



# Kinetics of the non-isothermal fusion-welding of unlike ethylene copolymers over a wide crystallinity range

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## ABSTRACT

The non-isothermal fusion-welding of unlike polyethylene materials has been studied using three linear ethylene copolymers covering the crystallinity range 16–77% and displaying partial miscibility of the binary blends. Welding was carried out by putting into intimate contact under slight pressure the molten surfaces of two flat beams quickly heated up far above the melting point by means of infrared radiations. Particular attention was paid to the wetting of the beams using ultrasonic measurements. The interface adhesion strength was determined by means of double cantilever beam method. Homo- as well as hetero-welding proved to be highly efficient for only a few seconds of contact of the two beams in the molten state. The critical strain energy release rate of the interface reached values  $G_{IC} \geq 6 \text{ kJ/m}^2$  for contact time less than 10 s. The time window of efficient welding proved to be intermediate between the number-average and weight-average values of the terminal relaxation time according to melt rheology. This is consistent with Wool's criterion assuming that perfect self-welding of amorphous polymer requires reptation of chains over their whole length through the interface. The longer chains yet seemed not to be able to achieve complete tube renewal during the experimental time window of efficient welding. It is suggested that the reptation of the shortest chains contributes to the restoration of the entanglement network of the longest chains within a time scale much shorter than the reptation time of the latter ones. The surprising efficiency of hetero-welding in agreement with Wool's criterion is attributed to the interfacial miscibility of the unlike copolymers. The concomitant role of cocrystallization in the process is pointed out for such semi-crystalline polymers.

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## 1. Introduction

Polyethylene (PE) is a class of polymers displaying a very large variety of molecular architecture due to different kinds of polymerization methods and copolymerization with several kinds of  $\alpha$ -olefin co-units [1]. Molecular architecture includes various contents of short and long chain branches that strongly influence the mechanism of crystallization and consequently the crystallinity index and the hierarchically organized microstructure of the semi-crystalline material [2,3]. This results in a very large panel of mechanical properties ranging from stiff thermoplastics to soft elastomers [4–6]. Association of components consisting of different ethylene-based polymers is an attractive challenge for

manufacturing parts with mechanical property gradient. Co-extrusion or co-injection is widely used in the industry for joining different elements into ready-to-use parts with simple shapes. Alternatively, welding or sealing of thermoplastic polymers may be used in this goal for achieving complex parts.

In the case of chemically different polymers, hetero-sealing is expected to be readily achieved in the case of miscibility that is likely to promote interdiffusion [7–9]. However, thermodynamic incompatibility is rather a rule than an exception in the domain of high polymers. This makes often necessary the use of a third-component for generating molecular binding between immiscible polymers. Amphiphilic block or grafted copolymers with reactive chemical groups proved to be efficient agents for creating covalent bonding through the interface of the unlike parts in close contact [10–12].

If semi-crystalline polymers have been largely concerned with welding studies owing to multiple applications requiring fast processing, more particular attention has been focused at PE-based

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materials. Welding is generally applied to parts consisting of the same polymer, namely self-sealing, which needs no intervening component for establishing interfacial adhesion thanks to the natural self-diffusion of the chains through the interface in the melt. This property is largely used on industrial scale for joining PE pipes into pipelines. Sealing of packaging films is also a common example of PE industrial welding. A major advantage of this latter technique is its fast achievement which refers to the hot-tack property. The extremely short time afforded to the material for welding in this latter process means that chain interdiffusion occurs over a very thin interfacial layer only, and notwithstanding results in very strong adhesion.

The PE self-welding is well known to efficiently occur for very short welding time in agreement with self-diffusion kinetics [13–18], owing to chain intertwining. However, cocrystallization of the chains emanating from the two parts has also been ascribed a major contribution to the welding efficiency [14,16,19,20], in spite of very few experimental evidences.

Studies regarding the welding of unlike PE materials are quite scarce in comparison to the profusion of works regarding their miscibility, both in the melt and in the solid state (see introduction of Ref. [21]). In the perspective of building structures with property gradient consisting of unlike PE materials, miscibility appears to be a key point for the achievement of welding. In a previous study, we reported on the liquid and solid state miscibility of three ethylene copolymers covering the range of crystal weight fraction 16–77% [21]. Partial miscibility and evidences of some degree of cocrystallization at the boundary of the phase-separated domains of all binary blends let foresee favorable welding capabilities of unlike pairs of these copolymers. In this paper we did not argue on the eventual occurrence of crystallization-driven phase separation in unlike blends, we just report experimental evidences of phase separation in the melt and in the solid state at equilibrium.

