METHODS USED IN THE ANALYSIS AND TESTING OF COMPOSITE MATERIALS WITH RUBBER MATRIX AND FA AND PVC ADDITIVES

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ABSTRACT: In the current context of excessive use of plastics and rubber materials, which are difficult to degrade, increasing levels of environmental pollution and global warming problems due to high industrialization, research is focusing on new materials, especially composites, with low environmental impact, made from waste resulting from other manufacturing processes but also after the end of their life cycle.

The recycling of rubber waste, polyvinyl chloride (PVC), and fly ash (FA) resulting from the combustion of coal in power plants for electricity production is an activity that can contribute to sustainable development, considering the three components (economic, social, and environmental).

KEY WORDS: Composite materials, industrial waste, rubber, fly ash, PVC

INTRODUCTION

Composite materials with a rubber matrix and FA additives can be used as components for construction materials (mortar, cement, concrete) or as insulating materials. For their manufacture, it is important to choose the right combination process for the two components. Usually, their manufacture is characterised by the following steps:

- FA collection: it is collected after coal combustion in power plants; it may contain fine particles and harmful chemicals, so it must be handled with care;
- FA preparation: it is processed to remove impurities and obtain a suitable grain size for mixing with rubber;
- mixing with rubber: this can be done by extrusion, using twin-screw extruders [1];
- Insertion of additives and modifiers: these are inserted to improve the properties of the composite; plasticizers, hardening agents, lubricants, and other chemical additives are used, depending on the specific requirements of the application.
- actual formation of the composite material: it can be extruded into profiles, pressed to obtain plates or other shapes;
- vulcanization: provides strength and durability to the final material;
- finishing and testing: excess material is removed, and samples are subjected to strength, flexibility, vibration, acoustic, thermal insulation, and other tests.

The final stage after manufacturing a composite material is its actual testing. Tests are carried out to ensure that the material meets certain characteristics in accordance with the purpose for which it was made. These characteristics can be highlighted through testing or experimental analysis.

Several experimental tests were carried out to determine the mechanical properties of composite materials with a rubber matrix and PVC inserts[3]. The first test was a tensile test, performed on a Schopper machine with a pulling speed of 460 mm/min. The modulus of elasticity, tensile strength, and elongation at break were determined in accordance with ISO 37/2012 [2]. Flat test pieces were used in accordance with the specifications in this standard (Figure 1).

In Figure 1, L denotes the length of the test specimens, which is given in Table 1.

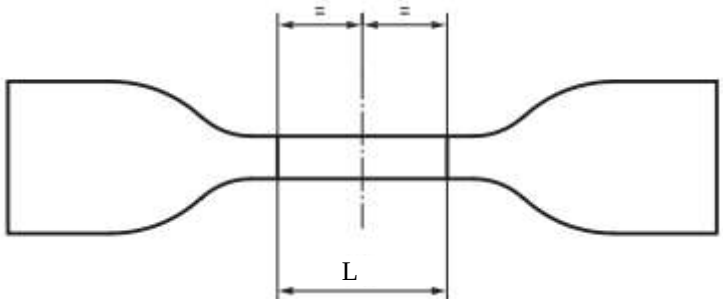

Figure 1. Standard test piece for tensile testing [2]

Table 1. Length of test specimens for tensile testing [2]

Specimen type	1	1	2	3	4
Length of calibrated section [mm]	25	20±0.5	20±0.5	10±0.5	20±0.5

In addition to the tensile test, a Shore hardness test was also performed, scale A according to ISO 7619/2011 [3,4]. A penetrator came into contact with the material under study, using a sufficiently large force. The holding time was 3 s for vulcanized rubbers and 15 s for thermoplastic rubbers. The dimensions and shape of the penetrator are given in Figure 2 according to ISO 7619. Another test for rubber composite materials and PVC inserts described was the accelerated aging resistance test, which was performed according to the specifications [3,5].

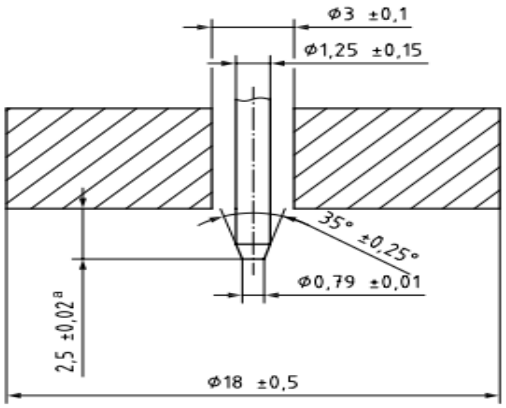

Figure 2. Dimensions and shape of the penetrator for scale A hardness [4]

Accelerated aging and heat resistance tests are designed to estimate the relative resistance of rubber to deterioration over time [6]. To this end, the rubber is subjected to controlled deterioration influences for defined periods, after which the corresponding properties are measured and compared with the corresponding properties of unused rubber. In accelerated aging, the rubber is subjected to a test environment designed to produce the effect of natural aging in a shorter time.

