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Recycled and devulcanized rubber modified epoxy-based composites reinforced with nano-magnetic iron oxide, Fe_3O_4

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ABSTRACT

Rubber modified epoxy based composites were designed by low cost production methods. Basically, clean and recycled materials were used to provide a solution for manufacturing of lightweight, cost efficient composites in industrial applications such as automotive and aeronautical engineering. In the present study four different compositions have been developed and characterized for their potential usage as structural materials. The matrix was prepared by treatment of epoxy with 10% recycled rubber. Nano-magnetic iron oxide, Fe_3O_4, was added to the matrix as reinforcement elements in different percentages. Nickel and aluminium were also add as auxiliary additional elements. Measurements of magnetic permeability and dielectrically properties have been carried out for electronic devise applications basically in aeronautical engineering. Dynamic Scanning Calorimeter (DSC) and Dynamic Mechanical Analysis (DMA) were carried out to determine thermo-mechanical properties. Static tests have been carried out by 3-point bending (3PB) tests for mechanical characterization. Furthermore, creep and wear behaviour of these compositions were evaluated by means of nanoindentation tests to analyze time dependent behaviour of these composites. Macro scratch tests were made in very high cycle test conditions for their measurements in long time resistance. Microstructural and fracture surface analyses have been carried out on the scanning electron microscopy (SEM).

All of the experiments; scanning electron microscopy, nanoindentation, static (3PB), test results expose a combined effect of toughening mechanisms high strength and ductile, lightweight and low-cost composites based on the rubber modified epoxy composites reinforced with nano magnetic iron oxide and auxiliary fine nickel and nano aluminium powders.

1. Introduction

Epoxy-rubber based structural composite materials are utilized more and more in the last decades thanks to their large spectrum of functional properties and performances. In order to realize an efficient engineering development process, the material property data needs to be obtained by different characterization steps and it is a requirement for material suppliers and engineers. The materials properties such as ease in manufacturing, flexibility and polymer-based dielectrics facilitate the usage of these composites in different industries [1]. To improve the brittleness of epoxies, adding a rubber phase such as commercially available styrene butadiene rubber with different functional terminal groups has been studied by different researchers [2].

Furthermore, using of fresh scrap rubber gives an economic and environmental aspect to this study. The volume fraction of the toughening rubber phase generally varies from 5 to 20%. But, the incorporation of rubber phase increases the viscosity of the epoxy resin mixture whereas the crosslink density, elasticity modulus and tensile strength diminish [3–5].

Another important point is that, the functionalities of these composites are increasing significantly in advanced electronics, electromagnetics and electric power systems such as actuators, AC motors, embedded capacitors, piezoelectric and high energy density pulsed-power devices [6]. In this regard, microwave absorbing property also attracts attention for many researchers. In detail, there are certain parameters needed to be taken into consideration in manufacturing of microwave absorbing materials, such as the weight, thickness, types of filler, filler content, environmental resistance and mechanical strength [7]. In this respect, ferrites are considered to be the best magnetic material for electromagnetic wave absorbers thanks to their outstanding magnetic and dielectric properties. However, they are heavy and expensive.

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In other respects, polymers are used to protect the electronic devices from electromagnetic interference (EMI) due to the flexibility, lightweight and cost effectiveness. Nevertheless, polymers are electrically insulating and transparent to electromagnetic wave. Therefore, ferrite materials are incorporated into polymer matrices to effectively eliminate EMI [8]. Many works have been done on polymer-based composites filled with magnetic materials in micrometer - size, such as Fe_3O_4/YIG [9]. However, conventional magnetic particles filled polymer-based composites have some drawbacks in corresponding the criterion in thin and lightweight microwave absorber because of high filler content [10]. For this reason, it is decided to use Fe_3O_4 instead of conventional magnetic fillers.

Fe_3O_4 nanoparticle, was selected in this study mainly due to its genuine and novel physiochemical properties which can be attained according to their particle size (quantum size effect), morphology, shape and engineering form [11]. Also, it is found attractive to enhance the magnetic permeability of epoxy based composites, by a good synchronization between the electrical and thermal conductivities [12]. Moreover, addition of Ni and Fe_3O_4 thermite powder mixtures to the matrix has been shown to have significantly affect the energetic of the reaction between the powders [13]. Hence, a balanced mixture of these characteristics can result in superior structural and energetic properties.

