Structured Radiation-Grafted Polymer Films and Membranes

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ABSTRACT: The patterning of radiation-grafted polymer films and membranes on a 1-mm scale was investigated as a means of improving the mechanical properties of these materials. Stress–strain measurements indicated that no positive effect was achieved. J Appl Polym Sci 100: 292–294, 2006

Key words: mechanical properties; membranes; polystyrene; radiation

INTRODUCTION

Styrene-grafted poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) films and membranes prepared from them by sulfonation suffer from rather poor mechanical properties. This is illustrated by the fact that, with an increasing amount of polystyrene incorporated into an FEP film, the elongation at break drastically decreases.[1,2] The incorporation of fibers into the base material before grafting has been proposed as one possibility for increasing the mechanical strength of such radiation-grafted materials.[3]

As a potential alternative way of obtaining a composite material with improved mechanical properties, one may think of limiting the grafting reaction to only part of the film area. More specifically, we were interested in the preparation and investigation of materials with a gridlike structure of pure (or at least lower grafted) FEP and isolated domains of higher grafted material. The expectation was that the FEP grid in this structure would act as a more flexible buffer zone that would increase the macroscopic elongation at break of the material.

For preparing such structured materials, we fell back on using a mask during irradiation, a technique that had already been used many years ago to prepare patterned polymer films and fabrics for other purposes.[4–6]

EXPERIMENTAL

Radiation-grafted polymer films and membranes of different degrees of grafting were prepared by the preirradiation method, as described previously:[1,7] 25-μm-thick Teflon FEP 100A films (Du Pont de Nemours & Co., Wilmington, DE) were electron-beam-irradiated under air with a dose of about 3 kGy and an acceleration voltage of 1.05 MeV. For the preparation of patterned samples, the films were brought into tight contact with a metal wire grid with a wire diameter of 0.3 mm and a distance between the wires of 0.6 mm. The irradiated films were inserted into a solution of styrene/divinylbenzene (9:1 v/v) in isopropyl alcohol, and the solution was deoxygenated via purging with N_2 and was heated to 60°C for different periods of time. The grafted films were washed with toluene and vacuum-dried. The degree of grafting of each film was determined by weighing and is given as the relative weight increase during grafting, that is, as the weight ratio of polystyrene to FEP.

Sulfonation of the grafted films was carried out with 2 vol % chlorosulfonic acid in dichloromethane at room temperature for 5 h, and this was followed by base and acid treatments for the hydrolysis of the sulfonic acid chloride groups.

Stress–strain measurements were carried out with an Instron 4464 materials testing machine (Instron Corp., Norwood, MA) and were evaluated with respect to the elongation at break. Dumbbell-shaped samples with a neck 4 mm wide and 15 mm long were elongated at a rate of 15 mm/min. For every sample, the results of five measurements were averaged. All membrane samples were dried under identical ambient conditions before the measurements.

RESULTS AND DISCUSSION

As is evident from Figure 1, covering the film with a wire grid during irradiation did not have any

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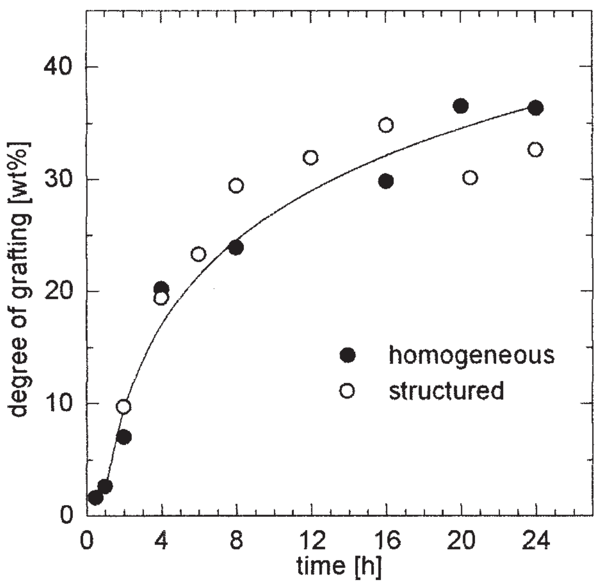