In the case of heat resistance tests, the rubber is subjected to long periods at the same temperature that it will experience in service. Two types of methods are presented in this International Standard, namely an air oven method using low air velocity and an air oven method using forced ventilation for high air velocity.

Samples similar to those used for tensile tests and hardness determination were used for accelerated aging resistance testing [3]. The test duration was 7 days at a temperature of 70 ± 1°C. The results were compared with those obtained from samples that were not subjected to the aging process.

Abrasion resistance was determined according to ISO 4649/2008 cylindrical method, using a pressing force of 10 N [7]. Abrasion resistance was expressed as relative volume loss in relation to calibrated abrasive paper. An abrasion tester with abrasive fabric and normal electrocorundum abrasive on a fabric substrate with a grain size of 212–80 μm (PE 80) was used, whose abrasiveness must be 180–220 mg for the control rubber. The samples were obtained from laminated mixtures and then pressed with a rotating die. The samples were cylindrical in shape, with a diameter of 16 mm and a minimum height of 6 mm. The diagram of the apparatus used is shown in Figure 3 [7].

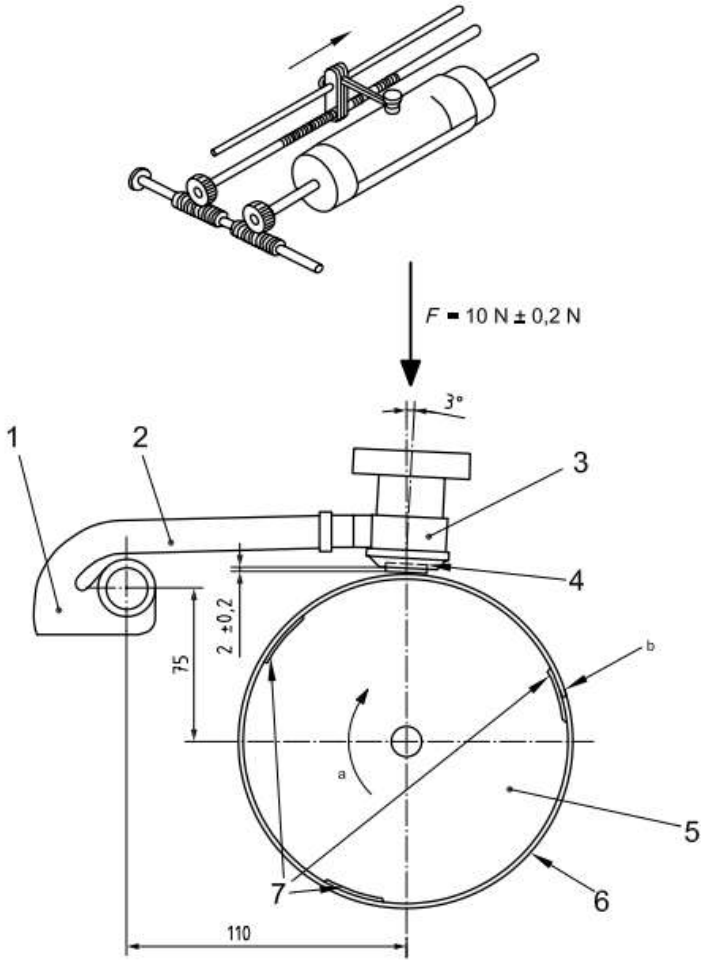

Figure 3. Equipment used to determine abrasion resistance [7] (1. – hammer; 2- oscillating arm; 3 – sample holder; 4- test sample; 5- cylinder; 6- abrasive sheet; 7- double-sided adhesive tape)

Resistance to repeated bending is determined according to SR 7645 [3,8]. A De Mattia type testing machine is used, Figure 4. The machine has fixed parts, equipped with clamps to hold one end of each sample in a fixed position, and similar parts, but with oscillating movement, to hold the other end of each sample. The displacement is 57 ± 0.5 mm and is such that the maximum distance between each set of opposite clamps is 75 ± 1 mm. The oscillating parts are arranged so that their movement is rectilinear and in the direction and in the same plane as the common center of each set of opposing

clamps. The planes of the gripping surfaces of each set of opposing clamps remain parallel throughout the movement [8].

