

CERAMIZABLE POLYMER COMPOSITES – POSSIBILITIES AND CHALLENGES

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1. Introduction

Ceramization of polymer composites can be defined as creation of mechanically resistant, porous ceramic structure of good barrier properties on their surface when faced high temperature or fire [1, 2]. The protective layer limits diffusion of flammable products of polymer decomposition, what together with smaller amount of oxygen being able to reach fire zone and reduction of heat transfer to the material, additionally adversely affecting the material decomposition, makes development of fire more difficult. Additionally, the continuous and porous ceramic phase being created, is likely to limit release of harmful and toxic products of polymer combustion and to reduce smoke generation during fire. Ceramization requires to fill polymers with a composition of fluxing agent, i.e. glass frit of relatively low softening point (flux particles), and powdered mineral fillers of high thermal resistance (refractory fillers). The above ceramization system is able to create the ceramic layer on polymer surface, being able to protect bulk of the material from heat/fire and external load. Mechanism illustrating formation of porous ceramic layer is presented in Fig. 1.

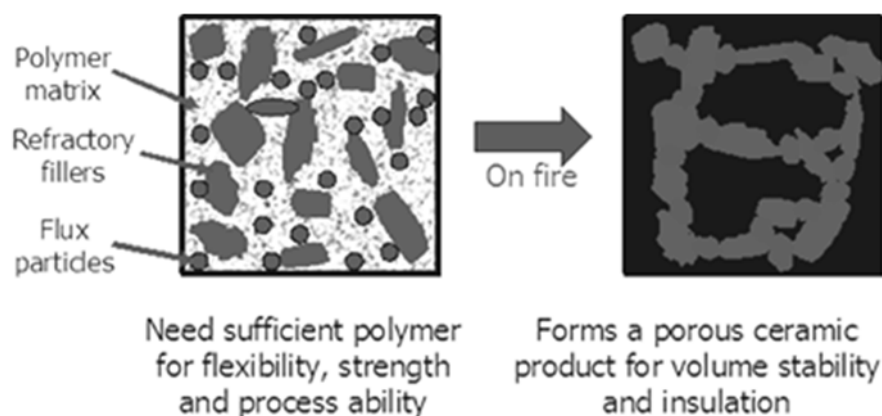


Fig. 1 Scheme illustrating ceramization process of polymer composites

Adequate qualitatively and quantitatively composition of flux - mineral fillers ceramization systems, grinding degree of their particles, and the way of modification of their surface, altogether enable effective processing and mechanical properties of the polymer composites, as well as assure morphology of pores (size distribution and amount), being responsible for mechanical strength, heat and gas insulation of the ceramic layer formed on polymer surface under high temperature, to be controlled. It has been confirmed that properly designed ceramization system can protect polymer composites used in cable, paint, sealing or other engineering applications from loss of their functions under fire conditions for at least 1 hour [3, 4].

Selection of appropriate refractory fillers for ceramizable composite is extremely important, because after polymer matrix degradation, they serve as a backbone of the ceramic structure. Mineral fillers can also increase flame retardancy of the composites by their endothermic decomposition, release of chemically bound water and formation of a layer of oxides that protects

bulk of the composite against further thermal degradation [5]. Also size of filler particles influences mechanical strength of ceramic phase being formed. Reduction in the average particle size allows not only for better dispersion of filler, but also increases the surface area of filler where ceramic, created from fluxing agents or decomposition of polymer matrix can be deposited. The size of filler particles also most often influences flame retardancy of polymer composites, smaller particles act in solid phase performing creation of more barrier char, increasing flame resistance [6]. On the other hand, with particle size decreasing, their ability to aggregation and agglomeration increases what can cause completely opposite effect, if the affinity between polymer matrix and/or fluxing agent and the filler surface is poor [7]. In some cases it makes necessary to fillers' surface, in order to assure its good wettability by melted "precursors" of ceramic phase [8]. Recent research in the area of ceramifiable composites has focused on the development of new ceramization-promoting additives [9, 10] and special components, e.g. carbon fibers, making strength of the ceramic phase formed after heat treatment/fire increased [11].

2. Experimental

2.1 Materials

Effects of ceramization is to be discussed on the example of four silicone rubber composites, designated as: F, S, W and N. The materials have similar base made of silicone rubber filled with pyrogenic silica in the amount of 50 phr. Another 50 phr of fillers, being admixed to the base, constitute mineral phase, which differs significantly according to composition and the kind of components. The fillers selected: mica (muscovite) and ZnO - composite F, quartz - composite S, wollastonite (CaSiO_3) - composite W, as well as wollastonite and quartz - composite N, differ intentionally according to their content, aspect ratio, dimensions and size distribution of particles.

