



Polyethylene ionomers as thermally reversible and aging resilient adhesives

Silvia D'Auria^{a,b,1}, Peter Neuteboom^{b,2}, Roberta Pinalli^{a,3}, Enrico Dalcanale^{a,*}, Jérôme Vachon^{b,*}

^a Department of Chemistry, Life Sciences and Environmental Sustainability and INSTM UdR Parma, University of Parma, Parco Area Delle Scienze 17/A, 43124 Parma, Italy

^b SABIC Technology & Innovation, STC Geleen, Urmonderbaan 22, Geleen, The Netherlands

ARTICLE INFO

Keywords:

Ionomer
Adhesion
Aluminum
LDPE
Aging
Reprocessability

ABSTRACT

Low-density Polyethylene (LDPE) is a widely used thermoplastic polymer in various industries due to its versatility and cost-effectiveness. However, its inherent limitations, including low strength, poor UV resistance, and poor adhesion properties, have spurred efforts to enhance its applicability. We recently developed a LDPE ionomer based on ion pair comonomers (IPC) that can extend the range of application where traditional LDPE are limited. In this work, we report the effect of the reaction conditions on IPC content and melt flow index (MFI) for the PE ionomer obtained by copolymerizing ethylene with the ion pair dimethyl-amino methacrylate and methacrylic acid. The resulting ionomers exhibited improved mechanical properties, including higher elongation and stress at break, making them superior to conventional LDPE. The developed ionomers display enhanced adhesion properties on aluminum substrates with respect to LDPE. Remarkably, the adhesives exhibit thermal reversibility, making them suitable for applications requiring disassembly. Accelerated aging tests demonstrate the ionomers' durability, with some even showing increased adhesion after exposure to harsh conditions. Overall, this study highlights the potential of PE-based ionomers as advanced materials that combine the benefits of thermosets and thermoplastics, while offering outstanding adhesive properties when the IPC content is higher than 1 mol %.

1. Introduction

Polyethylene (PE) is the most used thermoplastic polymer and the market leader in many applications in the global plastic industry. PE success is due to the combination of strong resistance to solvents, exceptional flexibility, low cost, lightness, and easy processing. PE finds application in many common objects, ranging from single-use plastics like plastic bags and packaging, to durable goods in automotive, electronics, medicine, fiber, and textiles.[1,2] However, its use is limited by its low strength and stiffness, low upper service temperature, stress cracking, and poor UV resistance. To overcome those issues, and drastically improve its properties, crosslinking of polyethylene is performed using both physical (electron beams, gamma rays, or ultraviolet

radiation)[3] and chemical (initiators like silanes,[4,5] peroxide or azo compounds) methods.[6,7] Additionally, the hydrophobic nature of PE makes it less suited for a wide range of applications, like heat sealing, extrusion coating, printing, or adhesive bonding. In the specific case of adhesion, the hydrophobicity of PE is reduced by introducing hydrophilic groups on the surface of the polymer via plasma treatment/corona discharge,[8] flame treatment,[9] oxidation by acids,[10] or chlorination.[11] However, only the first two techniques have received substantial commercial recognition, with the use of specific and dedicated equipment. As alternative materials, the best performing adhesives in terms of mechanical properties and chemical stability are thermosets, which, besides their higher production cost compared to polyolefins, cannot be reprocessed after their use.[12] On the contrary,

* Corresponding authors.

E-mail addresses: silvia.dauria@unipr.it (S. D'Auria), peter.neuteboom@sabic.com (P. Neuteboom), roberta.pinalli@unipr.it (R. Pinalli), enrico.dalcanale@unipr.it (E. Dalcanale), jerome.vachon@sabic.com (J. Vachon).

¹ Department of Chemistry, Life Sciences and Environmental Sustainability and INSTM UdR Parma, University of Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy; SABIC Technology & Innovation, STC Geleen, Urmonderbaan 22, Geleen, The Netherlands

² SABIC Technology & Innovation, STC Geleen, Urmonderbaan 22, Geleen, The Netherlands

³ Department of Chemistry, Life Sciences and Environmental Sustainability and INSTM UdR Parma, University of Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy

<https://doi.org/10.1016/j.eurpolymj.2024.113000>

Received 15 January 2024; Received in revised form 27 March 2024; Accepted 29 March 2024

Available online 3 April 2024

0014-3057/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Table 1

Reaction conditions used during the copolymerization and measured MFI. All the experiments were performed at 2000 bars.

Name	IPC content vs ethylene (mol%)	CTA content vs ethylene (mol%)	Temperature (°C)	MFI at 190°C/ 2.16 kg (g/10 min)
P1	0.05	0.07	180	0.1
P2	0.05	0.07	200	1
P3	0.05	0.07	250	12.2
P4	0.1	None	180	0.4
P5	0.1	None	200	1.6
P6	0.1	0.07	220	13
P7	0.1	0.07	250	25.3
P8	0.2	None	200	8.3
P9	0.2	0.07	220	25
P10	0.2	0.07	250	52.5

thermoplastic polymer-based adhesives exhibit a lower strength but permit the disassembly of the glued material upon heating.[13] Since the amount of adhesive materials used annually exceeds seven billion pounds, there is a growing interest in polymers that combine the high-performance of thermosets with the reprocessability of thermoplastics.[14,15,16] In this perspective, the design of innovative adhesives is focusing on covalent and non-covalent adaptable networks, whose reversible crosslinking can be triggered by specific stimuli.[17,18,19,20] Herein, we report the study of a polyethylene-based ionomer with outstanding adhesion properties. Such polymer was synthesized by copolymerizing ethylene with a combination of dimethyl-amino terminated methacrylate and methacrylic acid present as an ion pair comonomer (IPC). The selection of the comonomers was made based on their price, their commercial availability at an industrial scale and their low toxicity since both are approved in European Union as comonomer in plastic packaging for food contact application.[21] The direct copolymerization of a few mole percent of IPC and ethylene via high-pressure free radical copolymerization with a suitable initiator has been already demonstrated to be an effective method for physically crosslinking PE via ionic interactions, which resulted in improving its mechanical properties.[22] The introduction of ionic moieties to the PE matrix combines, to some extent, the thermoset and thermoplastic advantages, providing both excellent mechanical and adherence properties but still ensuring the disassembly of glued material during the melt process of non-covalent crosslinked network.