Figure 1 Grafting kinetics for homogeneously and inhomogeneously irradiated 25-μm FEP films in 50% styrene/divinylbenzene (9:1 v/v) in an isopropyl alcohol solution at 60°C.

marked influence on the grafting kinetics; within the reproducibility limits of ±10%, very similar degrees of grafting were obtained for masked and unmasked films. Nevertheless, a clearly inhomogeneous distribution of the grafting component was obtained for the masked samples, as is easily seen by the naked eye (Fig. 2): because of the lateral expansion of the grafted zones, a regular pattern of little bumps was

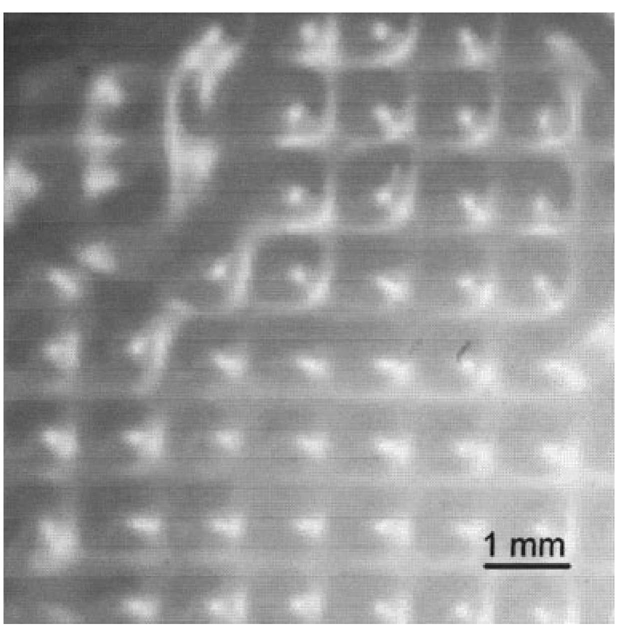

Figure 2 Light microscopy picture of a structured FEP-*g*-poly(styrene-co-divinylbenzene) film.

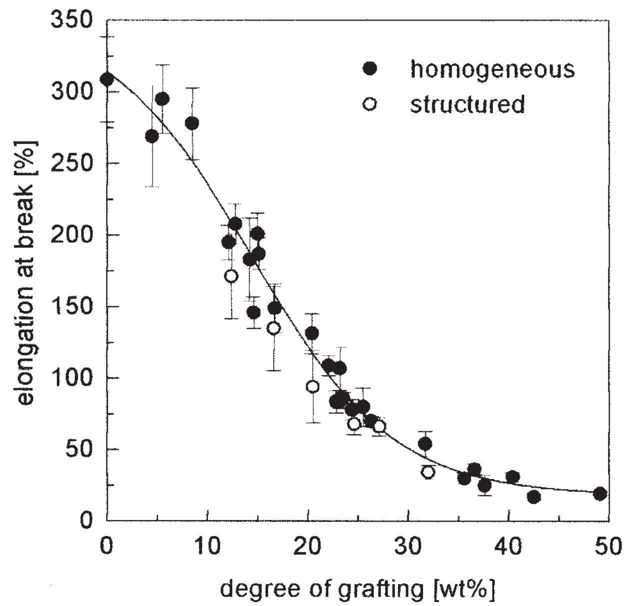

Figure 3 Elongation at break of radiation-grafted 25-μm FEP films parallel to the extrusion direction of the FEP base material. The continuous line gives the average value for the homogeneously grafted films.

formed during the grafting reaction. This structure was retained during sulfonation.

