

Crosslinking versus interdiffusion in two pot one pack acetoacetoxy-amine based binder system

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ABSTRACT

A two-pot-one-pack waterborne crosslinking system is studied by following the crosslinking and interdiffusion between the polymer particles functionalized with acetoacetoxy on one hand and with polyethyleneimine on the other. FTIR spectroscopy and rheological measurements are used to follow the evolution of crosslinking, while pyrene excimer fluorescence is used to analyse the interdiffusion of polymer chains between neighbouring particles during film formation. Both crosslinking and interdiffusion proceed slowly at room temperature. However, crosslinking is complete after 24 h at 60 °C, while interdiffusion does not proceed further at this temperature. TEM images confirm the presence of a honeycomb structure in the final film, produced by the crosslinked moieties between polymer particles that can act as a barrier for interdiffusion of polymer chains between particles. Nevertheless, strong films are produced even in the absence of significant interdiffusion, due to the crosslinks between particles.

1. Introduction

The primary purpose of crosslinking of polymer chains is to enhance their final properties such as the solvent resistance, durability and mechanical performance of the materials [1]. Moreover, the crosslinking can be achieved during the main polymerization step or after it, as a post-crosslinking [2]. The main difference between crosslinking and post-crosslinking is the way the materials are being processed afterwards, as a too early crosslinking may hinder a correct processing of the polymeric material [2,3].

This basic concept also applied to polymeric coatings made from waterborne latexes. In these waterborne systems, the film formation process plays a vital role on defining the final properties of the film. More specifically, the relative rate of diffusion of polymer chains between polymer particles and crosslinking between polymer chains are key variables playing a crucial role on the development of the final film properties [4,5]. Three possible scenarios could be occurred. Firstly, if the rate of crosslinking is faster than diffusion, or crosslinking occurs during the main polymerization step, a highly cross-linked structure is formed inside each polymer particle, which provides no chance to chains for diffusion during film formation. This is how weak films, with low cohesive strength, can be obtained from highly crosslinked polymers [3,5,6]. Geurts et al. found this problem for polymer particles containing

epoxy moieties, when they tried to crosslink them with diamines. As the initial polymer particles already had a high gel content, the reaction between epoxy groups and diamines was not favoured [7]. Secondly, if the rate of diffusion is faster than crosslinking a strong film can be prepared, as the crosslinks will occur on a fully diffused system [8–10]. Finally, if the rate of crosslinking is comparable to diffusion rate, the polymer particles diffuse to some extent to the boundaries and then crosslinking may occur in the interface, restricting the full diffusion of polymer chains between polymer particles.

Therefore, in order to design hard and solvent resistant coatings from waterborne latexes, it is not only important to follow crosslinking reactions during the production of the films but also the interdiffusion of polymer chains. There are basically three methods to measure the polymer chain interdiffusion during film formation. Two of them use fluorescence i.e., Fluorescence Energy Transfer (FRET) and Pyrene Excimer Fluorescence (PEF) [5,11]. The third method is small angle neutron scattering (SANS) [12,13]. PEF is a relatively new fluorescence method to measure the interdiffusion. It is based on the fact that excited molecules emit light at different wavelengths if they are isolated or in close contact, forming an excimer [14]. Pyrene is the most often used molecule in this technique because it can be excited by UV-light [15]. To carry out PEF measurements, two equivalent latexes are prepared, one labelled with the compound that forms the excimer and the other

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unlabelled. Then both latexes are blended and the film formation is followed by fluorescence. When the latex blend film starts to dry, the local concentration of pyrene decreases, as it will diffuse to the surrounding particles, not containing pyrene, and as a result the fluorescence coming from the excimer decreases. The diffusion speed of the polymer can be deduced by calculating the excimer/monomer ratio [14,16].

In 1950's, the hydroxyl/melamine based crosslinking system was applied in waterborne latexes [9,17]. It was the first time that crosslinking chemistry was introduced in waterborne systems and it was found that the chemical resistance and mechanical properties of the crosslinked films improved compared to the non-crosslinked counterparts. However, the major drawback of this chemistry is the use of formaldehyde, which was released during film formation. The high toxicity of the melamine based crosslinking system shifted the trend toward less toxic system i.e., carboxylic acid based chemistry. However, the aziridines used to crosslink the carboxylic groups at room temperature also presented toxicity problems [18]. Diacetone acrylamide/adipic acid dihydrazide based crosslinking system has also been reported by Liu et al. to crosslink acrylic dispersions, producing films with improved mechanical strength and chemical resistance [19].

Acetoacetoxyethyl methacrylate (AAEMA) was introduced in the market in the late 1980s, and since then its use for crosslinking reactions of waterborne latexes has been widely explored. AAEMA is preferred because it provides environmentally friendly coatings that are less toxic and able to cure at room temperature [20]. From the early studies by Geurink et al. in two pack systems with AAEMA functionalized latexes and water soluble polyamine crosslinkers, and their first trials of two-pot one-pack system [20], multiple patents presenting their use for the crosslinking of waterborne polymeric dispersions have appeared based on this system [21–24]. However, the rate of crosslinking and interdiffusion has not been deeply studied in this AAEMA-amine system.