2. Experimental

2.1. Materials and methods

Synthesis. Ionomers P1-10 were synthesized by free radical polymerization of ethylene in the presence of the IPC (see Table 1 for details). SABIC® LDPE 1922 N0, with a melt flow rate (MFR) of 22 g / 10 min (190 °C; 2.16 kg) and density of 0.919 g cm⁻³ was obtained from SABIC. Unless otherwise specified, solvents and chemicals used for the synthesis of the IPC and all the ionomers were purchased from Sigma Aldrich and used as received. All solvents employed were laboratory grade and used as received.

Synthesis of IPC.

Methacrylic acid (40.5 mL, 0.48 mol) was dropped into 2-(dimethylamino)ethyl methacrylate (81 mL, 0.48 mol) in a 2-neck flask equipped with an ice bath and a mechanical stirrer. The mixture was stirred at 0 °C and after 30 min a gel was formed. The formation of the product was confirmed via NMR.

¹H NMR (400 MHz, CDCl₃), δ (ppm): 1.94 (6H, m), 2.45 (6H, s), 2.86 (2H, t, J = 5.6 Hz), 4.36 (2H, td, J = 5.6, 1.6 Hz), 5.52 (1H, m), 5.58 (1H, m), 6.07 (1H, m), 6.13 (1H, m), 7.05 (1H, bs).

¹³C NMR (101 MHz, CDCl₃), δ (ppm): 18.37; 18.69; 44.09; 56.36; 60.88; 124.44; 126.33; 135.90; 138.22; 167.15; 171.96.

2.1.1. Synthesis of ionomers via radical polymerization

The ionomers were synthesized through a copolymerization between ethylene and the IPC according to the following general procedure: the polymerization was carried out in an autoclave reactor by using a pressure of 2000 bars with an impeller velocity fixed at 1540 rpm, at a different temperature (180, 200, 220, 250 °C) for 30 min. Before being injected with high-pressure ethylene, the IPC (1 eq. of ethylene for 0.05, 0.1 or 0.2 of IPC) was dissolved in methanol (50 wt%). Luperox®11 M75 (1.5 g/L), dissolved in heptane, was added as initiator together with propanal (0.07 mol%), used as CTA. The polymers were recovered from the bottom of the autoclave directly to a recuperation vessel through a let-down valve. Two recuperation vessels were used: the first one was used when stabilizing the conditions and then switched to the 2nd recuperation vessel once the polymerization conditions were steady for collecting the copolymer. The polymer was recovered in a fine powder form. Elemental analysis (EA) was used to determine the composition of the copolymer through nitrogen quantification. The specific conditions and quantities of IPC are specified in Table 1.

2.2. Characterization

Nuclear magnetic resonance (NMR). NMR spectra of the monomers were recorded using a Bruker Avance 400 (400 MHz) spectrometer at room temperature in CDCl₃ as solvent. High-temperature NMR spectra of the polymers were recorded on a Bruker AVANCE III (500 MHz) equipped with a cryogenically cooled probe head at 80 °C or 120 °C in deuterated tetrachloethane (TCE-d₂). 10 mg of each polymer were dissolved in 600 μL of TCE-d₂ and 10 mg of stabilizer butylated hydroxytoluene BHT were added. Chemical shifts are reported in parts per million (ppm) and given in reference to the residual solvent peaks at 7.26 ppm in CDCl₃, at 6.00 ppm for TCE-d₂.

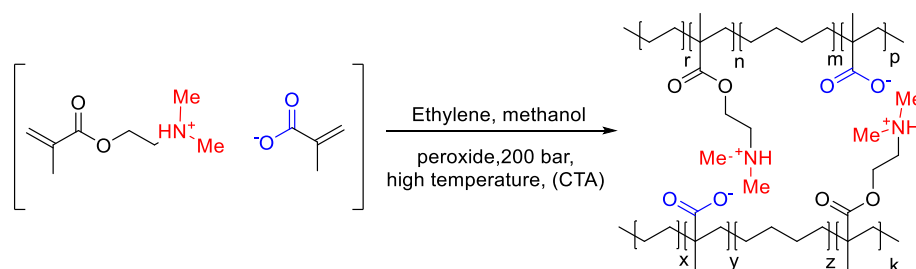
Elemental Analysis (EA). Elemental analysis was carried out with a CHNS Thermo Fisher FlashSmart instrument. Samples (5 mg for each sample) were burned in the presence of oxygen. The nitrogen content was determined by means of thermal conductivity (TC) and volumetric analysis.

Gel permeation Chromatography (GPC). The measurements were performed at 150 °C using a Polymer Char GPC-IR® built around an Agilent GC oven model 7890, equipped with an autosampler and the viscometer and refractive index detector. 1,2-Dichlorobenzene (o-DCB) was used as an eluent at a flow rate of 1 mL/min. The data were processed using Calculations Software GPC One®. Molecular weight and dispersity were determined in oDCB at 150 °C with respect to a polystyrene standard.

Rheology. Compression molded disks for rheology (for each disk of diameter 25 mm and thickness 1.2 mm, 2 g of each polymer were used) were measured using an Anton Paar 502MCR, equipped with a parallel plate geometry and under nitrogen environment. First, a strain sweep was carried out to determine the linear viscoelastic regime of the polymer samples. The subsequent measurements were carried out within the linear viscoelastic regime. Complex viscosities were monitored during a temperature ramp of 5 °C/min from 190 °C to 90 °C using a strain amplitude of 1 % and with an angular frequency of 1 rad/s. Complex viscosity vs temperature of P5, P8, P6 and P7 is reported in Figure S25.

Differential scanning calorimetry (DSC). Differential scanning calorimetry was performed on a TA Instruments Q20 equipped with a RCS 90 cooling system. About 2–4 mg of polymeric sample was weighed inside an aluminum pan. DSC measurements were carried out under nitrogen atmosphere from 40 °C to 200 °C at a constant heating/cooling rate of 10 °C min⁻¹. Enthalpy, melting, and crystallization temperatures were determined from the second heating and cooling cycle.

Thermogravimetric analysis (TGA). Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere using a Perkin Elmer TGA 8000. Samples (2–5 mg for each sample) were heated to 600 °C at a heating rate of 10 °C min⁻¹.



Scheme 1. Copolymerization reaction of IPC and ethylene.

Preparation of tests specimens for lap shear tests according to ASTM D1002. Aluminum bars (dimensions of 100 mm x 25 mm x 1 mm) were used as adherent, and the surface was carefully cleaned with EtOH. To prepare the polymer joint, 10 g of powder was pressed in a mold of 10 cm x 10 cm x 0.5 mm at 180 °C, and three rectangular stripes (12.5 mm x 25 mm x 0.5 mm) were cut and cleaned with EtOH. The metal slabs were placed so that they overlapped with the appropriate area and the polymer films were placed between them (Figure S25). Metal slabs of the same thickness were employed to support the upper aluminum slabs in order to align them in a plane. The entire setup was placed inside the compression molding machine, and then a force of 100 N and a temperature of 180 °C were applied for 5 min.

