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Radiation-grafting of ethylene glycol dimethacrylate (EGDMA) and glycidyl methacrylate (GMA) onto silicone rubber

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HIGHLIGHTS

- EGDMA/GMA onto SR were obtained by direct gamma-radiation and the chemical method.
- Grafting of SR-g-(EGDMA/GMA) depends on dose, temperature, and monomer concentration.
- SR-g-(EGDMA/GMA) may be suitable for development of the immobilization of enzymes.

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ABSTRACT

Silicone rubber (SR) was modified with a graft of ethylene glycol dimethacrylate (EGDMA) and glycidyl methacrylate (GMA) using either gamma-radiation or azobisisobutyronitrile (AIBN). The graft efficiency was evaluated as a function of monomer concentration, absorbed dose, reaction temperature, and concentration of AIBN. The hydrophilicity of the grafted films was measured by contact angle and their equilibrium swelling time in ethanol. Additional characterization by infrared (FTIR-ATR) spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) is also reported.

1. Introduction

In recent years, there has been remarkable growth in the research and development of synthetic polymers for biomedical, microelectronics, and other advanced technological applications (Rosiak et al., 2003; Lafarge et al., 2013). In the particular case of biomaterials, most polymers that have the desired mechanical properties needed for biological applications tend to have a hydrophobic character, which makes them prone to the attachment of platelets and bacteria, and opens up the necessity to attempt the modification of their surface properties (Uyama et al., 1999). In this context, graft-processing technology represents a useful tool for the modification of polymeric materials because it enables their surface modification with different functional groups such as amides, amines, carboxylic acids or epoxies, without changing their mechanical properties (Muñoz-Muñoz et al., 2012; Alvarez-Lorenzo et al., 2010). Furthermore, unlike other surface modification methods such as coatings, graft-processing offers the advantage that the grafted polymer layer is more stable, there is a better control of the grafted polymer chains, and several different polymers can be grafted onto the same substrate (Minko, 2008).

The process of carrying out a graft polymerization revolves around the creation of active sites on the surface of the substrate material (*grafting-from*), or on the polymer chains that will be grafted onto the substrate (*grafting-to*). In the particular case of *grafting-from*, these active sites can be created through the surface-activation of the substrate via chemical pathways, or using high energy sources such as *UV*-radiation, plasma treatments, electron beams, and gamma radiation (Minko, 2008; Dargaville et al., 2003). In this regard, the use of gamma radiation for graft polymerization is a well-known alternative method to chemical approaches because it circumvents the use of initiators that will have to be removed at later stages (e.g. azobisisobutyronitrile (AIBN), benzoyl peroxide, dicumyl peroxide, or mixes of Ce(IV) and Fe(II) with peroxides), and it also serves as a way to sterilize the material while it is being irradiated (Jenkins et al., 2001). Thereupon, it is not surprising that radiation-induced copolymerization

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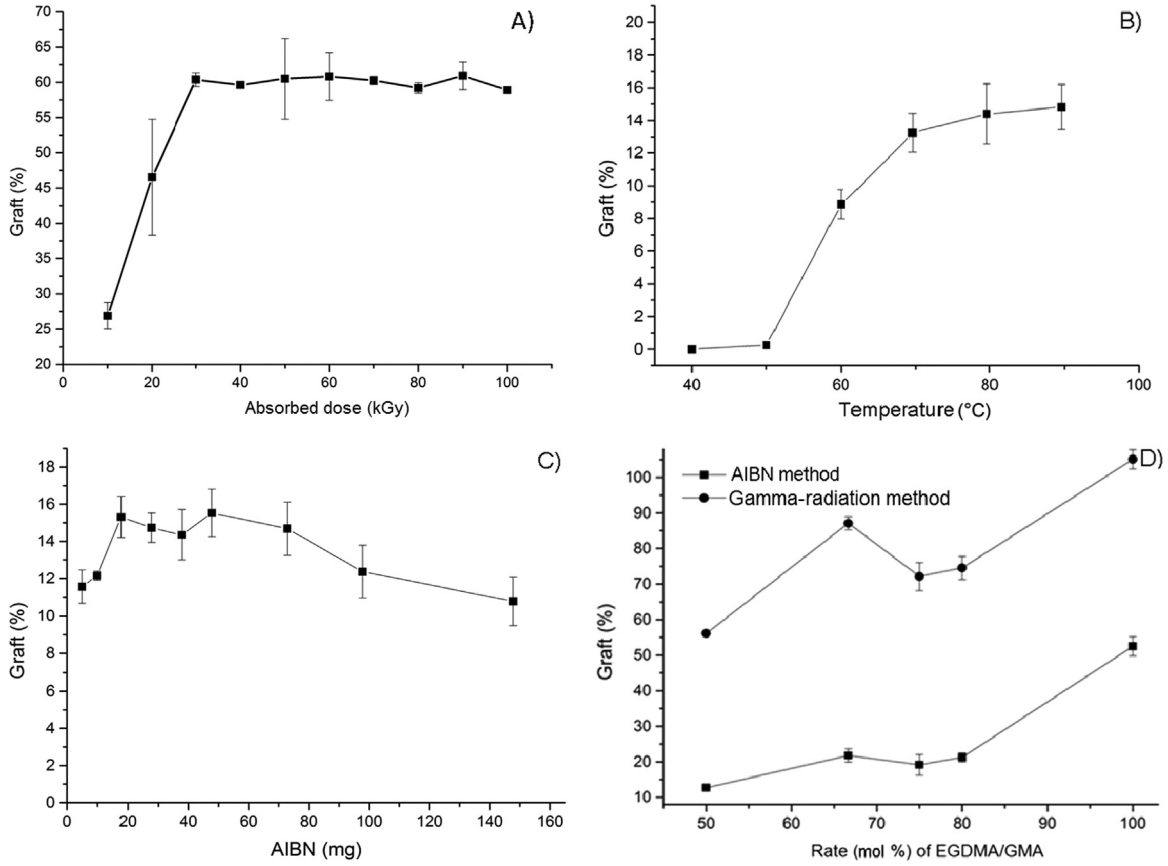