In our previous work, we reported the kinetic study of the crosslinking between hexamethylenediamine (HMDA) functionalized polymer particles and AAEMA functionalized polymer particles, in a two-pot one pack system [25]. This way, the use of water soluble amine crosslinkers was avoided, favouring the REACH implementation of the crosslinking coating system. The kinetic study showed that crosslinking reaction evolves slowly at room temperature, as opposed to what seemed to be widely supposed and that temperature had a significant effect on driving the crosslinking degree to its completeness. Nevertheless, the functionalization of the amine bearing particles with longer polyethylenimine (PEI) groups, instead that with short diamines (such as HDMA), seems to produce better final properties in the two-pot one-pack system [23].

Therefore, the objective of this work is to follow the evolution of crosslinking and interdiffusion in two-pot one pack binder system, pot-1 (component-1) prepared by AAEMA functional polymer particles and pot-2 (component-2) by PEI based functional polymer particles. To follow the kinetics of the crosslinking reaction, FTIR spectroscopy and rheological measurements were carried out, analysing also the effect of temperature. On the other hand, the interdiffusion of polymer chains was followed by PEF experiment, while the crosslinking reaction was also occurring. Film morphology was analysed by TEM of the cryosectioned films with different PEI contents. All this information was used to justify the mechanical properties of the crosslinked films obtained with different amine functionality contents and at different annealing conditions.

2. Experimental part

2.1. Materials

Methyl methacrylate (MMA) and butyl acrylate (n-BA) monomers were supplied by Quimidroga, while methacrylic acid (MAA) and acetoacetoxy ethyl methacrylate (AAEMA) in technical grade were also used

as monomers and supplied by Sigma-Aldrich. Sodium lauryl sulfate (SLS) and Disponil A3065 were used as emulsifiers, sodium bicarbonate as a stabilizer and potassium persulfate (KPS) as initiator. All these materials were supplied by Sigma-Aldrich. Ammonium hydroxide and the fluorescent monomer 1-pyrenemethyl methacrylate were also purchased from Sigma-Aldrich. Polyethyleneimine (Lupasol G20) with average molecular weight of about 1300 g/mol was kindly supplied by BASF Corporation. Deionized high-purity water was used for the emulsion polymerization and obtained through a Merck Millipore plant.

2.2. Synthesis of MMA/BA/AAEMA latex

For the production of the latexes, a seeded semibatch emulsion polymerization procedure was used. Initially, a seed was prepared by batch emulsion polymerization (Table 1) at 80 °C for 2 h.

This seed was used to produce the final latex by seeded semibatch emulsion polymerization with two feeding steps. We used 10 to 90 ratio of seed/monomer in the two feeding stages. The seed quantity used during the first stage of feeding was 42.78 g with no additional water, and the first feed presented in Table 2 was fed at 0.442 g/min. In the second stage of feeding 31.5 g of extra water was added to maintain the final solids content at 50 % and a feeding rate of 0.23 g/min for the second feed was used. AAEMA functional monomer was included in the recipe in this second feeding stage. We named the latex obtained this way as component 0 (C-0).

Once C-0 latex was prepared, the emulsion was cooled and ammonium hydroxide (NH₄OH) (28 %) was added in 5 min under continuous stirring to one fraction of it. The NH₄OH was added in a mol ratio of 2:1 in NH₄OH:AAEMA. This way AAEMA functionalized and protected component 1 (C-1) latex was prepared.

For the preparation of amine functionalized component 2 (C-2) latex, a fraction of C-0 latex was reacted with polyethyleneimine (PEI). The Mw of the PEI used in this work, LUPASOL G-20, was 1300 g/mol. PEI is composed of $-\text{CH}_2-\text{CH}_2-\text{N}(\text{H})_x-$ repeating units, x being 0, 1 or 2. Considering an average molecular weight of 43 g for this repeating unit, it can be estimated that this PEI will be composed of 30 of these repeating units. Assuming an even distribution of N, NH and NH₂ groups, it can be said that each PEI molecule will have 20 amine groups able to react with AAEMA moieties. In order to prepare C-2 latex, we selected a molar ratio of 7.7 reactive amine groups per AAEMA functional groups, or one PEI molecule per 2.6 AAEMA molecules in the C-0 latex. Component-2 was prepared by adding slowly C-0 latex into PEI solution. From these components, C-1 and C-2, a blend latex was prepared with equal weight ratio of both components (Blend latex). For comparison purposes, a lower amine/AAEMA ratio was also selected, namely 0.2. This component-2 was named C-2_0.2ratio.

In order to study the interdiffusion of the polymer chains by PEF, fluorescent labelled and unlabelled latexes were prepared. Batch emulsion polymerization was used for the preparation of the seeds, in which 1-pyrenemethyl methacrylate was introduced in the case of the labelled latex. Then the shell was prepared by semibatch emulsion polymerization by using the whole seed. The formulation used for both seed and shell formation for the preparation of labelled and unlabelled latexes is presented in Table 3.

Once the two latexes (labelled and unlabelled) were prepared, three

Table 1
Formulation of the seed produced by batch emulsion polymerization.

Ingredients	Charge (g)
Methyl methacrylate	31.29
Butyl acrylate	31.34
Water	250.31
SLS	1.255
NaHCO ₃	0.326
K ₂ S ₂ O ₈	0.31

Table 2

Formulation used in the two growing steps of the seed by semibatch emulsion polymerization for the synthesis of MMA/BA/AAEMA latex (C-0).