Aging test procedure. Initial conditions: 168 h at $T = 23 \pm 2$ °C and %RH = 50 ± 6 . After initial conditions, the joints were exposed to accelerate aging tests used in the automotive sector: the samples are completely wrapped with cotton. Then the wrapped sample is wetted evenly with demineralized water. The sample is completely wrapped in aluminum foil before it enters a PE bag. Subsequently, the air is pressed out of the PE bag by hand and the polyethylene bag is welded completely airtight. The package sample is stored at $T = 70 \pm 2$ °C and %RH = 100 ± 6 for 168 h (7 days) and immediately exposed to $T = -20 \pm 2$ °C for 16 h. Thereafter, the sample is thawed at room temperature, the package removed and the test piece reconditioned for 2 h at $T = 23 \pm 2$ °C and %RH = 50 ± 6 .

Lap shear tests. Lap shear tests were performed with a Zwick type Z020 tensile tester equipped with a 10 kN load cell. A grip-to-grip separation of 195 mm was used. The samples were pre-stressed to 0.1 N and with a test speed of $100 \text{ mm} \cdot \text{min}^{-1}$.

3. Results and discussion

A study on high-pressure/high-temperature free radical polymerization has been carried out using a dedicated high-pressure autoclave equipment, by testing different reaction conditions such as temperature, IPC concentration and chain transfer agent (CTA) content. Among the several IPC tested so far to prepare ionomers, the dimethylamino terminated one was chosen for its superior mechanical properties.[22] The IPC (Scheme 1) was synthesized via an acid-base reaction by mixing the dimethyl-amino terminated methacrylate and methacrylic acid without the use of solvents.[22] ^1H NMR spectroscopy was used to confirm the formation of the ion pair by monitoring the chemical shift of the protons before and after the formation of the salt (Figure S1). Ten ionomers were prepared by varying the three parameters listed above (Table 1). The general procedure for the polymerization reaction, described in detail in the experimental section, was implemented. The IPC was mixed with high-pressure ethylene through a static mixer at different feed ratio (0.05, 0.1, or 0.2 mol%). Afterwards, the initiator Luperox®11 M75 and propanal as CTA were added to the mixture. Luperox®11 M75 is a 75 % active weight solution of t-butyl peroxyvalate and is a typical peroxide used for the polymerization of ethylene to make LDPE. Being in a liquid form, it is an easy to handle peroxide with good reactivity as containing a relatively high amount of active oxygen (6.80–6.98 wt%). Propanal is an ideal and efficient CTA

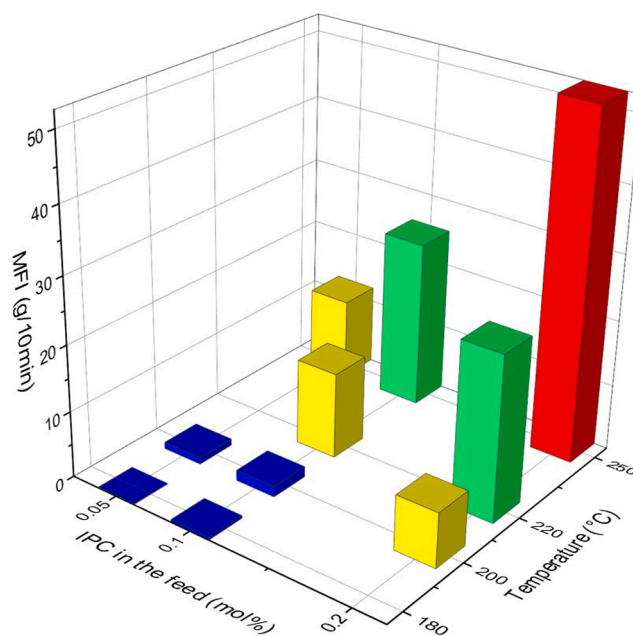


Fig. 1. Effect of the temperature and IPC content in the feed on the MFI of the final ionomers.

for ethylene polymerization to make LDPE. It is considered as a relatively fast-acting CTA with a high transfer coefficient (C_s) value ($C_s = 0.33$ at 130 °C and 1360 atm), as calculated by Mortimer.[23] This means that propanal H-abstraction is fast and easy to transfer to the growing polymer chain thus effectively reducing chain length of PE. The resulting solution was heated at 60 °C before being injected in the reactor, set at a fixed temperature ranging from 180 °C to 250 °C (Scheme 1, Table 1). In all the experiments, the reactor pressure was kept constant at 2000 bars.

A crucial aspect to consider is the use of the CTA. The experiments conducted without propanal as CTA led to ionomers with very low MFI at low concentration of IPC (entries P4 and P5 of Table 1). The concomitant formation of long chain branching and ionic crosslinking resulted in material with poor flow properties. Such high viscosity causes processing issues, therefore using a CTA to control the chain length during synthesis proved to be a critical feature to achieve a proper mechanical and processing quality. Interestingly, by raising the IPC content in the ethylene feed (from 0.05 to 0.1 and 0.2 mol%) the MFI values increased even without the presence of CTA, indicating that in such conditions, the IPC can operate as CTA by itself (entries P5 and P8 in Table 1). This CTA effect of the IPC is even more pronounced at higher temperatures, as illustrated in Fig. 1. The temperature effect on MFI is evident on the P1-P3 series: temperature increase leads to higher MFI. Therefore, the MFI of the resulting ionomers is both temperature and IPC concentration dependent.