The present work presents processing of devulcanized recycled rubbers blended with epoxy resin to create novel composites in economic way. Main objective of this research is to determine the magnetic and mechanical properties of these composites. During this study, physical properties such as glass transition temperature and phase transitions were determined with dynamical mechanical analysis (DMA) and differential scanning calorimeter (DSC). Then, bending tests were realized with smooth specimens. After that, nano indentation as well as scratch tests have been carried out to see the time dependent behaviour and wear characteristics. In addition, surface hardness was determined by means of Shore D hardness measurement. Also, magnetic and dielectric properties were examined by means of special equipment. At the end, fracture surfaces were observed by means of scanning electron microscopy (SEM) to study the toughening and damage mechanisms.

2. Experimental conditions

2.1. Materials processing

When the recycled rubbers are blended with epoxy matrix to create new composites, the durability of the final product is highly dependent on the compatibility of epoxy and the rubber type. Lack of the compatibility results in weak interfacial adhesion and this situation poses an obstacle to obtain a toughened composite. Also, the intensity of interfacial adhesion between the matrix and the toughened phase plays a key role in terms of toughening mechanisms. A strong adhesion is required at the interface for the relieving of the applied load. Physical interactions and molecular interlocking can either increase or decrease the adhesion between the toughened phase and the matrix. For an effective toughening, an intermediate bonding, which is not too strong or too weak, is thought as the key issue.

However, epoxy resins are usually incompatible with the recycled rubber particles and it causes to a poor interface [14]. For this reason, fresh scrap rubber should be devulcanized. In fact, devulcanization is known to be an operative practice for manufacture of recycled rubbers to increase flowing capacity and also to be remolded during manufacturing of new designed composites. During this process, Sulphur links are tried to be broken and also generated new other links, it means that the structure of the material is modified entirely as renewable process.

In the frame of the present work, a new combined method was used to devulcanize fresh scrap rubber (SBR) with a particle size varying from 30 to 130 μm. This combined method contains a pre-chemical treatment of rubbers followed exposing them to microwave heating in a short time that is applied in two stages in practical point of view. It means that 2 min microwave heating for each stage for a total heating of 4 min in order to avoid degradation of the main chains. During the chemical treatments, acrylic acid was used as a catalyzer for surface activation of the fine rubber particles after a short silanization process. After that, a drying process was carried out at 80 °C during 24 h under adiabatic conditions. At the final stage, much effective spark effect was carried out by means of microwave heating for devulcanization process [15–18]. By this way, a good cohesion is supplied at the interface between epoxy resins and rubber powders to improve the properties of the recycled rubber coming from the sportive affaires. It means that are fresh clean scrap and completely different from ground tire [19–23].

In the second stage, after the chemical treatment and devulcanization of rubbers, solid epoxy resin was mixed with fine rubber powders in pre-defined ratios, then the blend was milled for 2 h with a fast-rotating toothed-wheel mill to obtain fine and homogeneous compound for 2 h. This mixture used as a matrix after that the new designed composites are manufactured by using classical powder metallurgy methods. After the addition of reinforcements, mainly iron oxide particles which are manufactured via sol-gel method in the laboratory of Supmeca-Paris [17,18], milling process is carried out during 4 h.

After having a homogeneous powder compound, the composite specimens were manufactured by using double uniaxial action press at a temperature of 180 °C under a pressure of 70 MPa during the heating of 30 min. All of the specimens (30/50 mm in diameter) were cooled slowly in the press. All of the specimens were post-cured isothermally at 80 °C for 24 h.

The compositions of iron oxide reinforced epoxy-recycled rubber based composites (called as ENRF I-II-III hereafter) were given in Table 1.

After hot compaction, test specimens were cut from the cylindrical samples. In Fig. 1 powder form of the composites, compacted composites in different diameter and 3PB test specimens are presented in Fig. 1.

2.2. Thermal analyses and physical characterization

Differential scanning calorimeter (DSC) analyses were performed on DSC Q10N2 apparatus of TA Instruments, USA, from −80 °C to 400 °C in air flow with a 1 dm^3/min flow rate and heating rate of 10 °C/min. Dynamic properties, storage modulus (E′) and mechanical loss angle tangent (tan δ) of the epoxy based composites were investigated using a Dynamic Mechanical Thermal Analyzer Q800 system (TA Instruments). The data were obtained at a frequency of 1 Hz, 0.1% strain in the temperature range from −80 °C to 200 °C using a heating rate of 3 °C/min under single cantilever bending mode. The dimensions of the investigated samples were as follows: width 10 mm, length 30 mm, and the thickness were 3 mm.

Table 1
Chemical composition of the “epoxy – rubber” based composites prepared for this work.

Composite code	Weight percentage of reinforcement particles			
	Fe_3O_4	Ni	Al	Matrix
ENRF I	10	5	10	75
ENRF II	20	5	10	65
ENRF III	30	5	10	55

Ratio of Matrix (90% Epoxy and 10% Rubber Powder)