Ingredients	First feeding (g)	Second feeding (g)
	Growth of the seed	Addition of functional monomer
Methyl methacrylate	24.76	12.23
Butyl acrylate	24.51	12.15
Water	27.92	14.24
SLS	0.99	0.4915
Disponil A3065	1.34	0.662
Methacrylic acid	0.467	0.20
K ₂ S ₂ O ₈	0.2	0.1
Acetoacetoxy ethyl methacrylate (AAEMA)		4.4

Table 3

Formulation used to produce the seed by batch emulsion polymerization and the final latex by semibatch emulsion polymerization for the synthesis of labelled and unlabelled latexes for PEF study.

Ingredients	Seed (g) (labelled latex)	Seed (g) (unlabelled latex)	Feed (g)
Methyl methacrylate (MMA)	2.19	2.19	6.025
Butyl acrylate (BA)	2.19	2.19	6.025
SLS	0.087	0.087	0.245
NaHCO ₃	0.0217	0.0217	–
K ₂ S ₂ O ₈	0.0217	0.0217	0.064
Disponil A3065	–	–	0.33
Water	17.57	17.57	6.9
Methacrylic acid (MAA)	–	–	0.096
Acetoacetoxy ethyl methacrylate (AAEMA)	–	–	0.88
1-Pyrenemethyl methacrylate	0.887	–	–

blends were prepared from them, one control blend (named as Blank Blend) and the other two were crosslinked blends. For the preparation of Blank Blend, a ratio of 5:95 between labelled to unlabelled latex was used, without the addition of any PEI. So Blank Blend contained to C-0 like latexes, in which the crosslinking moiety had not been included. For the preparation of the crosslinked blends, first C-1 and C-2 components from both unlabelled and labelled latexes were prepared. For the preparation of unlabelled C-1, the mol ratio of 2:1 between NH₄OH to AAEMA was used. During the preparation of labelled and unlabelled C-2, we prepared two different C-2 by using different amounts of PEI. The polyethyleneimine was added to maintain a mol ratio of 0.2 and 7.7 between N–H of PEI and acetoacetoxy groups respectively. Therefore, two blends were prepared by mixing equal amounts of component-1 and 2. First blend was named as “PEI-0.2-ratio” having C-2 with 0.2 NH to AAEMA ratio and second blend named as “PEI-7.7-ratio” having a ratio of 7.7. The following weight ratio of components was selected for the preparation of the crosslinked blends: 5 % of labelled C-2, 45 % of unlabelled C-2 and 50 % of unlabelled C-1. This way the total ratio of labelled to unlabelled latexes was 5/95, as in the Blank Blend.

Table 4 presents the codes used along the work to define the samples studied.

2.3. Latex and film characterization

The solids content of the seed and the latex was obtained gravimetrically, and it was used to analyse the evolution of the conversion during the polymerization reaction. The particle size of polymer particles was measured by Dynamic Light Scattering, DLS (Malvern® Zetasizer Nano). For the analysis, samples were diluted to such a low concentration that it can safely be assumed that no monomer was present in the polymer particles, namely that the unswollen particle sizes were measured.

Table 4

Samples code used.

Sample code	Definition of samples	
	Single latexes	Two pot
C-0	Latex functionalized with AAEMA	
C-1	C0 + NH ₄ OH	Blend latex (C-1 + C-2_7-7 ratio)
C-2	C0 + PEI (7.7 NH/AAEMA)	
C-2_0.2 ratio	C0 + PEI (0.2 NH/AAEMA)	Blend latex 0.2 (C-1 + C-2_0.2 ratio)
Labelled C-0	C-0 labelled with pyrene	Blank Blend (5 % labelled C-0 + 95 % C-0)
Labelled C-2_0.2 ratio	Labelled C-0 + PEI (0.2 amine/AAEMA)	PEI-0.2-ratio (5 % labelled C-2_0.2 ratio + 45 % C-2_0.2 ratio + 50 % C-1)
Labelled C-2_7.7 ratio	Labelled C-0 + PEI (7.7 amine/AAEMA)	PEI-0.2-ratio (5 % labelled C-2_7.7 ratio + 45 % C-2_7.7 ratio + 50 % C-1)

For the kinetic analysis of the evolution of the crosslinking reaction, FTIR spectra were recorded using a Nicolet iS50 equipment. The spectra were registered with the resolution of 4 cm⁻¹ with scan number 32. The samples were prepared by casting over CaF₂ support. The RT film formation was carried out at 23 °C with relative humidity of 55 % and for high temperature treatment, the film was placed in an oven with static air at 60 °C. Dynamic Mechanical Thermal Analysis (DMTA) were carried out using a dynamic mechanical thermal analyser Triton 2000 DMA, Triton Technology Ltd. with single cantilever bending geometry. We investigated the rheological properties by calculating the E', E'' and tan delta at 2 °C heating rate/min heating rate. On the other hand, we performed time sweeps at 60 °C for 1500 min for PEI containing system. After the time sweep, another temperature sweep was carried out to compare with the initial sample.

Tensile tests of the free standing films annealed at room temperature (23 °C with relative humidity of 55 %) and at 60 °C were performed on Universal testing machine TA.HD plus Texture Analyser at a crosshead speed of 0.42 mm/s. Samples with approximate length of 55 mm and 0.55 mm of thickness were used.