Cast film extrusion tests were performed at temperatures between

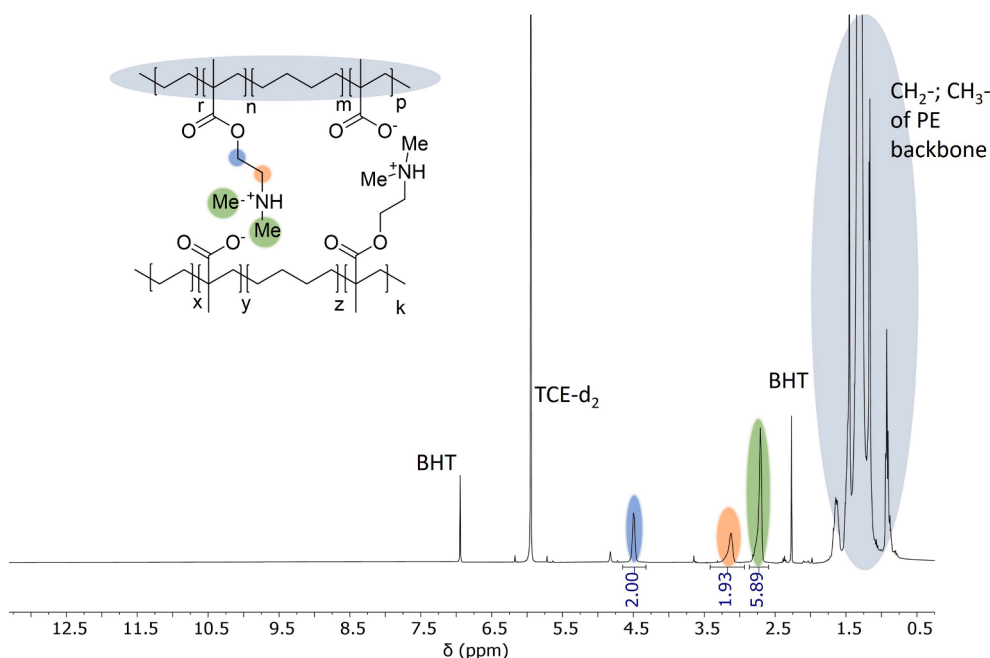


Fig. 2. ^1H NMR (500 MHz, 120°C) of P1 in TCE-d_2 (10 mg of butylated hydroxytoluene BHT stabilizer were added in the NMR tube).

Table 2

The content of IPC was calculated via nitrogen elemental analysis, melting temperature (T_m), the heat of fusion (ΔH_f), and crystallinity (X_c) obtained via DSC. As references, a commercial LDPE is used.

Name	Content of IPC (mol%)	T_m ($^\circ\text{C}$)	ΔH_f (J/g)	X_c (%) ^a
LDPE	–	105	131.9	46
P1	0.5	114	157.0	53
P2	0.45	112	157.8	54
P3	0.39	108	144.5	49
P4	0.81	111	145.7	50
P5	0.69	110	143.7	49
P6	0.73	109	152.8	52
P7	0.33	106	137.3	47
P8	1.28	105	125.3	43
P9	1.35	105	135.4	46
P10	0.75	103	123.2	42

a) Calculated considering the heat of fusion of 100 % crystalline polyethylene $\Delta H_f^0 = 286.2 \text{ J g}^{-1}$. [23].

150°C and 190°C to determine the ionomer processability, a critical aspect in the manufacturing stage. [24] The temperature of the extruder was chosen according to the MFI of the polymer (Figure S7). TGA analyses showed no weight loss up to 250°C (see Figures S13-S17 SI). The films obtained resulted to be uniform and transparent with a thickness of $\sim 50 \mu\text{m}$ (Figure S8).

The ionomers produced in the autoclave were characterized through ^1H NMR, and elemental analysis. The ^1H NMR spectra were conducted at 120°C , using TCE-d_2 as solvent. As an example, the spectrum of P1 is reported in Fig. 2: where it is possible to identify the diagnostic peaks of the dimethyl amino moiety and the two methylene groups connecting the ester and the amino group.

The ^1H NMR spectrum confirms that the polymerization reaction proceeds without the formation of noticeable side products, providing a pure polymer free from unreacted monomers (no vinyl groups present). Nitrogen elemental analyses were done to quantify the content of IPC embedded in the final polymers, since nitrogen is diagnostic of the presence of IPC. As shown in Table 2, the content of IPC in the polymer is dependent both on the initial content of IPC added in the reactor feed and on the temperature of the reaction.

Gel permeation chromatography (GPC) was performed on one ionomer (P2) dissolved in 1,2-dichlorobenzene at 80°C to determine the molecular weight. The resulting chromatogram (Figure S9) shows an extremely broad molecular weight giving an apparent molecular weight $M_w = 324.400 \text{ g/mol}$ and a polydispersity index (DPI) $M_w/M_n = 39$. These values are not realistic for a LDPE polymer, suggesting the persistence of ionic aggregates in solution that give rise to an apparent abnormally high molecular weight, as already observed in a previous study. [22].

Table 2 shows the thermal data, obtained via DSC, of the ionomers with commercial LDPE as reference. All the ionomers show thermograms comparable to the LDPE one (Figure S10-S14). The melting temperatures obtained from the second heating run, range from 103°C to 114°C , in line with the crystalline fraction of the ionomers (42 % to 65 %, Table 2). Being the ionic moieties mainly confined in the amorphous fraction, [22] the IPC content influences the degree of crystallinity of the ionomers, together with the reaction temperature. In fact, if we compare ionomers obtained at the same temperature (Table 1 and 2), the crystallinity of the ones with a higher IPC content is invariably lower.

To investigate the microstructure of the polymer, the average lamellar thickness (Table S1) has been calculated following the Gibbs-Thomson equation (equation (1)): [26]

$$l_c = \frac{2\sigma_e}{\rho \cdot \Delta H_f^0} \cdot \frac{T_m^0}{T_m^0 - T_m} \quad (1)$$

where $\sigma_e = 90.4 \text{ mJ m}^{-2}$ is the surface energy for polyethylene, [27,28] $\rho = 1 \text{ g cm}^{-3}$ is the density of the crystal phase. $\Delta H_f^0 = 286.2 \text{ J g}^{-1}$ is the heat of fusion, [23] and $T_m^0 = 418.6 \text{ K}$ is the equilibrium melting temperature of polyethylene. The obtained lamellar thickness values, between 8.4 nm and 8.7 nm are consistent with the typical values of LDPE, [29] suggesting that the inclusion of the IPC does not affect in a meaningful way the microstructure of the polymer. However, the higher addition of IPC in the feed results in a slightly smaller lamellar thickness of the ionomers. The most significant and desired effect of the addition of IPC into the polyethylene backbone consists in the non-covalent cross-linking of the chains through ionic interactions between the carboxylate and ammonium groups. Such feature leads to an improvement in the