The samples used for this test were obtained by cutting from rubber plates and are rectangular in shape. The test was performed by monitoring the crack marks on each sample at intervals of 1 h, 2 h, 4 h, 8 h, 24 h, 48 h, 72 h, and 96 h [3].

Figure 4. De Mattia machine [9]

Swelling resistance was tested by immersion in liquids and determined according to ISO 1817 by changing the mass and volume using the following method: test samples of known weight (W 1) and volume (V 1) were immersed in different solvents: water, sunflower oil, soybean oil, animal fat, 70% sulfuric acid, 50% nitric acid, 50% caustic soda, isooctane, toluene, 70% isooctane solution, and 30% toluene solution, in diffusion test bottles and kept at room temperature for 22 hours [3,10]. After this period, they were removed from the bottles and weighed. This procedure is used if the sample is completely immersed in the solutions. If only one surface of the sample is immersed, then a device such as the one in Figure 5 [10] is used.

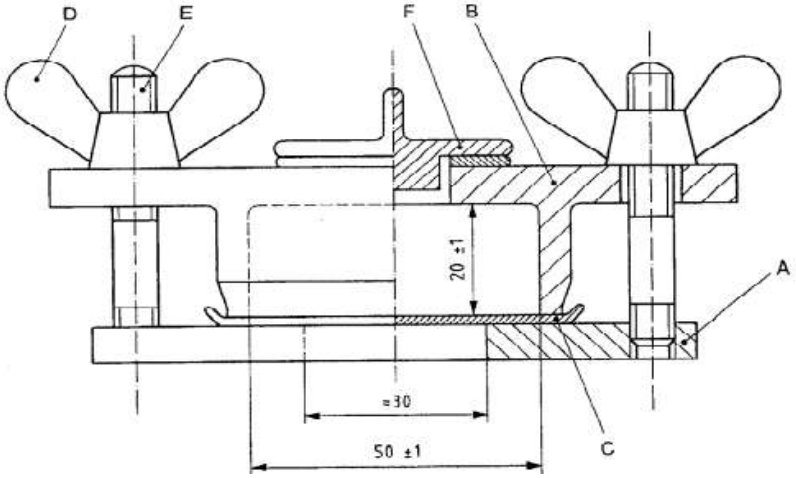

Figure 5.a. Device for immersing a surface of the sample in liquid according to ISO 1817 [10]

Figure 5.a. shows the following components: A – base plate, B – cylindrical piece, C – test piece, D – flange nut, E – bolt.

Other tests and analyses commonly used in research related to rubber matrix composite materials are microscopic ones. One of the most widely used is scanning electron microscopy (, SEM) because the equipment has very high magnification powers and can analyze and highlight

structural homogeneities/inhomogeneities, defects, inclusions, or aspects related to the type of surface fracture following destructive testing, etc. For example, aspects of the fracture section for tensile test specimens were investigated using scanning electron microscopy. Figure 5.b) [11]