Fig. 1. Grafting yield as a function of (A) adsorbed dose with a monomers-toluene concentration of 20 vol% and a 1:1 EGDMA/GMA mol ratio; (B) temperature, for the chemical method (AIBN), using a 40 vol% monomers-toluene concentration and a 1:1 EGDMA/GMA mol ratio; (C) milligrams of AIBN initiator using a 40 vol% monomers-toluene concentration and EGDMA/GMA 1:1 mol ratio; and (D) different EGDMA/GMA mol ratios for both methods, with a monomers-toluene concentration of 20 and 40 vol% for the gamma-radiation and chemical method, respectively.

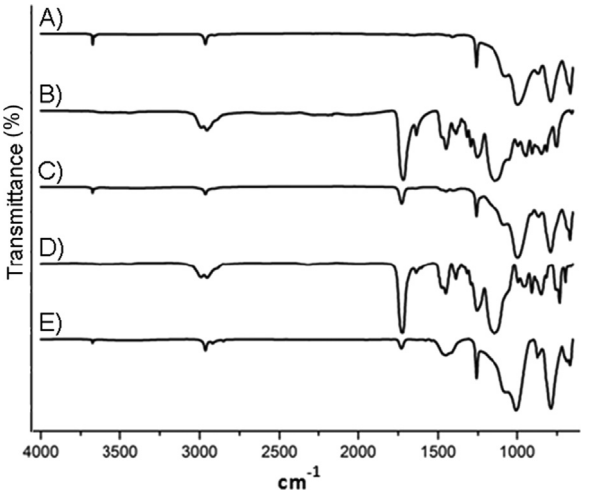

Fig. 2. FT-IR spectrum of (A) pristine silicone film, (B) poly(EGDMA-co-GMA) and (C) SR-g-(EGDMA-co-GMA), both obtained using the gamma-radiation method; and (D) poly(EGDMA-co-GMA) and (E) SR-g-(EGDMA-co-GMA), both obtained using the chemical method with AIBN as initiator.

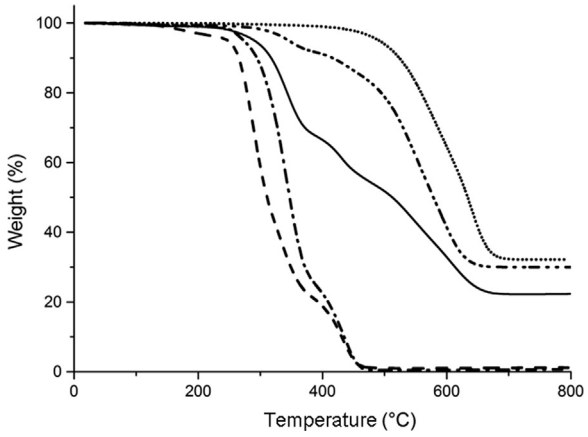

Fig. 3. TGA analysis of (———) SR-g-(EGDMA-co-GMA) (60.5%) modified using the gamma-radiation method; (— - —) SR-g-(EGDMA-co-GMA) (15.4%) modified using the chemical method, (•••••••••••) pristine silicone; (— - —) poly(EGDMA-co-GMA) obtained by the gamma-radiation method; and (— —) poly(EGDMA-co-GMA) obtained by the chemical method (AIBN).

and crosslinking has been increasingly used for the creation of novel biomaterials (Estrada-Villegas and Bucio, 2012).

In general, there are two pathways towards radiation induced graft polymerization: the pre-irradiation and the direct method. The pre-irradiation method can be further classified into either a trapped radical or peroxide method. The use of either method will depend upon the materials used, taking into consideration whether the compounds are susceptible towards degradation or crosslinking, or if they favor homopolymerization rather than grafting (Ivanov, 1992).

In this work, silicone rubber (SR) was modified with a binary graft of ethylene glycol dimethacrylate (EGDMA) and glycidyl methacrylate (GMA) using two different methods: 1) the direct radiation method, and 2) the chemical method using AIBN as an initiator. This graft will allow the immobilization of enzymes by subsequent reactions using the epoxy group from GMA.