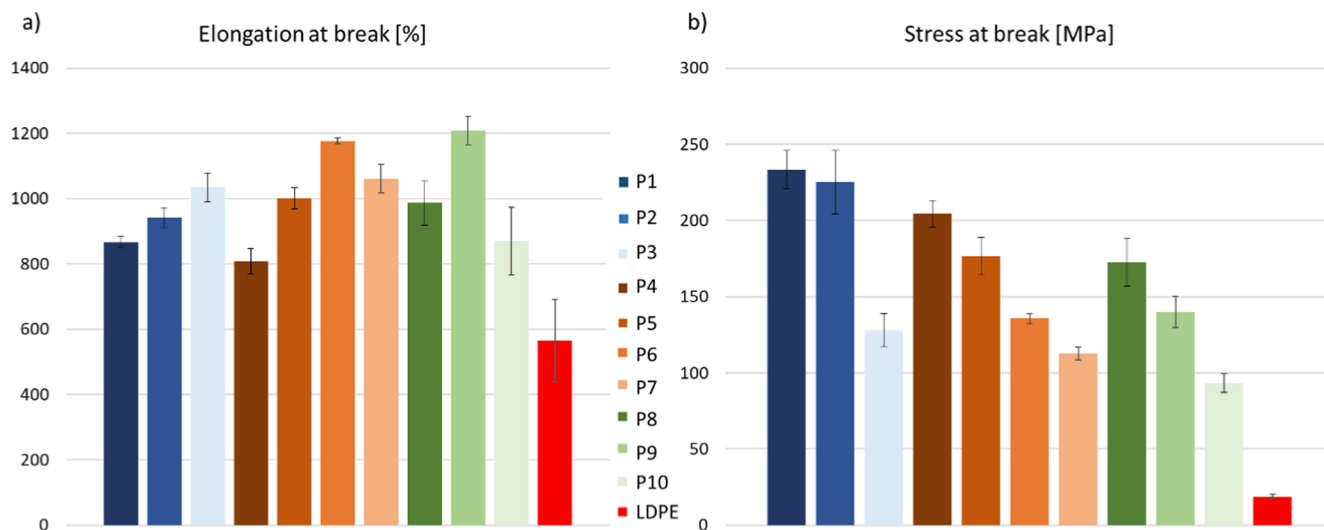


Fig. 3. Histogram of a) elongation at break, and b) stress at break for P1-P10 (blue, brown and green bars) and LDPE (red bar). Each bar represents the average of 5 measurements.

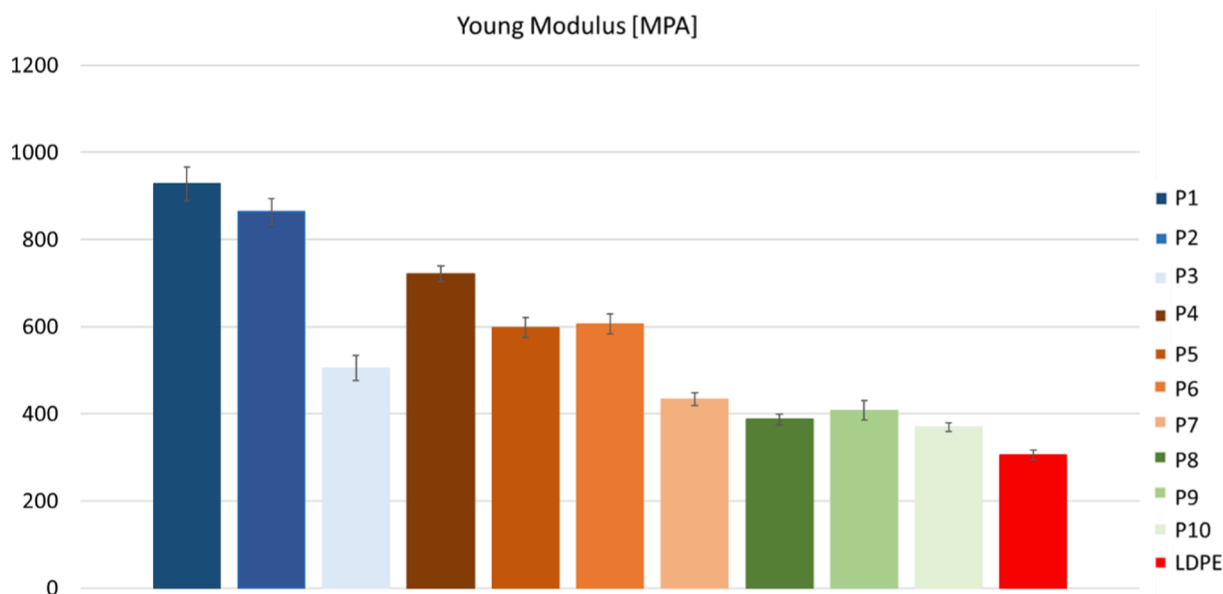


Fig. 4. Histogram of Young modulus values for P1-P10 (blue, brown and green bars) and LDPE (red bar). Each bar represents the average of 5 measurements.

Table 3
Samples used for adhesive tests.

Name	Content of IPC (mol%)	MFI (g/10 min)	T_m (°C)	X_c (%) ^{a)}
P7	0.33	25.3	106	47
P6	0.73	13	109	52
P10	0.75	52.5	103	42
P8	1.28	8.3	105	43
P9	1.35	25	105	46

a) Calculated considering the heat of fusion of 100 % crystalline polyethylene $\Delta H_f^0 = 286.2 \text{ J g}^{-1}$. [25].

mechanical properties of the polymer compared to an ordinary LDPE, obtaining superior mechanical performances without sacrificing the processability of the thermoplastic. This is illustrated by the tensile performance of the ionomers, which was tested on films prepared via

film casting. All ionomers present higher elongation and stress at break compared to LDPE (Fig. 3), a clear indication of the positive effect of the IPC on the mechanical properties of the ionomers.

A significant increase of the Young modulus is observed only for the ionomers with less IPC content (blue and brown bars in Fig. 4). These results correlate roughly with the degree of crystallinity of the ionomers: the higher the X_c the larger is the modulus.

3.1. Ionomers adhesion properties

To study adhesion properties of ionomers on aluminum, lap shear tests were performed according to ASTM D1002, a standardized method to evaluate the adhesion strength of polymers. Five ionomers were selected (Table 3), of which lap shear specimens were prepared using the setup illustrated in Figure S21. These samples, which cover a broad range of MFI values, were chosen between all the ionomers described above, to compare the adhesive qualities of samples with low (P7), medium (P6 and P10), and high IPC contents (P8 and P9).