The morphology of films was studied by means of Transmission Electron Microscopy (TEM). TEM analysis was carried out with a Tecnai™ G2 20 Twin device at 200 kV (FEI Electron Microscopes). The films were cryosectioned with a Leica EMUC6 cryoultramicrotome at 30 °C below the Tg of the sample, with a Diatome 45° diamond 30 knife, and the observations were made in the microscope (TEM), after RuO₄ staining. The fluorescence measurements were conducted by using Fluoromax-4 apparatus (Horiba Jobin-Yvon) equipped with 450 W Xenon arc lamp. Thin Blend latex films were applied on quartz crystal by spin coating (8000 rpm, without diluting the latex). The samples were deposited in the equipment, excited with 340 nm and measured in the range of 360 nm to 600 nm. The signal was collected at 45° orientation to the beam. The measurements were carried out after annealing the film during different times at room temperature and at 60 °C.

3. Results and discussions

3.1. Kinetics of crosslinking reaction

The particle size of C-0 was 130 nm and the latex had a solids content of 47 wt% with 95 % of monomer conversion. There was no change in solids content during the formation of C-1 by the addition of NH₄OH. However, it decreased to 40 wt% solids content during the formation of C-2. The particle sizes of C-1 and C-2 measured right after their preparation were 130 and 134 nm respectively.

FTIR spectroscopy analysis was used to study the chemical structural changes during the synthesis of C-1, C-2 and the crosslinked Blend. The FTIR spectra of C-0, C-1, C-2 and Blend film casted at room temperature

will be presented in the two regions that present the most significant changes: the region from 3800 cm^{-1} to 3000 cm^{-1} , named as N-H stretching region and the region from 1800 cm^{-1} to 1500 cm^{-1} , named as carbonyl stretching region. Both regions have been analysed

separately for the formation of C-1, C-2 and Blend in Fig. 1. The assignment of the different infrared absorptions can be found in the Supplementary information (Table S.1).

In the NH stretching vibration region, in addition to the band due to

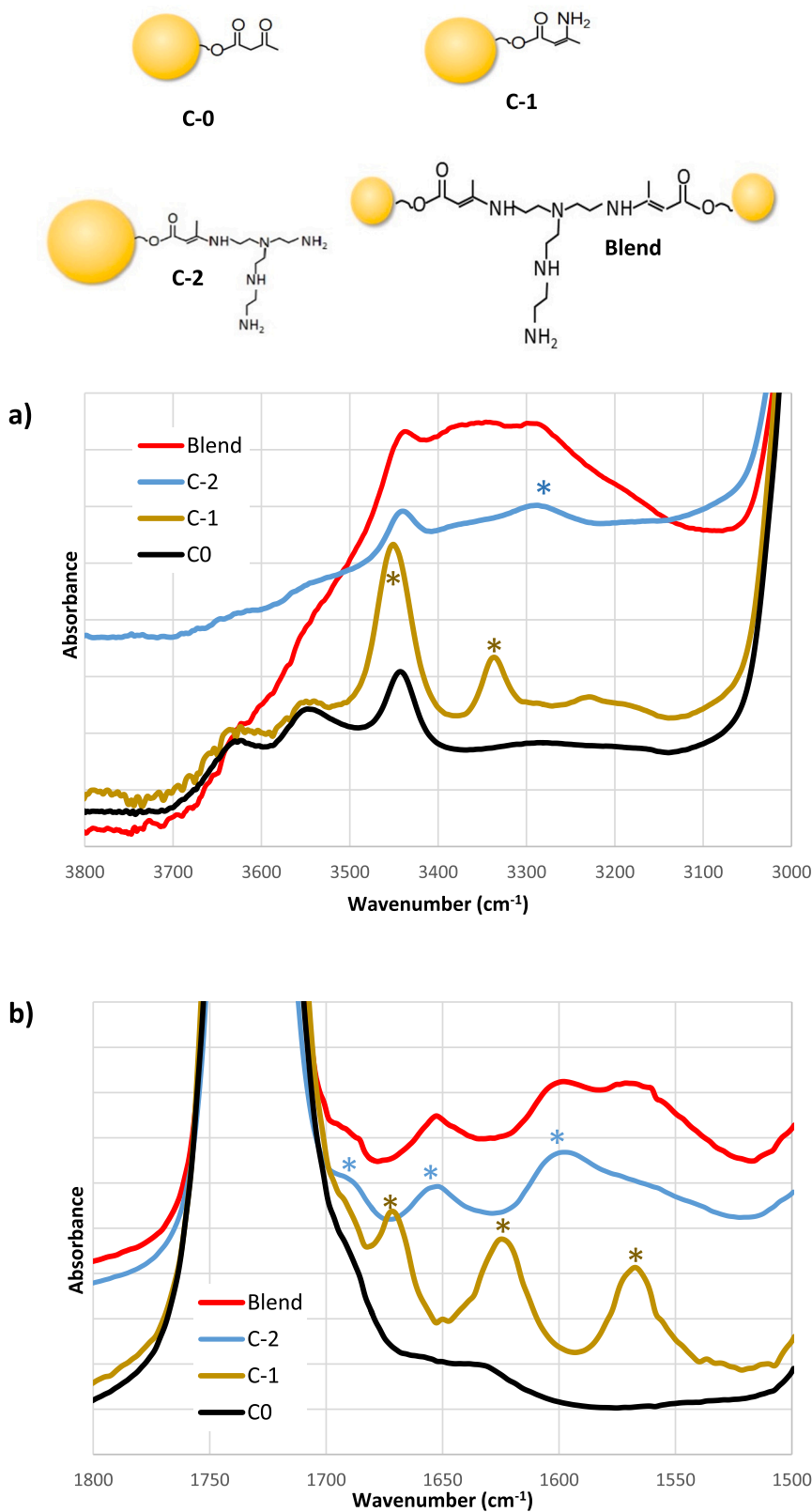


Fig. 1. Model chemical structures of C-0, C-1, C-2 and crosslinked Blend particles and FTIR spectra of a) N-H stretching region and b) carbonyl stretching region of C-0, C-1, C-2 and Blend films prepared at RT (1 day).

