On the role of free carboxylic groups and cluster conformation on the surface scratch healing behaviour of ionomers

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ABSTRACT

While ionomers are well known for their healing ability under ballistic impact conditions, the present work focusses on elucidating the effect of both the free carboxylic content and the cluster state on well-controlled isothermal low temperature healing of surface scratches in ionomer blends. It is shown that under the conditions explored the healing efficiency depends primarily on the amount of free carboxylic groups and the presence of clusters plays a secondary role. A free carboxylic end group concentration of about 3 mol% is required to obtain optimal healing.

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1. Introduction

Intrinsic healing polymers are materials in which the healing capability is provided by the polymer network itself which increases its mobility upon a certain minimal chemical, mechanical or thermal energy input. In the case of healing polymers using reversible chemistries the increased mobility leads to a local viscous flow of the material in the vicinity of the damage site followed by a process of spontaneous restoration of the chemical and physical bonds and a (partial) recovery of the original mechanical or functional properties [1]. One of the first and most studied intrinsic self-healing polymers are the so-called ionomers as these have shown the ability to autonomously close and seal holes produced by pointed high speed impact objects [2–4]. Ionomers are partially neutralized polymers which bulk properties are deeply affected by ionic interactions within discrete regions of the polymer structure [5]. The strong Coulombic interactions between the ion pairs yields ionic aggregates acting as multifunctional "electrostatic" crosslinks [6] and as a result, a supramolecular network (spatially distributed clusters) of physical (reversible) crosslinks are formed. The final polymer structure and thus physical and mechanical properties strictly depend on neutralization level and neutralizing ions [7,8]. Likewise it is also expected that the polymer architecture will have a major influence on the healing capabilities of intrinsic healing polymers [9].

Ionomers are currently being considered for relatively new applications [10]. In particular their adequate mechanical properties in combination with a remarkable autonomous healing capability after ballistic impact at low, mid and hyper velocities [11] have led to various suggested applications such as multilayer composites for spacecraft debris protection shields [12] and self-sealing layers in tank reservoirs for low velocity impact [4,13]. In order to further extend their application range without losing their most crucial properties ionomers have been blended with other polymers this leading to significant improvements [14,15].

Upon ballistic impact there is substantial but undefined degree of heating of the region close to the impact site due to the work of bullet-polymer friction and the work of deformation. As a result, the material is raised to a temperature well above both the declustering and secondary crystal phase melting temperature (or characteristic ionomer transition temperatures) [16,17] and even above the primary crystal phase melting temperature. The actual healing after passage of the bullet proceeds via a two stage-process with a fast initial elastic recovery of the molten material, followed by a much slower viscoelastic response leading to inter-diffusion and reformation of the original ionomer microstructure [4,18]. Most studies on the healing mechanism of ionomers found in literature focused on elucidating the role of the neutralization level and the cluster content in the healing process after ballistic impact [18–20] with almost no focus on the possible effect of amount of free carboxylic groups identified by Kalista as a potential driver for the healing process [4]. In more recent times the effect of phase morphology on the healing efficiency in ionomers and ionomer based blends has gained attention [18,21]. Puncture studies performed under pseudo-static conditions highlighted the importance of the microstructure controlling the elastic response involved in the healing process [22]. Despite all these efforts, and while it is clear the relevance of polymer architecture on healing [9], the role of the different physical and chemical parameters in the healing of ionomers is not yet clear. The lack of clarity is the unavoidable result of the highly transient and poorly defined state of the ballistic impact site with large gradients in both the local deformation and the thermal fields.

In this work we introduce the use of well controlled scratching experiments at room temperature with subsequent isothermal healing treatments to separate in a more controlled way the viscoelastic and viscoplastic contributions to healing. The role of clusters and carboxylic groups in the healing process of poly[ethylene-co-(methacrylic acid)] ionomers at temperatures well below the polymer melting temperature was elucidated. The equilibrium cluster state as well as the number of free carboxylic end groups was varied intentionally by blending the ionomer with adipic acid, which is known to have a large effect on the ballistic healing behaviour [18,22]. The surface scratch healing behaviour is analysed by confocal microscopy and linked to the chemical and microstructural information obtained from additional infrared and X-ray tests.

2. Experimental section

2.1. Materials

In this study two series of poly(ethylene-co-methacrylic acid) zinc ionomer based blends (Table 1) were prepared using a mini-extruder with a twin screw configuration at 150 °C with the aim of varying the free carboxylic content as well as the equilibrium cluster content:

– Series 1 (EMAA-Zn/EMAA): Pellets of Nucrel 960® (DuPont™) containing 5.4 mol% of methacrylic acid groups (MAA) were blended in different proportions with pellets of Surlyn 9520® (Dupont™) containing 3.5 mol% MAA out of which 71% were neutralized with Zn^{2+} ions.
– Series 2 (EMAA-Zn/AA): Pellets of Surlyn 9520® (EMAA-Zn) were blended in different proportions with adipic acid powder (AA), $(CH_2)_4(COOH)_2$.

After blending and palletising the extrudate two types of specimens were prepared by compression moulding using a hot press: (i) ionomer coated galvanized steel plates for scratch healing tests and (ii) free standing ionomer films for general polymer characterization. The compression moulding was performed at a pressure of 0.67 MPa, a mould temperature of 130 °C and a pressing time of 5 min. Kapton® foils were used to separate the samples from the heated flat die surfaces. The samples were water-cooled to room temperature before releasing the pressure. The thickness of both coatings and free-standing films was around 160 ± 10 μm as measured by a PosiTector® 6000 thickness gage. The coatings and films had a smooth surface and a homogeneous appearance. After moulding the samples were stored at room temperature for at least 30 days to equilibrate the microstucture. The equilibration conditions were based on earlier work on the kinetics of the secondary phase formation [23].

2.2. Scratch procedure and healing quantification

For the creation of well-controlled surface scratches a microscratch tester (MST) from CSM Instruments with a 100 μm radius sphere-conical diamond indenter tip (Rockwell) was used. The scratch length (5 mm), load (2 N) and the scratching speed (10 mm/min) were kept constant in all experiments. Four scratches were created per sample.

The scratching procedure consisted of the following steps:

(i) A pre-scan at 0.03 N load. This step allows automatic correction during the scratch process for sample tilting or topology variations.
(ii) A scan at a 2 N load. This scan creates a surface deformation of the polymer (scratch) with a maximum penetration depth (P_d) as shown in Fig. 1a.
(iii) A post-scan at 0.03 N load. This step allows determination of the scratch depth just after load (R_d) and determination of the fast viscoelastic recovery. The residual depth (R_d) is also indicated schematically in Fig. 1a.

The immediate viscoelastic recovery (VE_R) was quantified using the parameters directly given by the MST instrument during the scratch procedure (P_d and R_d) using the following equation [24]:

$$VE_R(\%) = (1 - R_d/P_d)100 \tag{1}$$

The change in scratch profile and depth (at room temperature) after stepwise annealing at a fixed temperature of 70 °C for times up to 240 min was measured with a laser scanning confocal microscope Olympus OLS 3100 (software LEXT OLS 6.0.11) using a 20× objective. The