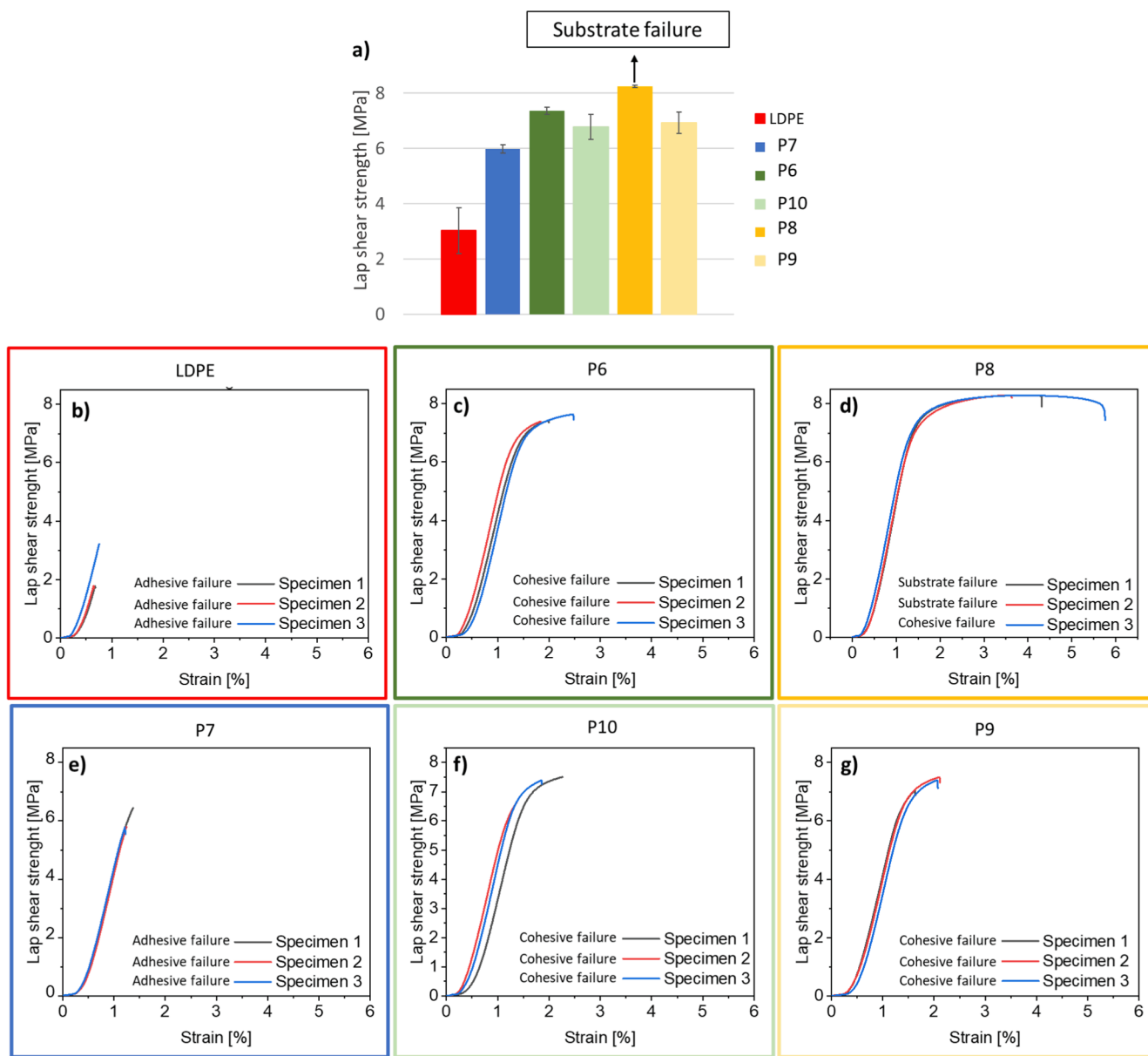


Fig. 5. a) Average maximum lap shear strength. The arrows indicate the ionomers which achieved substrate failure. b)-g) stress-strain curves of LDPE and of the ionomers obtained from lap shear tests.

There are three types of failures to be considered, adhesive, cohesive, and substrate failure. Failure owing to limited adherence between the glue and the adherent is referred to as an adhesive failure and is usually named delamination.[30] Cohesive failure occurs when the structural integrity of the glue is not as strong as its adherence to the substrates, and the breakdown of the adhesive itself occurs. The last possible failure consists of the breakdown of the substrate, indicating that the proper strength of the adhesive bond with the substrate is achieved. In Fig. 5, the stress-strain curves of LDPE and the ionomers tested are displayed and the failure of the joint can be deduced by the stress-strain profiles. Fig. 5a,b shows how LDPE is ineffective in adhering to aluminum since only a small stress led to the separation of the two metal slabs through adhesive failure. All the ionomer joints exhibit a considerable increase in adhesion when compared to LDPE (at least twice), showing that even a small number of ionic groups can significantly enhance PE's hydrophilic properties. P7, the ionomer with less IPC content (Fig. 5e), has the worst performance; all its three specimens show an early adhesive failure that occurs just after a sudden increase in stress. P6, P9, and P10 (Fig. 5c,g,f),

were slightly better than P7 as both cohesive and adhesive failures were observed. P8 (Fig. 5d) remarkably caused a substrate failure indicating a very strong adhesion to the substrate (Figure S22). The expected straight correlation between IPC content in the polymer and adhesive strength is not followed, which indicates that other parameters play a role. The upper limit of the ionomers adhesive strength was evaluated by testing them using steel bars. The strongest ionomer resulted to be P8, reaching a value of 12 MPa (see Figure S23).

Lap shear tests at different temperatures were performed to verify the reversible nature of the adhesives based on ionomers. Fig. 6 reports the trend line of the decrease of the adhesive strength with the increase of the temperature: at 60 °C and 80 °C the ionomers still exhibit a higher adhesion with respect to LDPE, at 100 °C (nearly the melting point of the polymers) a complete collapse of the adhesion strength is observed for all the samples.