the carbonyl harmonic at 3430 cm^{-1} , two bands around 3336 cm^{-1} and 3430 cm^{-1} could be observed for C-1, assigned to the NH_2 stretching of the primary enamine. These two bands did not appear in the spectrum of C-2 that was characterized by a broad absorption centred at 3290 cm^{-1} . This band was assigned to the secondary enamine stretching that was overlapped with the NH_2 and NH stretching and the polyethyleneimine. Finally, in the Blend, the bands of primary and secondary enamine stretching could be found.

In the carbonyl stretching region of C1, three bands appeared at 1670 , 1624 and 1562 cm^{-1} related to carbonyl stretching next to the primary amine, $\text{C}=\text{C}$ stretching and NH_2 bending of the primary enamine respectively. However, the spectrum of C-2 was characterized by the bands related to the secondary enamine (1690 cm^{-1} $\text{C}=\text{O}$ stretching and 1654 cm^{-1} $\text{C}=\text{C}$ stretching and NH bending) and to the remaining polyethyleneimine bending at 1606 cm^{-1} . In the Blend, bands related to primary and secondary enamine and to the remaining polyethyleneimine could be found.

Ideally, the crosslinking reaction between the protected acetoacetoxy group of C-1 and the amine functionalized C-2 should be complete, when all the primary amines coming from the protection of acetoacetoxy by NH_4OH in C-1 disappear due to the reaction with PEI amines. However, the infrared results (Fig. 1) showed that the bands related to primary enamine from C-1 at 1562 cm^{-1} remained in the spectrum and accordingly full conversion was not obtained after one day of film formation at room temperature. Therefore, it was decided to follow the crosslinking reaction quantitatively by FTIR for different times and annealing temperatures. Thus the FTIR spectra of the Blend film annealed at room temperature for one, two and three days was analysed, and then after annealing at $60\text{ }^\circ\text{C}$ for 1 h, 3 h and 24 h. Fig. 2 presents the low wavenumber region for such analysis. In this region, the evolution of primary amines absorption at 1562 cm^{-1} was followed for the quantification of the crosslinking.

For the quantification study, the area of the primary amine peak coming from C-1 at 1562 cm^{-1} at different crosslinking times was measured and the conversion was calculated according to Eq. (1), considering that the conversion was negligible at time 0.

$$\% \text{Crosslinking} = \left(1 - \frac{A_{1562}(t)}{A_{1562}(0 \text{ days})} \right) * 100 \quad (1)$$

Fig. 3 presents the crosslinking percentage obtained during annealing at room temperature for three days and for 1, 3 and 24 h at $60\text{ }^\circ\text{C}$. It was noticed that the reaction proceeded slowly for 3 days at RT and only

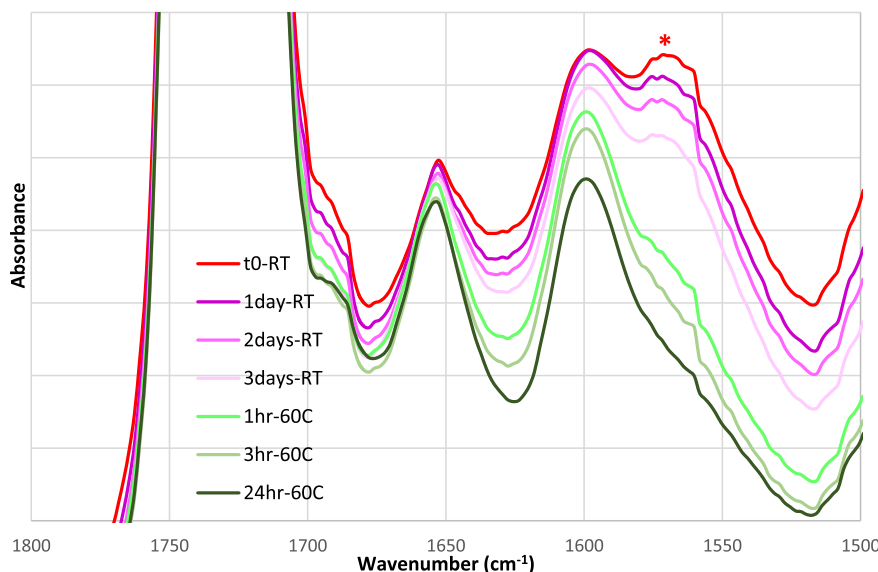


Fig. 2. FTIR spectra in the carbonyl stretching region after annealing the Blend film at RT for 1, 2 and 3 day and then 1, 3 and 24 h at $60\text{ }^\circ\text{C}$.

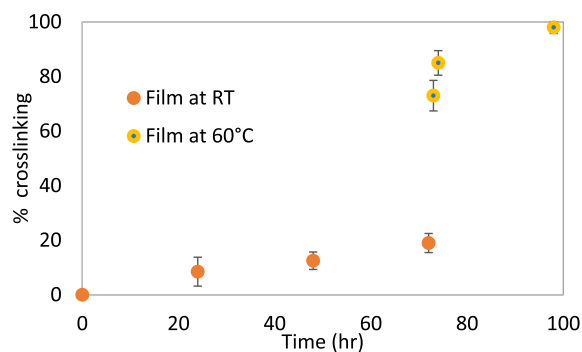


Fig. 3. Crosslinking degree in Blend film calculated via FTIR analysis with time and temperature.

