial sectors. Plastics typically are made through human industrial systems. Most modern plastics are derived from fossil fuel-based chemicals like natural gas or petroleum.

Plastics are broadly classified as **thermoplastics** and **thermosetting plastics**.

Thermoplastics do not undergo chemical change in their composition when heated and thus can be molded repeatedly. Examples include polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC)[3].

Thermosets or thermosetting plastics can be heated to melt but can be shaped only once. After they have solidified, they stay solid. If reheated, thermosets decompose rather than melt as an irreversible chemical reaction occurs [4]. Vulcanization of rubber and Bakelite are typical examples of thermosetting plastics.

A polymer composite is a multi-phase material that is formed by impregnating fillers with a polymer matrix for reinforcement, resulting in synergistic mechanical properties that cannot be achieved from either component alone.

A polymer matrix composite (PMC) is a composite material composed of a variety of short or continuous fibers bound together by a matrix of organic polymers. They can transfer loads between the fibers of a matrix. Lightweight, high resistance to abrasion and corrosion, high stiffness and strength along the direction of their reinforcements make polymer compositesa versatile material for advanced industrial applications including cryogenic and space technologies.

IV. ADVANCES IN THE CHARACTERIZATION OF POLYMER COMPOSITES

Research and developmental works on polymer composites have gained tremendous momentum in recent years and its new area of applications are being explored

Polymer for Cryogenic application highlighting Methods, Mechanisms, and Perspectives is reviewed [5] it is observed that polymeric materials become more brittle, and the adverse effect of thermal stress induced by temperature is significant. The research and development of thermoset and thermoplastic polymers related to the cryogenic compatibility of modified thermoset polymers and the improving mechanisms of the reported modification methods, the cryogenic application potential of some commercial thermoplastic polymers and the recent advance in the use of polymer, especially at liquid oxygen environment are explained. Moreover, future research scopes have been proposed with particular reference to aerospace engineering.

An investigation revealed that cryogenic treatment improves wear, abrasion, erosion, and corrosion resistivity, and durability and stabilizes the strength characteristics of various metals, alloys, plastics, and composites [6].

Carbon fiber reinforced polymer (CFRP) composites are widely used in aerospace crafts as a load-bearing component as they are lightweight but have reasonable mechanical strength. The effects of cryogenic temperature from 77 K to 298 K and cryogenic stability after 50, 100, and 150 cycles on the mechanical properties and failure modes of Carbon fiber-reinforced polymer composite laminates with various stacking sequences are investigated [7]. In-situ static tensile and three-point bending tests are performed. X-ray computed tomography (X-ray CT) results revealed significant degradation in tensile strength and modulus of laminates with the decrease in temperature because of changes in failure mode.

The flexural properties improved by over 50% and the degradation in properties of quasi-isotropy laminates is more significant than that of unidirectional due to the coupling effect of thermal expanding mismatch between material (fiber and matrix) and layer. Quasi-isotropy laminated exhibited greater micro-crack volume fractions (more than 6-fold after 150 cycles). The micro-cracks gradually expanded and nucleation occurred within the interfacial layers as thermocycling rises. The results provide important information regarding the structure design of cryogenic composite tanks under complex working environments based on temperature effect.

Polymer-based composites become brittle and micro-cracks are developed due to differential thermal coefficients of expansion (CTEs) between the polymer matrix and the impregnated filler materials. It is found that the use of single-walled (SWNTs) and multi-walled carbon (MWNTs) nanotubes could enhance the mechanical properties of polymer-based composites. The efficiency and effectiveness of stress transfer in the composites are normally affected by interfacial bonding properties. The viability of using coiled carbon nanotubes (CCNTs) and randomly-oriented Nano clay-supported nanotubes (NSCNTs) to enhance the mechanical properties of epoxy resin at the cryogenic temperature are explained in detail with experimental studies [8].