Accelerated aging was commonly employed to speed up the degradation of the adhesive joint caused by temperature and moisture. To achieve the aging of the adhesive ionomers, lap shear specimens were

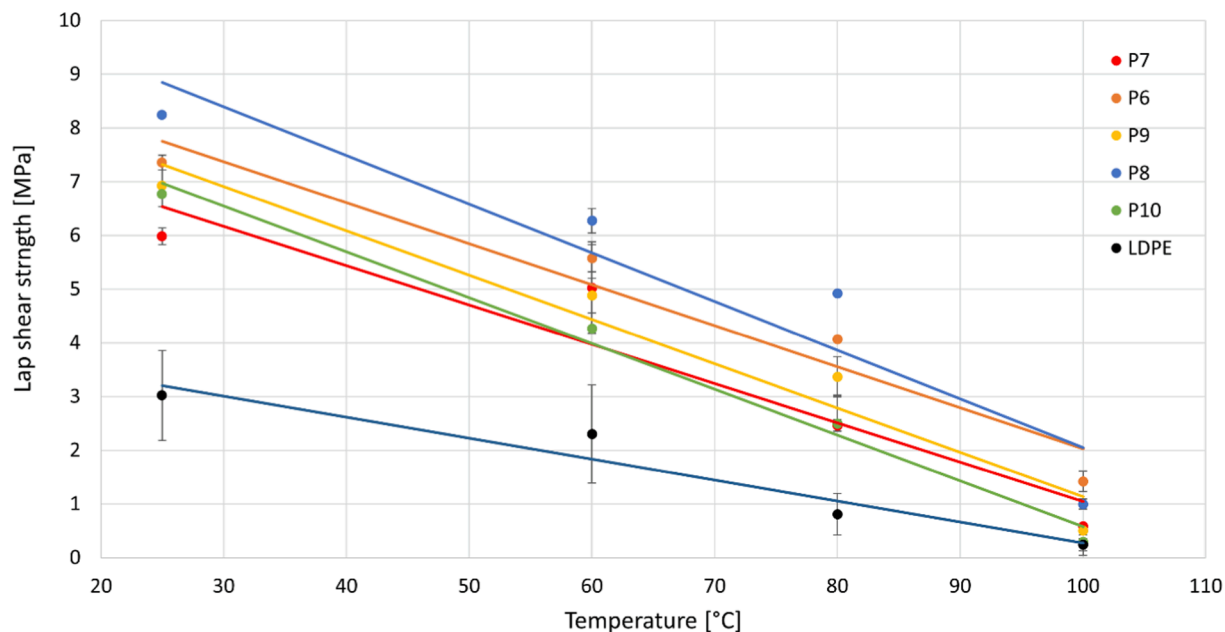


Fig. 6. Trend of the adhesive strength with the temperature 25 °C, 60 °C, 80 °C and 100 °C.

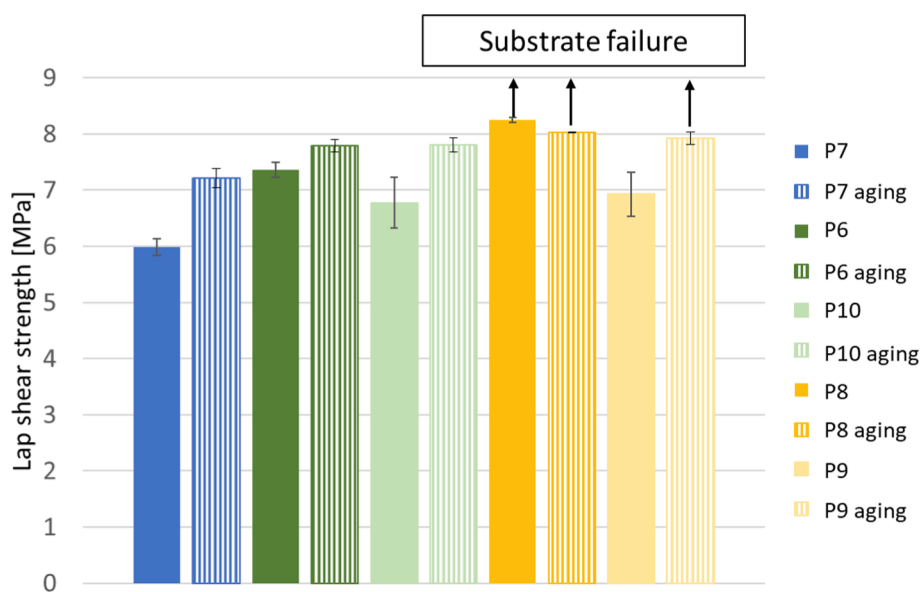


Fig. 7. Lap shear strength for the ionomers before (solid-colored bars) and after (striped-colored bars) aging procedure. The arrows indicate the ionomers that achieved substrate failure.

subjected to aging conditions described in the experimental section. Afterward, the same lap shear procedure employed above (ASTM D3163) was used to evaluate whether the mechanical performance of the glue has withstood the aging test. Fig. 7 shows the average strength of three specimens for each sample before and after the aging process.

Surprisingly, the strength of the adhesives was mostly unaltered or even increased for some samples (P7, P9, and P10) after the climate durability test. The stress-strain curves displayed in Figure S20, show a clear trend consistent with the IPC content of the ionomer. P7, the polymer with less IPC content (0.33 mol% respectively), has the worst adhesive performance (~6 Mpa). P6 and P10, having an intermediate IPC content (0.73 mol% for P6 and 0.75 mol% for P10) increase their adhesive strength, reaching values around 8 MPa. Lastly, P8 and P9 with the highest IPC content (1.28 mol% and 1.35 mol% respectively) display the highest adhesive strength with consequent substrate failure

(Figure S24). To explain the better performance after aging of most specimens, we speculate that the seven days spent at 70 °C may have caused the repositioning of the ionic moieties closer to the metal surface, favoring the adhesion of the ionomers with the highest IPC content.

4. Conclusions

In this work, the effect of introducing an ionic comonomer into LDPE on the mechanical and adhesive properties of the resulting copolymers is investigated. Several ionomers are synthesized via high-pressure/high-temperature free radical copolymerization of ethylene with an IPC formed by the salt of dimethyl-amino terminated methacrylate cation with the anion of methacrylic acid. The polymerization reaction conditions are varied to examine the effects of temperature, IPC content, and chain transfer agent (CTA) on the final copolymer. Raising the

temperature results in a limited inclusion of the IPC comonomer and in a decrease of MFI. The use of a higher IPC content in the feed leads to ionomers with lower viscosity, making the use of CTA unnecessary.

The incorporation of IPC into the hydrophobic backbone of LDPE generates an ionic crosslinking, leading to a reversible crosslinked-LDPE. The introduction of the ionic cross-linking improves both the mechanical properties (higher elongation and stress at break) and the adhesion capabilities on aluminum compared to LDPE, allowing at the same time the processing *via* cast film extrusion and compression molding. Furthermore, the dynamic nature of the ionic cross-linking leads to a thermally-reversible adhesive.