20 % of conversion was achieved in this time. The annealing at $60\text{ }^\circ\text{C}$ speeded up the process, as around 70 % conversion was already achieved after 1 h, 74 % conversion 3 h and almost 100 % conversion after 24 h, to complete the crosslinking reaction as shown in Fig. 3.

The crosslinking reaction kinetics were also studied by rheological measurements. Fig. 4 presents the evolution of moduli value with time, performed by a time sweep test at constant temperature of $60\text{ }^\circ\text{C}$. We found that the moduli (both E' and E'') values initially increased significantly and then reached a certain plateau. The significant increase

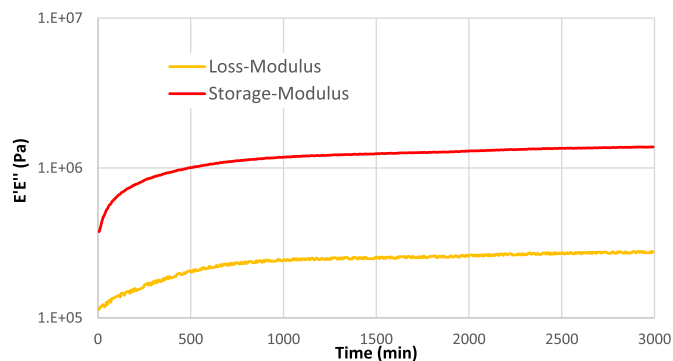


Fig. 4. Time sweep at $60\text{ }^\circ\text{C}$ and 0.1 Hz for Blend film initially annealed at RT.

of moduli with time was due to the crosslinking reactions occurring between C-1 and C-2 components in the film. These data match the crosslinking degree calculated by FTIR, where it was also seen that crosslinking reaction evolved rapidly in the initial hours of annealing at 60 °C, but around 24 h were required to fully convert the reaction. In these rheological measurements, it can be seen that around 1500 min are needed to reach to the plateau of the moduli, very similar to the 24 h (1440 min) observed by FTIR. In our previous work, hexamethylenediamine (HDMA) was used as amine moiety in C-2, instead of oligomeric PEI [25]. In that case, the full crosslinking reaction took just 100 min at 60 °C, suggesting that the smaller size of HDMA in the amine functionalized C-2 particles favoured the crosslinking reaction with the AAEMA functionalized C-1 particles, compared to the larger PEI functionalized C-2 particles.

However, taking a look to the crosslinking % at RT derived from FTIR, it could be noticed that the rate was low, but steady. Therefore, the Blend film casted at RT was left at that temperature for 30 days, and its rheological properties were analysed by DMTA. Fig. 5 presents the tan δ curves of Blend film annealed at RT for 3 days and 30 days, and the same films annealed for 1 day more at 60 °C (see the corresponding storage and loss moduli in Fig. S.1 of the Supplementary material).

Two main changes were found in tan delta curve of the Blend annealed at RT 3 days and that of the film further annealed at 60 °C for one day. First, there was a decrease in the intensity of tan delta peak and the second change was the shift of the peak toward higher temperature (from 33 to 44 °C). The first change might appear because after annealing at 60 °C for 1 day full crosslinking was achieved, leaving a lower amount of amorphous phase and decreasing the segmental chain mobility, and the intensity of the peak. The reason for the second change was the formation of more crosslinked joints that increases the T_g value for sample annealed at 60 °C. However, it can be noticed that the Blend film annealed at RT for 30 days, presented the same tan delta curve as the film annealed at 60 °C for one day. And the curve was not further changed, when the Blend films annealed for 30 days at RT was further annealed at 60 °C for one more day. Therefore, it can be concluded that full crosslinking can also be achieved at RT for this system, but with much longer annealing times.

3.2. Evolution of polymer interparticle diffusion

In order to study the diffusion of polymer chains between polymer particles during the film formation process of this crosslinked system, PEF experiments were used. 1-pyrene methyl methacrylate monomer was used for labelling the latexes. Labelled and unlabelled C-0 latexes were synthesized, with a particle size of 73 nm and a solids content of 37

wt% for the labelled latex and 90 nm particle size and 38 wt% solids content for the unlabelled latex. First, the interdiffusion was studied by PEF in a control non-crosslinked system. Therefore, a non-crosslinked control blend containing a 5/95 weight ratio of labelled C-0 latex to unlabelled C-0 latex was prepared, in the absence of any amine crosslinking moiety. Fig. 6 shows the fluorescence spectra of this control film prepared at different temperature and annealing times.

The pyrene monomer fluorescence peak (I_M) appears in the region from 392 to 398 nm. The excimer emission (I_E) is located between 450 and 540 nm. The spectra in Fig. 6 have been normalized to the pyrene monomer fluorescence peak. It can be seen that during the film annealing process, the ratio between the intensity of the band associated to the excimer, and that of the monomer ($R = I_E / I_M$) decreases. The decrease in the excimer band can be explained by the decrease of the local concentration of pyrene containing polymer chains, as they diffuse out of the labelled particles into adjacent unlabelled ones.