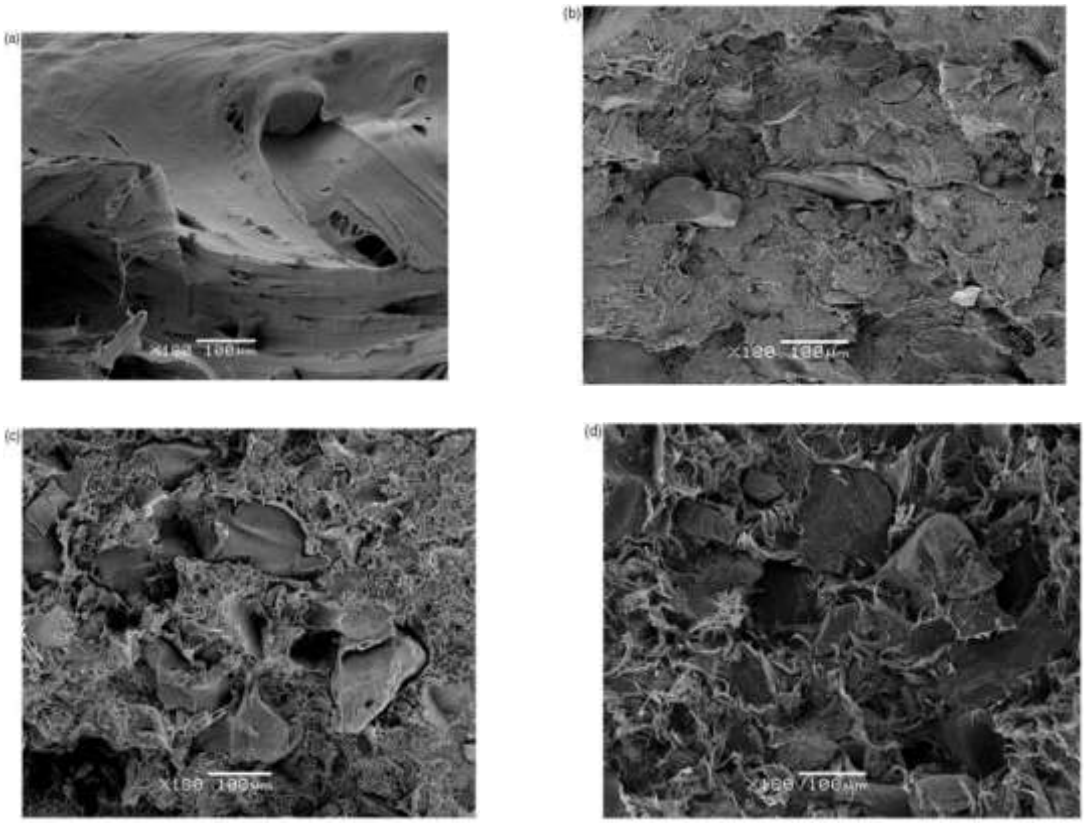

Figure 5.b. SEM micrographs of HDPE-GTR for several concentration percentages: (a) HDPE/GTR-10%; (b) HDPE/GTR-20%; (c) HDPE/GTR-40%; and (d) HDPE/GTR-70% [11].

SEM (Scanning Electron Microscopy) was used to analyze the fracture surface of the tensile-tested samples. It is possible to analyze the effects of this filler material in the matrix by observing the environment of the reinforcing particles. Several images of the samples were analyzed according to particle size and GTR (recycled rubber granules) concentration. A JEOL 5610 microscope was used, and the samples were previously coated with a thin layer of gold to prevent static charge accumulation on the surface [12].

SEM images show relative differences in their results depending on particle size and concentration [11]. In terms of particle size, when particles are small, they adhere better to the matrix due to their high specific roughness and small pore and crack size. On the other hand, large particles cause an increase in defects and cracks in the matrix, worsening interfacial adhesion. The concentration of GTR also influences the microstructure of the composite, worsening the bond at the interface in all cases, forming agglomerates that cause cracks and pores of considerable size on its surface.

The thermal behavior of composite samples with rubber matrices is studied using differential scanning calorimetry (DSC) of heat flow [11]. The measurements were performed using a Mettler TA4000 thermoanalyzer coupled with a DSC 30 device. The sample mass was between 3.0 and 3.5 mg and was small enough to avoid problems caused by heat and material transfers. The temperature and enthalpy were calibrated using indium (In) and lead (Pb) as standards ( ). The samples were heated from 40°C to 200°C at a heating rate of 10 K/min

and using synthetic air as the purge gas at a flow rate of 40 mL/min.

The calorimetric study indicates that the differences in melting enthalpy are small when the GTR concentration is varied, which means that the matrix is only slightly modified by the presence of the filler in terms of its crystalline structure. However, this melting enthalpy tends to increase slightly for compounds with particle sizes below 200 μm and low GTR concentrations (5-10%) due to the nucleation effect of GTR particles inside the HDPE. In general, particles larger than 200 μm cause a decrease in melting enthalpy in all cases, demonstrating greater fragility.

A tensile stress study similar to that in [3] was also performed, but using the American standard ASTM D638-14 [13]. Another type of test presented in [11] was dielectric analysis. Dielectric analysis was performed only with particles smaller than 200 μm. The dielectric parameters and magnitudes were measured by dielectric analysis with BDS40 equipment [14], which has a built-in Novotherm temperature sensor from Novocontrol [15], using a compression mold with a diameter of 2 cm and a thickness of 400 μm. The measurements were performed in a frequency range from 1 to 1/100 and 3 to 10^{6}Hz, with a temperature scan between 30°C and 120°C and at a speed of 3°C/min using the aforementioned sensors. Analysis of the results showed that the actual conductivity, permittivity, and dielectric loss factor increase with the concentration of GTR in the respective compounds. As with similar materials, conductivity exhibits sublinear dispersive behavior in all cases. On the other hand, permittivity decreases with frequency in composite samples, but remains constant in pure HDPE.