The polymer materials need to possess good mechanical and physical properties at cryogenic temperatures such as liquid helium (4.2 K), liquid hydrogen (20 K), liquid nitrogen (77 K), and liquid oxygen (90 K) temperatures, etc. Mechanical and physical properties of polymers and filled polymers materials at cryogenic temperature are highlighted with a details discussion on cryogenic tensile behaviors, shear strength, impact strength, and fracture toughness etc. Thermal creep and dielectric properties of polymers are also summarized [9].

The material properties such as tensile, compressive and shear strength, stress-strain behavior, mechanical and thermal fatigue response, fracture toughness, impact resistance, tribology thermal expansion and thermal conductivity and abrasion resistance of polymer composites are presented highlighting the challenges of cryogenic experiments towards characterization[10].

The tribological behavior of Poly Tetra Fluro Ethylene (PTFE) composites against steel at cryogenic temperatures is investigated. The results showed that the friction coefficient decreases with the temperature down to 77 K, but below 77K, It did not follow a linear evolution. The cryogenic environment has a great influence on the tribological performance of the polymer composites. SEM and AFM analyses revealed that the PTFE matrix composites investigated have transferred material onto the disc down to very low temperatures [11].

High strength, stiffness, and low weightpropel composite materials and FRPs into new arenas. Due to the heterogeneous nature and anisotropic behavior of FRPs, a structural designer has faced challenges in predicting the integrity and durability of FRP laminates. Cryogenic fuel tanks for storing Liquefied Natural Gas (LNG) and liquid hydrogen are the unique structural applications of FRP at low temperatures. Micro cracks as well as delamination in the composites due to thermal residual stresses may develop which provide a pathway for the ingress of moisture or corrosive chemicals leading to loss of cryogenic fluids in the tanks. Matrix resins become brittle and do not allow the relaxation of residual stresses to take place. Polymers are well below their glass transition temperature and show little viscoelastic behavior when exposed to a cryogenic environment. Mechanical properties of FRP composites such as carbon, glass, and Kevlar fiber-reinforced polymers with different resin matrix at cryogenic temperatures are discussed [12].

The mechanical performance of carbon nanotube (CNT) reinforced polymer composites subjected to tension in a cryogenic environment is experimentally and numerically evaluated. Tensile tests are performed on CNT/polycarbonate composites to identify the effects of CNTs tensile properties, and finite element computations are also conducted using a model for the representative volume element (RVE) of CNT reinforced composites for computing the effective composite elastic modulus and the stress state within the composites. The numerical findings are then correlated with the experimental results [13].

Thermal/mechanical response and damage growth in polymeric composites at cryogenic temperatures are investigated [14]. The research paper presents experimental data on the residual mechanical properties of a carbon fiber polymeric composite, IM7/PETI-5, before and after cryogenic treatment. Tension modulus and strength are measured at room temperature, -196°C, and -269°C on five different specimen ply lay-ups,[0] 12, [90112, [-+4513s, [-+2513s and [45,903,-45,03,-45,903,45]. Specimens were preconditioned with a onset of coupons being isothermally aged for 555 hours at 184 °C in an unloaded state. And Microscopic examination of the surface morphology of the specimen after exposure to cryogenic temperature shows evidence of degradation along the exposed edges of the material.

The Characterization of cryogenic delamination growth behaviour in woven glass fibre reinforced polymer (GFRP) composite laminates subjected to Mode II fatigue loading are reported in the literature by conducting testsat room temperature, liquid nitrogen temperature (77 K) and liquid helium temperature (4 K) using the four-point bend end-notched flexure (4ENF) test method, The research findings give an ideaof the fatigue delamination growth mechanisms in the woven glass fiber reinforced polymer GFRP laminates under Mode II loading at cryogenic temperatures [15].

To assess the damage trends in cryogenically cycled (upto1000 cycles) carbon/polymer composites, (six carbon/polymer composites of three materials, two lay-ups each) are cycled by repeated submersion of 5 cm x 5 cm flat plates in liquid nitrogen. It is observed that reducing the ply thickness by 30% in the IM7/5250-4 delays surface ply micro-cracking by up to 200 cycles and the surface ply micro-crack densities are nearly equal by 100 cycles regardless of the ply thickness [16].