Then, the same procedure was applied to crosslinked blends, in which the labelled latex was surface modified with different PEI contents to produce C-2 labelled compounds. Fig. 7 presents the evolution of I_E/I_M ratio with time and temperature in the non-crosslinked Blank

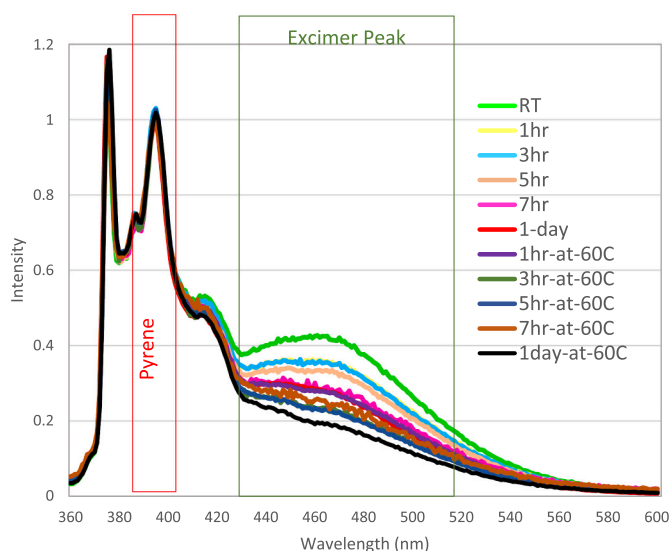


Fig. 6. Fluorescence spectra of the uncrosslinked control blend latex film containing 5 % of labelled C-0 latex and 95 % of unlabelled C-0 latex, annealed at RT and 60 °C for different times.

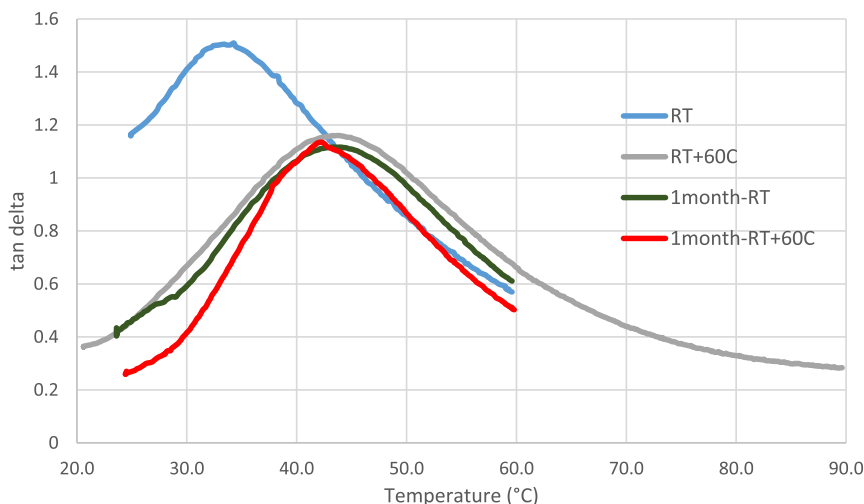


Fig. 5. Comparison of tan delta curves of the Blend film annealed at different T and time conditions.

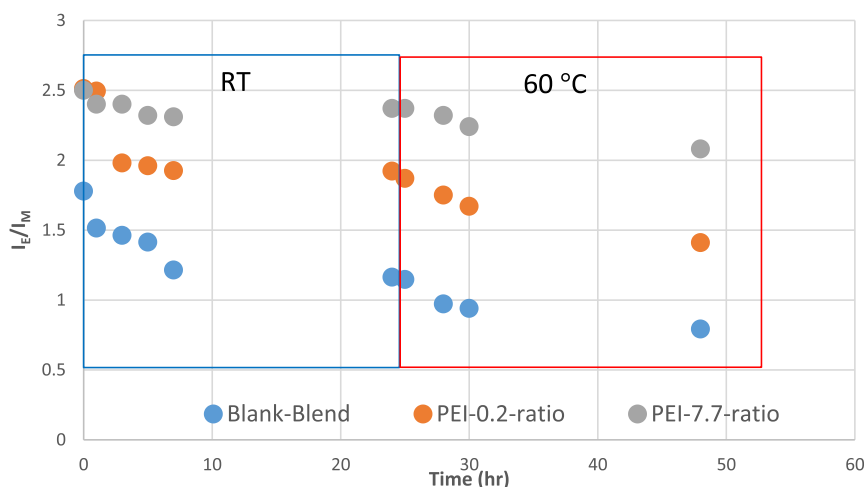


Fig. 7. I_E/I_M ratio of the uncrosslinked Control Blend and crosslinked Blend films annealed at RT and then annealed at 60 °C for different times.