2.2 Techniques

Performance of the composites during fire testing has been explained based on the results of their thermal analysis (TGA/DSC and microcalorimetry), as well as morphological studies (microporosimetry and SEM) and breaking strength analysis of ceramized phase produced due to heat treatment. The composites studied were ceramized under various conditions:

- by firing in an open flame (measured temperature exceeded 1000°C) with 2 min. soaking time, or
- by heating in a laboratory furnace, from room temperature up to 600, 800 or 1000°C , with the heating rate of $20^\circ\text{C}/\text{min.}$, followed by 20 min of soaking.

3. Results and discussion

SEM analysis of the composites subjected to ceramization makes possible to reveal the influence of heat treatment conditions on structure of the materials. The most significant changes are presented in Fig. 2.

Microscopic analysis of samples ceramized in a laboratory furnace at 800°C (see the left column of pictures) demonstrates significant differences among the composites studied. The material N contains the highest amount of pores, contrary to other composites, for which pores are more difficult to be identified. Detailed information on pore size distribution of the composites studied is presented by microporosimetric analysis. The porosity of composites N and to small extent S, contrary to the other materials studied, is represented by two population of pores: sub-micro and micro ones. Porosity of the composites depends on ceramization conditions. The smallest pores, of sub-micrometer dimensions, disappear when the materials have been fired directly in a flame (see the right column of pictures). The total degree of material porosity also

another 20-30 deg to be completed for the materials W and N, whereas the composite S requires temperature exceeding even 800°C. It decides the composition of fluxing system required for each of the composites and determines temperature range in which their ceramization process can take place effectively.

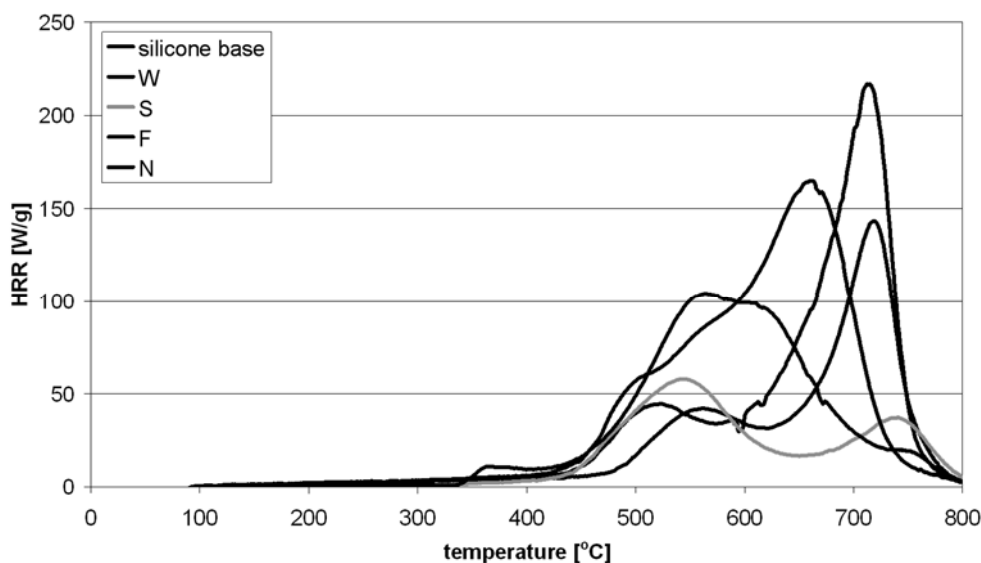


Fig. 3 Heat release rate (HRR) of the composites studied.

Created ceramic phase should exhibit limited thermal shrinkage, what allows to avoid problems concerning breaking or delamination of the surface layer from a polymer substrate [15]. Apart good heat insulation, prolonging the time to material ignition and the decrease of a heat release during fire, the micro-porous structure has to be strong enough to maintain the integrity of an electrical circuit. Thermal conditions of ceramization strongly influence shrinkage and mechanical strength of the composites studied. Generally, the higher shrinkage of material the lower strength of ceramized composite. The composite N is the only one which shrinks significantly when subjected to direct fire.

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