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Grafting of thermo-sensitive N-vinylcaprolactam onto silicone rubber through the direct radiation method

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HIGHLIGHTS

- SR grafted with PNVCL for stimuli-responsiveness.
- The effects of radiation dose and monomers concentration were evaluated.
- The modified surface-responsive SR-based devices for biomedical applications.
- PNVCL onto SR has a LCST near the range of physiological temperature.

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ABSTRACT

The modification of silicone rubber films (SR) was performed by radiation-induced graft polymerization of thermosensitive poly(N-vinylcaprolactam) (PNVCL) using gamma rays from a Co-60 source. The graft polymerization was obtained by a direct radiation method with doses from 5 to 70 kGy, at monomer concentrations between 5% and 70% in toluene. Grafting was confirmed by infrared, differential scanning calorimetry, thermogravimetric analysis, and swelling studies. The lower critical solution temperature (LCST) of the grafted SR was measured by swelling and differential scanning calorimetry.

1. Introduction

Radiation grafting is a suitable technique for surface modification of polymeric materials since it allows introducing active functional groups onto a polymer backbone (Alvarez-Lorenzo et al., 2010; Ramírez-Fuentes et al., 2007; Contreras-García et al. 2008). Radiation synthesis and fabrication techniques geared up the research on biomedical applications in the early 1960s, with Charlesby and Chapiro (Charlesby, 1960; Chapiro, 1962) being the pioneers of this area, and at present are in full swing. In this particular field, bio-compatibility is the most essential aspect to be considered. Radiation grafting is applicable to many substrates and monomer combinations, and unlike chemically initiated grafting, it does not require initiators (Vahdat et al., 2007). There are several radiation grafting methods, including: (i) the direct (or mutual) grafting method in which the polymeric material is irradiated in contact with a monomer, with the disadvantage of homopolymerization being a collateral effect; and (ii) the pre-irradiation method, which involves the irradiation of the polymer matrix in the absence of air and then grafting is initiated by the macroradicals trapped in the irradiated polymer; the radiation dose needed for this method is usually larger than in the direct method (Alvarez-Lorenzo et al., 2010; Bucio and Burillo, 2009).

Stimuli-responsive polymers are polymers that respond to changes in chemical and physical conditions, such as pH and temperature (Yuan et al., 2008). A number of studies have been carried out to explore the applications of these kinds of materials in the biomedical and biotechnological fields, including controlled drug delivery, tissue engineering, and gene transfection and sensors, due to their tunable and stimuli-responsive properties (Zhang et al., 2009). In the particular case of thermo-sensitive polymers, there can be two different responses. If the polymer is soluble below a certain temperature, it is said to have a lower critical solution temperature (LCST). Above the LCST, the material becomes increasingly hydrophobic and insoluble, and a gel is formed. In contrast, polymers that are hydrophobic below a critical temperature and hydrophilic above it are said to have an upper critical solution temperature (UCST) (Klouda and Mikos, 2008). Water-soluble polymers with an LCST have attracted a great deal

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of attention in recent years due to their potential applications in biomedicine and biotechnology.

N-vinylcaprolactam (NVCL) is a cyclic vinyl amide with a seven-membered lactam ring, and it can be categorized as a typical non-conjugated monomer that only undergoes radical polymerization. NVCL is structurally similar to N-vinylpyrrolidone (NVP) in that the alkene p-electrons are not conjugated with the C=O functional group (Nakabayashi and Mori, 2013). Recent studies have incorporated different monomers such as NVP and amino acid derivatives as spacers between the carboxylic acid groups of other compounds (Arlyapov et al., 2013). This modification increased the polymeric backbone flexibility and allowed greater access for acid/base reactions. In its polymer form, poly(N-vinylcaprolactam) (PNVCL) stands out not only because it has an LCST near the range of physiological temperature (32–34 °C) (Cheng et al., 2002), but it's also nonionic, water-soluble, nontoxic, thermo-sensitive, and biocompatible. Because of this, the aim of this work was to implement a procedure for the thermo-responsive grafting of PNVCL onto SR and to elucidate the influence of the synthesis variables, including monomer composition and irradiation dose, on the grafting yield and in turn on the hydrophilicity.

2. Materials and methods

2.1. Materials

Silicone rubber (SR) was obtained from Goodfellow (Huntingdon, UK), washed with ethanol for 24 h and then dried under reduced pressure. N-vinylcaprolactam was from Sigma Aldrich (St. Louis MO, USA) and distilled under reduced pressure before use. Toluene was from J.T. Baker (Mexico). Distilled water was used for all experiments.