Thermal/Mechanical Response of a Polymer Matrix Composite at Cryogenic Temperatures reported [17]. This paper presents experimental data on the residual mechanical properties of a carbon-fiber polymeric composite, IM7/PETI-5, both before and after cryogenic exposure. Tension, compression modulus, and strength are measured at room temperature, -196"C, and -269°C on five different laminate configurations.It is shown that trends in stiffness and strength that result from changes in temperature are not always smooth and consistent.

A yield-stress-based failure model is used to predict the temperature at which microcracking occurred in symmetrical cross-ply carbon-fiber/epoxy composite materials. Dynamic mechanical analysis was used to assess microcracking at cryogenic temperatures through the observation of discontinuities in the material properties during failure. The model accurately predicted the onset temperature for microcracking in three of the four cases, if a fiber-reinforced polymeric composite laminate's room-temperature properties are appropriately modified to take care of property variations at low temperatures [18].

Low-temperature properties of a unidirectionally reinforced epoxy fiberglass composite are studied [19]. The tension, compression, and in-plane shear properties of a unidirectionally reinforced fiber/epoxy composite are measured at 295K, 76K, and 4 K. The composite plate material is produced by the wet-filament winding method. The orthotropic material properties are dominated by the glass fiber properties if measured parallel to the direction of reinforcement and the epoxy resin matrix properties are dominated when measured transverse to the reinforcement. With the decrease in temperature, strength and elastic moduli are increased.

Effects of High and Low Temperatures on the Tensile Strength of Glass Fiber Reinforced Polymer Composites are studied [20]. The tensile strength of glass fiber reinforced polymer (GFRP) composites at high and low temperatures is experimentally determined. GFRP laminates are manufactured by the wet hand lay-up assisted by a vacuum bag to get an average fiber volume fraction of 0.45. Using simultaneous heating/cooling and loading, glass fiber epoxy and polyester laminates are examined for their mechanical performance in static tensile loading. The tension mechanical properties; stress and modulus are reduced with increasing temperature from 250 C to 800 C. Results from room temperature to a minimum temperature of - 200 C, indicate that there is no considerable effect on the tensile strength but a slight decrease of tensile modulus is observed on the GFRP laminates. The experimental findings highlight the structural survivability at low and high temperatures of the GFRP at the cryogenic environment.

The impact properties of glass fiber/epoxy composites in the cryogenic environment are experimentally determined [21]. GFRP samples are fabricated by vacuum infusion process with post-curing at 353 K for 3 h to ensure that a complete chemical reaction inside the samples is achieved. Samples are stored at room temperature (295 K), dry ice temperature (199 K), and liquid nitrogen temperature (100 K) conditions. The apparent damages and their size are visually examined and impact load, deflection, and energy absorption of each damage type are interpreted. Besides, the post-curing effect was also studied to verify its significance to the impact properties of composites. Experimental results show that post-curing could reduce the apparent damage and increase the energy absorption of GFRP composites.

V. CONCLUSION

The article described details of the experimental findings by the researchers on the effect of low temperature pertaining to the structural properties including tensile strength, impact strength, thermal fatigue, creep, brittleness, etc so that the designer can make a choice of the appropriate polymer composites for its application to a specific cryogenic field. Itis observed that most polymers become brittle at low temperatures but their strength increases. Fiberglass-reinforced epoxy resin or graphite-impregnated PTFE can sustain low temperatures without cracking and hence their structural survivability at cryogenic temperature is manifested. In addition, PTFE offers self-lubricating properties.

Centre for Rural and Cryogenic Technologies is in the process of developing a fiberglass-reinforced epoxy tube to be used in the cryogenic container which will not only withstand cryogenic temperature but also will act as heat insulating neck of the cylindrical metallic container.

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