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Welding of Nafion® – The influence of time, temperature and pressure

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HIGHLIGHTS

- We investigate the welding behavior of Nafion over a broad parameter range.
- The influence of time, temperature and pressure is measured and explained by theory.
- The welding behavior can be predicted by the reptation model from polymer dynamics.
- Time-temperature master curves for different pressures are constructed and discussed.
- Welding time and final strength are predicted using the model and measurement data.

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ABSTRACT

The properties of perfluorosulfonic acid ionomers (PFSIs) such as DuPont's Nafion® have been extensively characterized during the last decades. However, despite its importance for the upcoming industrialization of PFSI-based products no detailed investigation of the welding behavior of PFSIs has been performed. This paper investigates the welding behavior of Nafion® NRE-211 membranes common in both academia and industry over an industrially relevant parameter range of time, temperature and pressure. The strength evolution of the welded interface shows a linear dependence with square root of time and an Arrhenius temperature dependence. It is thus suggested that the welding behavior of Nafion® membranes can be predicted by the reptation model from polymer dynamics. Time-temperature master curves for a large range of parameters are constructed. Pressure is shown to have positive effects at very low welding times, but strongly negative effects at longer welding times, which can be explained by the model. Welding time and final strength of the fully healed interface are predicted using measurement and literature data. A short discussion on thermal transitions and on the role of crystallinity is also presented.

1. Introduction

Since the introduction of Nafion® by DuPont™ in the mid-1960s [1] perfluorosulfonic acid ionomers (PFSIs) have been extensively investigated for use as ion-conducting electrolyte in electrolysis cells, fuel cells and redox flow batteries as well as for different catalytic processes [2].

The hydrophobic Polytetrafluoroethylene (PTFE) backbone combined with the hydrophilic side chains result in the unique microstructural, thermomechanical and functional properties of PFSIs which despite thousands of publications have still not been fully understood [3]. One key characteristic of a PFSI molecule is the average distance between the hydrophilic side chains, characterized by the equivalent weight (EW) as molecular weight per mole of sulfonic acid groups. A typical equivalent weight of 1100 g mol^{-1} thus corresponds to an average of 6.6 TFE units between the side chains. The second distinct molecular feature of a PFSI molecule, the chemical structure and length of its side chain, has recently attracted increasing attention [4,5]. In contrast, the third molecular property, the molecular weight and its distribution, has received much less scientific attention. These molecular features as well as processing parameters and a slow equilibration to environmental conditions determine the microstructure and the resulting properties of PFSIs.

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Today's understanding of the microstructure of PFSIs has mainly evolved from scattering and diffraction investigations performed since the 1970s. In an early investigation of Nafion® in its acid and precursor form Gierke et al. discovered that PFSIs have low crystallinity that can be assigned to the PTFE backbone, increases with increasing equivalent weight and decreases from the precursor to dry acid and wet acid form. Moreover, water filled clusters of around 5 nm size are detected, which increase in size and number along with an increased macroscopic water uptake with decreasing equivalent weight. It is further proposed that with increasing water content the number of side chains and average size per cluster increases, but the number of clusters is reduced by a microstructural reorganization [6]. Though a wealth of excellent investigations and microstructural models have been published thereafter (e.g. Refs. [7–20]) these assumptions from 1981 are still the foundations of our current understanding.

Thermomechanical properties have also been widely investigated towards a better understanding of PFSIs. In 1977, Yeo and Eisenberg identified three distinct thermal transitions of 1365 EW Nafion® at 110 °C, 20 °C and −100 °C, which they denoted by alpha, beta and gamma transition, which is still the current terminology [3,21]. Since then, dynamic mechanical analysis (DMA) [13,18–22], differential scanning calorimetry (DSC) [10,11,12,18,23], modulated differential scanning calorimetry (MDSC) [24], thermogravimetric analysis (TGA) [12,23], dielectric spectroscopy [20,21] as well as wide-angle X-ray diffraction (WAXD) [6], small-angle X-ray scattering (SAXS) [18,19] and nuclear magnetic resonance (NMR) spectroscopy [18] at different temperatures have been used to detect and interpret thermal transitions in PFSIs with, however, often contradictory results. This can be explained by the use of different PFSIs, their long equilibration times, but also by experimental difficulties as the effects of concurrent solvent evaporation during heating. The consensus is that the different transitions can be assigned to different molecular origins as a common glass transition of the backbone, a melting of the crystalline regions, the overcoming of electrostatic interactions between the side chain end groups and, finally, the thermal decomposition of PFSIs that starts at around 300 °C.