2.2. Synthesis of SR-g-NVCL

Grafting was carried out by the direct method, at a dose rate of 7.1 kGy h^{-1} at room temperature; SR films were placed in pyrex ampoules alongside a solution of NVCL in toluene at different monomer concentrations; the ampoules were sealed off after degassing by a repeated freeze/thaw process, and irradiated with a ^{60}Co γ-source (Gammabeam 651 PT, Nordion International Inc.) at doses from 5 to 70 kGy. Afterwards, the grafted films were extracted with ethanol and then with water in order to remove the residual monomer and the homopolymer generated during the grafting process. Then, the films were dried under reduced pressure and the grafting yield was calculated as follows:

$$\text{Grafting yield}(\%) = 100\left[\left(W_g - W_o\right)/W_o\right] \quad (1)$$

where W_g and W_o are the weights of the grafted and initial films, respectively.

2.3. Structural and physical characterization

FTIR-ATR (attenuated total reflection) spectra were recorded using a Perkin-Elmer Spectrum 100 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT, U.S.A.). The decomposition temperature was determined under nitrogen atmosphere using a TGA Q50 (TA Instruments, New Castle, DE) from 25 to 800 °C at 10 °C min^{-1}. Differential Scanning Calorimetry (DSC) scans were recorded using a DSC 2010 calorimeter (TA Instruments, New Castle, DE) between 22 and 350 °C at 10 °C min^{-1}. For determination of equilibrium water uptake, weighed pieces of graft copolymers were immersed in distilled water for various periods of time. The swelling percentages were determined from the weights of the swollen (W_s) and dried (W_d) films as follows:

$$\text{Swelling} \quad (\%) = 100\left[\left(W_s - W_d\right)/W_d\right] \quad (2)$$

where W_s and W_d represent the weights of the swollen and dry samples, respectively.

The determination of thermodynamic transitions was performed by differential scanning calorimetry. Runs were recorded under a nitrogen atmosphere using a DSC 2010 calorimeter (TA Instruments, USA). The LCST of the grafted films was determined by DSC using a temperature range from 22 to 50 °C at 1 °C min^{-1} with the samples having been swollen in distilled water. The LCST was also calculated with water swelling measurements at temperatures from 22 to 40 °C, where the LCST was defined as the inflection point of the swelling vs. temperature plot (Boltzmann function fitting).

3. Results and discussion

The effect of the irradiation dose on the grafting yield was examined by performing graft polymerizations at fixed monomer concentrations varying the irradiation dose between 5 and 70 kGy. For a 60% monomer concentration, the grafting yield of PNVCL onto SR films is depicted in Fig. 1, where it can be observed that there is an increase in grafting percentage as the irradiation dose increases, which is not unexpected given that the number of latent initiating sites is expected to increase with increasing radiation dose, although not necessarily in a proportional manner. However, when the irradiation dose is greater than 30 kGy, the recombination of macroradicals becomes predominant and causes that grafting percentage to plateau. After a radiation dose of 40 kGy, the SR films have poor mechanical properties because of excessive degradation.

Fig. 2 shows the relationship between monomer concentration (NVCL in toluene) and grafting yield at a radiation dose of 40 kGy and room temperature. As the figure shows, the grafting percentage increases with increasing monomer concentration, reaching a maximum of 45% for a 60% monomer concentration. From the figure it can also be gathered that a higher monomer concentration favors "the gel effect" and crosslinking, which results in a slower termination step due to the lack of mobility of the growing chains, and thus and increase in the grafting yield.

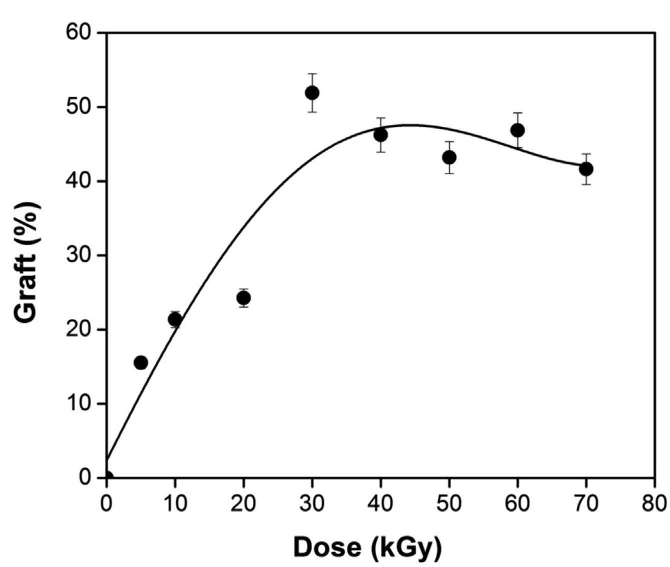

Fig. 1. Grafting percentage as function of dose of N-vinylcaprolactam onto silicone rubber films, 60% monomer concentration in toluene and dose rate of 7.1 kGy h^{-1}.