## 2. Experimental

### 2.1. Materials and preparation

The three polymers under investigation are a Ziegler–Natta high density ethylene–hexene copolymer (HD) from Total Petrochemicals, and a linear low density ethylene–octene copolymer (LL) together with an ultra low density ethylene–octene copolymer (UL) manufactured by DOW Chemicals via metallocene catalysis. The molecular characteristics of the three materials provided by the manufacturers are given in Table 1.

The HD copolymer is a cascade-reactor bimodal compound consisting of an actual homopolymer and a random copolymer with higher counit content than the average. More details on the molecular structure of the HD bimodal copolymer can be found in previous papers regarding the same material or similar ones [22]. The presence of an ethylene–hexene copolymer having a counit content greater than the average value in the HD bimodal copolymer is expected to be a favorable factor for compatibilisation with

the counit-rich low density copolymers, and therefore to promote welding of the unlike materials.

The polymer pellets were compression-molded at 180 °C for 10 min into sheets of various thickness in the range 1–3 mm and subsequently cooled down to room temperature (RT) at about 40 °C/min. Samples 20 mm wide and 60 mm long were cut out from the sheets for the welding experiments.

### 2.2. Structure characterization

Differential scanning calorimetry was carried out on a Q100 apparatus from TA Instruments at a heating rate of 10°/min, the sample weight being about 8 mg. The temperature and heat flow scales were calibrated using high purity indium and zinc samples at the same heating rate. The melting point,  $T_f$ , is taken at peak of the melting endotherm. The weight fraction crystallinity,  $X_c$ , was determined using the melting enthalpy of perfectly crystalline polyethylene  $\Delta H_f^c = 290$  J/g at the equilibrium melting point [23]. In first approximation, the temperature dependency of  $\Delta H_f^c$  was not taken into consideration in the  $X_c$  computation for the LL and UL copolymers that exhibit strong melting point depression.

Small-Angle X-ray Scattering data have been borrowed from previous experiments regarding binary blends of the various copolymers [21]. The 2D-patterns were recorded on the BM02 beamline of the European Synchrotron Radiation Facility (Grenoble, France) equipped with a 0.1 mm point-focusing collimation and a CCD camera from Princeton Instruments. More details on the experimental procedure are provided elsewhere [21]. The most probable long period,  $L_p$ , of the materials was computed from the correlation peak of the Lorentz-corrected intensity profile. The standard deviation of the data was about 0.5 nm.

### 2.3. Welding procedure

The welding experiments were performed using a home-made device [24] sketched in Fig. 1. This computer-assisted device affords easy control of the processing parameters, *i.e.* time, temperature and pressure. It is mainly constituted by a press with two copper plates on which the two beams to be welded are stuck. A movable infrared (IR) oven can be mechanically introduced between the two plates. The heating source consists of a platinum filament wound on an alumina plate. The copper plates and oven were oversized (120 × 30 mm) as compared with the sample size (60 × 15 mm) in order to provide uniform heating. This non-isothermal method mimics the industrial “mirror welding” technique for joining bulk parts such as pipes, in contrast to isothermal methods that involve heating the whole volume of the two parts.

The very powerful heating source can warm the outer surface of the two beams at temperatures above the melting point within a few seconds only. Three pneumatic jacks ensure the quick displacement of various mobile parts of the device: horizontal move and remove of the IR oven, up and down move of the upper plate of the press, and horizontal ejection of the sample at the end of the experiment.

Welding was performed through 4 steps illustrated in the scheme of Fig. 2. Step 1: after sticking the two beams to the copper plates of the press with a temperature resistant adhesive tape, the oven was pre-heated for 5 s. Step 2: the IR source heated at 370 °C was swept between the two beams for a period of time ranging from 3 to 10 s. This holding time of the IR oven between the beams is called *heating time*. Step 3: after removal of the IR source at a rate of about 100 mm/s, the two beams were quickly brought into intimate contact by the press under constant pressure of 0.4 MPa for 20 s. This level of pressure was chosen after several trials in

**Table 1**

Molecular and physical characteristics of the polymers: number- and weight-average molar weights,  $M_n$  and  $M_w$ ; counit content,  $\xi$ ; density,  $\rho$ ; crystal weight fraction,  $X_c$ ; melting point,  $T_f$ ; elastic modulus,  $E$ .

Material	$M_n$ (kDa)	$M_w$ (kDa)	$\xi$ (mol%)	$\rho$ (g/cm <sup>3</sup> )	$X_c$ (%)	$T_f$ (°C)	$E$ (MPa)
HD	14	174	0.1	0.959	77	133	1100
LL	50	104	5.0	0.902	32	100	70
UL	75	150	12	0.870	16	65	10

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