During the last decade the dependence of mechanical properties on environmental conditions as temperature and humidity has been further explored. Benzinger et al. find a drastic effect on Young's modulus, creep and relaxation rates [25–29]. Whereas water seems to have a plasticizing effect at temperatures below 70 °C, the hydrophilic clusters seem to have a stiffening effect at temperatures between 70 °C and 100 °C, which is supported by earlier results [22]. Recently, Patankar et al. showed that stress relaxation curves of PFSIs can be represented by master curves using time-temperature moisture superposition for a wide range of temperatures and humidities [30]. The same seems to apply to the fracture toughness of PFSI membranes characterized by a knife slit test [31,32].

Despite its importance for the upcoming industrialization of PFSI-based products the welding behavior of PFSIs has not been reported in detail before. In fact, it is sometimes suggested that welding of PFSI-based products should be conducted slightly above the glass temperature of a PFSI as a lower temperature could lead to insufficient melting [33] or a lack of molecular entanglements between the bond partners [34] and higher temperatures could lead to inferior product characteristics [33,34]. A detailed discussion of the underlying processes and resulting time temperature pressure trade-offs is lacking, however.

Polymeric parts can be bonded by a variety of joining technologies [35,36]. In contrast, PFSI-based parts such as membranes and electrodes for electrolysis cells, fuel cells or redox flow batteries require intimate contact between the bond partners, which is why welding seems to be the only appropriate joining technology. In welding, coalescence of the bond partners is typically reached by applying pressure and heat to the interface and the process is classified with respect to the heat source as thermal, friction or electromagnetic bonding [35]. In general, adhesion at the interface of two joined parts can be explained by a variety of possible adhesion models such as the thermodynamic adhesion model based on non-covalent bonds, the chemical adhesion model based on chemical bonds, the electrical adhesion model that interprets the two interfaces as a kind of capacitor, the diffusion model that is based on interdiffusion of matter across the interface and the mechanical adhesion model that is based on mechanical interlocking of the two bond partners and is probably the historically first explanation for adhesion. For polymers, it is now widely accepted that diffusion is the predominant adhesion mechanism in most cases [37–39].

From the basic idea of this adhesion mechanism presented by Voyutskii in the 1960s [40] today's models of polymer diffusion across an interface have evolved by a number of major works on polymer dynamics. Based on the work of Rouse on polymer dynamics in dilute solutions and melts [41], de Gennes [42], Doi and Edwards [43] also integrated the effects of molecular entanglements on chain dynamics and developed the “reptation model”. According to the model thermal motion of linear polymer chains in an amorphous material can be described as a correlated, curvilinear motion of monomers within local restrictions imposed by neighboring chains or distant chain segments called “tubes”. Starting with the chain ends, the chains leave their original tube by this random walk over time. After the molecular relaxation or reptation time T_r most of the chain has left its original tube. This model has first been applied to polymer interfaces by de Gennes, Prager and Tirell as well as Wool [38]. The latter characterizes the state of interdiffusion by several parameters such as the average length $l(t)$ of the chain ends that have left their original tube called “minor chains” resulting in the number of molecules $n(t)$ and the number of chain segments $p(t)$ crossing the interface. For a time $t < T_r$ these are defined as [38]

$$l(t) \approx 2\sqrt{(D_1 t/\pi)} = L \Big/ 2{*}(t/T_r)^{0.5}\sim t^{0.5} M^{-0.5} \tag{1}$$

$$\begin{aligned} n(t) &= \mathrm{n}_\infty{*}(t/T_r)^{0.25}\sim t^{0.25} M^{-1.25} \ \text{ with } \ n_\infty \\ &= 1,31\rho \mathrm{N_a}(C_\infty j/M_0) b_0 M^{-0.5}\sim M^{-0.5}. \end{aligned} \tag{2}$$

$$\begin{aligned} p(t) &= \mathrm{p}_\infty{*}(t/T_r)^{0.5}\sim t^{0.5} M^{-1.5} \ \text{ with } \ p_\infty \\ &= 3,93\rho \mathrm{N_a}(C_\infty j/M_0) b_0 M_c^{-0.5}\sim M^0 \end{aligned} \tag{3}$$

and

$$T_r \approx L^2 \Big/ (2D_1)\sim M^3 \tag{4}$$

with D_1 as the curvilinear diffusion coefficient of a chain with length L, the density ρ, the molecular weight M, the molecular weight of the monomer M_0, the number of backbone bonds per monomer j, the characteristic ratio C_∞, the bond length b_0 and the Avogadro constant N_a. The temperature dependence of D_1 can be represented by an Arrhenius equation [44]. At times $t > T_r$ the chains have reached their equilibrium conformation and the interface has disappeared locally. The structure of the interface then only depends on molecular properties as seen in Eqs. (1)–(3). The mechanical strength of the interface is particularly dependent on the molecular weight, such that the mechanical strength starts at low values, then above a certain molecular weight increases by several orders of magnitude and levels off for further increasing