The mechanical properties of the grafted films and membranes were determined by dynamic stress–strain measurements. The elongations at break, as ob-

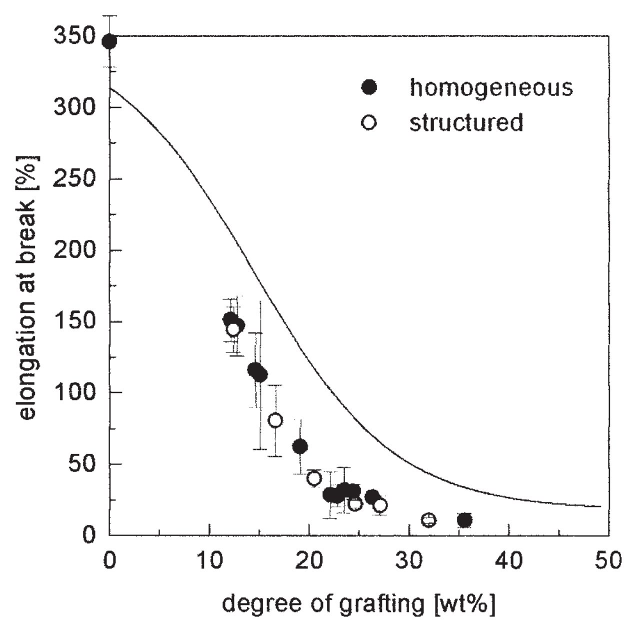

Figure 4 Elongation at break of radiation-grafted 25-μm FEP films perpendicular to the extrusion direction of the FEP base material. The continuous line gives the average value for the homogeneously grafted films parallel to the extrusion direction (cf. Figure 3).

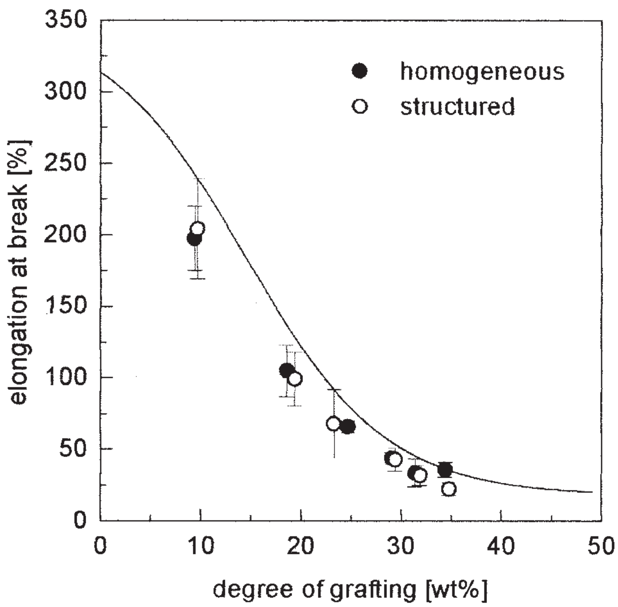

Figure 5 Elongation at break of radiation-grafted 25-μm FEP membranes parallel to the extrusion direction of the FEP base material. The continuous line gives the average value for the homogeneously grafted films parallel to the extrusion direction (cf. Fig. 3).

tained by these measurements, are presented in Figures 3–5. Noticeable differences can be observed for the measurements parallel and perpendicular to the extrusion direction of the original FEP film as well as films and membranes. Contrary to this, the mechanical properties of the structured and nonstructured films and membranes were essentially identical. A slight difference was discernible only for the stress–strain measurements of the grafted films parallel to the extrusion direction of the FEP film given in Figure 3. Here, slightly lower elongations at break were obtained for the structured films than for the average of the homogeneous films.

It had to be concluded that a less homogeneous distribution of the grafting component on a millimeter scale over the membrane area had no effect, and in particular no positive effect, on the mechanical properties of the grafted films. The elongation at break of the patterned films and membranes was essentially identical to the elongation at break of a homogeneous film or membrane with the same average degree of grafting. Higher elongations at break of the lower grafted regions were apparently compensated by lower elongations at break of the higher grafted zones.

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