Five ionomers with low (P7), medium (P6 and P10), and high (P8 and P9) IPC concentrations, covering a wide range of MFI, were selected. Preliminary adhesion tests on aluminum show that the insertion of IPC leads to improved adhesion performances, although there is no relationship between the IPC content and the strength of the joints. At this stage, the rheological properties of the material appears to play a role as well. An automotive accelerated aging protocol was employed to hasten the adhesive joint's deterioration by moisture and temperature. Remarkably, all the ionomers withstand the aging test. A clear correlation between IPC content and adhesive performance is observed: the higher the IPC content in the polymer, the stronger the adhesion. This behavior suggests that conditioning the specimens at a temperature close to the onset of the polymer's T_m raises their adhesive performances by allowing more IPC moieties to approach the metal surface.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This work was supported by the National Recovery and Resilience Plan (NRRP), Mission 04 Component 2 Investment 1.5 – NextGenerationEU, Call for tender n. 3277 dated 30/12/2021. Award Number: 0,001,052 dated 23/06/2022, CUP D93C22000460001, Project title: Ecosystem for sustainable transition in Emilia-Romagna.

Notes

The authors declare no competing financial interest.

CRediT authorship contribution statement

Silvia D'Auria: Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Peter Neuteboom:** Validation, Methodology, Investigation, Data curation. **Roberta Pinalli:** Writing – review & editing, Methodology, Data curation, Conceptualization. **Enrico Dalcanale:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Data curation, Conceptualization. **Jérôme Vachon:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

This work benefited from the equipment funded by the Departments of Excellence program of the Italian Ministry for Education, University and Research (MIUR, 2017-2022 and 2023–2027). Centro Interfacoltà di Misura “G. Casnati” of the University of Parma is acknowledged for the use of NMR and MS facilities. S.D., R.P., and E.D. acknowledge project VIT, funded through the European Union Horizon 2020 Program (H2020-MSCA-RISE-2020 under grant agreement no. 101008237).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2024.113000>.

REFERENCES

- [1] C. Vasile (Ed.), *Handbook of Polyolefins*, Marcel Dekker, New York, 2000.
- [2] W. Kaminsky (Ed.), *Polyolefins: 50 Years after Ziegler and Natta II: Polyolefins by Metallocenes and Other Single-Site Catalysts*, Springer, Berlin Heidelberg, Berlin, Heidelberg, 2013.
- [3] S. Dadbin, M. Frounchi, M. Sabet, *Polym. Int.* 54 (2005) 686.
- [4] R.P. de Melo, V. de O. Aguiar, M. de F.V. Marques, *Mat. Res.* 18 (2015) 313.
- [5] J. Morshedjan, P.M. Hoseinpour, *Iran. Polym. J.* 18 (2009) 104.
- [6] M. Narkis, I. Raïter, S. Shkolnik, A. Siegmans, P. Eyerer, *J. Macromol. Sci., Part B* 26 (1987) 37.
- [7] U.W. Gedde, M. Ifwarson, *Polym. Eng. Sci.* 30 (1990) 202.
- [8] R.H. Hansen, H. Schonhorn, *J. Polym. Sci. B Polym. Lett.* 4 (1966) 203.
- [9] P. Fabbri, M. Messori, *Modification of Polymer properties*, Elsevier 109 (2017).
- [10] Y.-L. Hsieh, Xu. Shanjing, M. Hartzell, *J. Adhes. Sci. Technol.* 5 (1991) 1023.
- [11] H.N.A.M. Steenbakkens-Menting, P.E.L. Voets, P.J. Lemstra, *J. Adhes. Sci. Technol.* 9 (1995) 889.
- [12] F. Awaja, M. Gilbert, G. Kelly, B. Fox, P.J. Pigram, *Prog. Polym. Sci.* 34 (2009) 948.
- [13] F. Chabert, F. Tournilhac, N. Sajot, S. Tencé-Girault, L. Leibler, *Int. J. Adhes. Adhes.* 30 (2010) 696.
- [14] K. Yamauchi, J.R. Lizotte, T.E. Long, *Macromolecules* 36 (2003) 1083.
- [15] C. Heinzmann, C. Weder, L.M. de Espinosa, *Chem. Soc. Rev.* 45 (2016) 342.
- [16] P. Sun, Y. Li, B. Qin, J.-F. Xu, X. Zhang, *ACS Materials Lett.* 3 (2021) 1003.
- [17] C. Heinzmann, S. Coulibaly, A. Roulin, G.L. Fiore, C. Weder, *ACS Appl. Mater. Interfaces* 6 (2014) 4713.
- [18] C. Heinzmann, U. Salz, N. Moszner, G.L. Fiore, C. Weder, *ACS Appl. Mater. Interfaces* 7 (2015) 13395.
- [19] J.H. Aubert, *J. Adhes.* 79 (2003) 609.
- [20] N. Ishikawa, M. Furutani, K. Arimitsu, *ACS Macro Lett.* 4 (2015) 741.
- [21] 2-(dimethylamino)-ethyl ester methacrylic acid (CAS 2867-47-2), approved comonomer (FCM No 455, with specific migration limit of 0.01 mg/kg); methacrylic acid (CAS 79-41-4), approved comonomer (FCM No 150, no specific migration limit). For details see: plastic-material-food-contact - ECHA (europa.eu).
- [22] S. D'Auria, A.M. Pourrahimi, A. Favero, P. Neuteboom, X. Xu, S. Haraguchi, M. Bek, R. Kádár, E. Dalcanale, R. Pinalli, C. Müller, J. Vachon, *Adv. Funct. Materi.* 33 (2023) 2301878.
- [23] G. Mortimer, *J. Polym. Sci.* 10 (1972) 163.
- [24] J.R. Wagner, E.M. Mount, H.F. Giles, in *Extrusion*, Elsevier, 181, 2014.
- [25] B. Wunderlich, C.M. Cormier, *J. Polym. Sci. A-2 Polym. Phys.* 5 (1967) 987.
- [26] Y. Furushima, M. Nakada, M. Murakami, T. Yamane, A. Toda, C. Schick, *Macromolecules* 48 (2015) 8831.
- [27] J.D. Hoffman, R.L. Miller, H. Marand, D.B. Roitman, *Macromolecules* 25 (1992) 2221.
- [28] J.D. Hoffman, R.L. Miller, *Polymer* 38 (1997) 3151.
- [29] D.V. Rees, D.C. Bassett, *Nature* 219 (1968) 368.
- [30] S. Omairey, N. Jayasree, M. Kazilas, *S.N. Appl. Sci.* 3 (2021) 769.