Two other types of experimental investigations are presented in [16]: thermal stability by thermogravimetric analysis (TGA) and dynamic mechanical stability by DMA analysis. The thermal stability of the sample was measured by thermogravimetric analysis (TGA) on a Mettler Toledo TGA/SDTA 851e (Switzerland) [17], operating under an $N_{(2)}$atmosphere at a heating rate of 20°C/min in the temperature range from 50 to 1,000°C. Dynamic mechanical analysis (DMA) of the sample was performed on a Mettler Toledo DMA/SDTA 861e instrument (Switzerland) in torsion mode at a constant frequency of 1 Hz and a heating rate of 3°C/min in the temperature range from -50 to 50°C under a flow of N_2 .

The behavior of conveyor belts under thermal shock was investigated [18]. Conveyor belts can operate under special conditions in terms of working temperature. In this regard, the most common thermal shock conditions consist of temperature cycles between -40 °C and 85 °C. Therefore, environmental conditions have a major influence on the functionality and reliability of conveyor belts. In order to detect latent weaknesses in the shortest possible time, a typical temperature test is often insufficient. Thus, the samples were subjected to several sudden temperature changes. Under these conditions, the elastic properties of the conveyor belts were determined both immediately after manufacture and after the application of thermal shocks.

A Zwick/Roell Z05 TN device [19] with testXpertII software version 3.6 produced by BRECON Vibrationstechnik GmbH Stolberger, Cologne, Germany, was used to measure the elasticity of the conveyor belts. This type of device has a wide range of equipment options that allow the zwickiLine to be used for testing plastics, elastomers, metals, composites, paper, cardboard, textiles, foams, food, and components.

A thermal chamber was used for the thermal aging of conveyor belts - the Temp Shock Votsch VT3 7012 S2 test chamber manufactured by Test Equipment Co., Ltd. Jin Hui Industrial Park, China [20]. This thermal chamber allows very rapid temperature changes in the range from -80 °C to +220 °C. This method of testing conveyor belts leads to improved manufacturing conditions for conveyor belts in order to increase their reliability.

The thermal aging application regime was established taking into account the following parameters:

- a total of 2000 cycles of variation between -40 °C and 85 °C;

- the acclimatization time varied, being 45 minutes for the first 700 cycles and 15 minutes for the rest.

An accommodation time of 15 minutes for the last 1300 load cycles was considered sufficient, given the small mass and relatively large surface area of the samples. Acclimatization was performed under forced conversion (ventilation). A temperature range between -40 °C and 85 °C was adopted, taking into account the actual conditions in which conveyor belts may be used. The penetrator used in the testing process had a spherical end with a diameter of 7.96 mm and a tip radius of 3.98 mm.

CONCLUSIONS

The following conclusions can be drawn from the study carried out in this chapter:

- Rubber, PVC, and FA waste have a wide range of practical uses, mainly in construction as a component of cement, with the manufacturing technology being casting.

- The manufacturing process for natural rubber can vary depending on the type of finished product desired and the technology used.

- The manufacturing process for synthetic rubber can vary depending on the type of synthetic rubber produced and the end application; there are several different types of synthetic rubbers, each with specific chemical compositions and properties, so processes may vary depending on these variables.

- The specific composition of composite materials with a rubber matrix and PVC additives may vary depending on the end use and performance requirements; the production of these composite materials requires a thorough understanding of the chemical and technical processes, as well as the appropriate additives to achieve the desired properties [21].

- The production of composite materials with a rubber matrix and FA additives involves both chemical and material processing technologies and requires a detailed understanding of the properties of the materials and the requirements of the end application.

- the production of composite materials with a rubber matrix and fly ash (FA) and PVC particle inserts is a complex process that requires rigorous control of the manufacturing technology because both FA and PVC particles pollute the environment and can affect health;

- there are a large number of technologies for obtaining composite materials with rubber matrix and FA or PVC additives, These are characterised by variations in working temperature, mixing speed, vulcanisation time (where applicable), pressing pressure (if hydraulic presses are used in the final stages), drying temperature and duration, etc. [22, 23].

- there are a large number of standardized tests and analyses that can be applied to composite materials with rubber matrices and FA or PVC additives depending on their field of application; analysis of the specialized literature has shown that destructive tensile tests and SEM micrographs are most commonly found in research studies [22, 23];

The choice of test methods for test specimens is a determining factor in establishing product recipes, dosages, quantities, and dimensions. The importance of testing materials cannot be ignored.

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