Blend film and in the crosslinked blend films (see the full set of fluorescence spectra of the crosslinked blends in Figs. S.2 and S.3 of the Supplementary material). In the case of the Blank Blend film, as seen in Fig. 7, the I_E/I_M ratio decreases slowly at room temperature, to reach some kind of plateau after 24 h, but it decreases further on annealing at 60 °C, to keep almost the same I_E/I_M ratio for further annealing at 60 °C. Therefore, it can be seen that polymer chains interdiffuse at RT (even if slowly) and there is a clear effect of temperature on speeding up the interdiffusion of polymer chains in this control system without crosslinking moieties. When crosslinking is included in the film, the interdiffusion extent changes depending on the PEI/AAEMA ratio. In case of blend “0.2-PEI ratio” the interdiffusion trend is similar to the non-crosslinked Blank Blend, showing a first low interdiffusion extent at room temperature that is enhanced at 60 °C. However, the initial I_E/I_M values are higher for the “0.2-PEI ratio” blend as compared to Blank Blend, suggesting some kind of hindrance to interdiffusion given by water molecules that could be retained by the hydrophilic PEI moieties. However, once those molecules would evaporate, the I_E/I_M ratio presents a sudden decrease, due to the interdiffusion of polymer chains among polymer particles. However, in case of the crosslinked “7.7-PEI ratio” blend, the I_E/I_M ratio was maintained almost constant at RT and there was just a slight decrease while annealing at 60 °C, suggesting a negligible interdiffusion of polymer chains between polymer particles

for this crosslinked system. According to Narayanaswami et al., the excimer to monomer intensity ratio (I_E/I_M) is reduced three fold when the distance between pyrene units goes from 5 Å to 20 Å [26]. Considering the values that are presented in Fig. 7, it can be said that such reduction is observed for the Blank Blend sample (when no crosslinking PEI was included in the sample). However, when a significant number of PEI moieties are inserted in “7.7-PEI ratio” blend, the I_E/I_M ratio only reduced from 2.5 to 2.08 at the end on the annealing at 60 °C. Therefore, a movement of the pyrene having chains of less than 1 nm could be expected.

TEM analysis was carried out in order to see if the crosslinked Blend films (PEI-7.7 ratio and PEI-0.2ratio) presented defects or holes in its structure, as a consequence of this lack of polymer interdiffusion between polymer particles, or between C-1 and C-2 particles in the final film. Fig. 8 shows the TEM images of the Blend film (PEI-7.7 ratio) annealed at RT and annealed at 60 °C, cryosectioned and stained with RuO₄. The amines moieties are stained with RuO₄ and appear dark in the interparticle spaces. Apparently, there is no difference in the TEM images of the film annealed at RT and that of the film annealed at 60 °C, but in a closer look it seems that boundaries are not that sharp in the annealed film as in the RT annealed film. Fig. 9 shows the TEM images of the Blend film (PEI-0.2 ratio) annealed at RT, cryosectioned and stained with RuO₄. The presence of slightly visible honeycomb structure

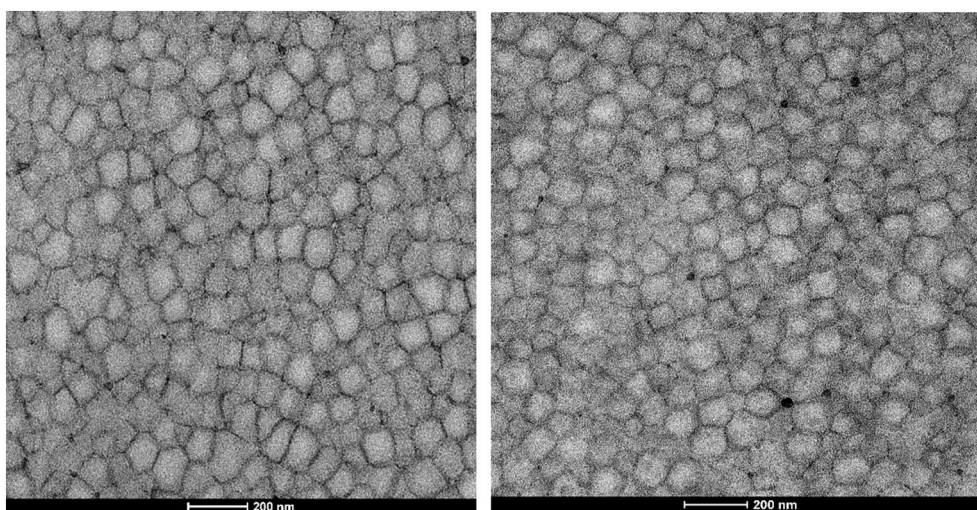


Fig. 8. TEM images for Blend film (7.7 ratio PEI) cryosectioned and stained for 5 min with RuO₄. The image on left was taken from the RT annealed film and right image from the film annealed at 60 °C.

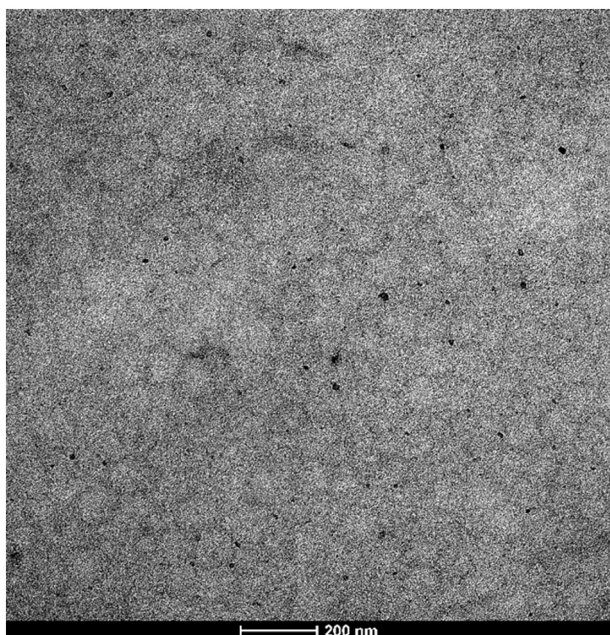


Fig. 9. TEM images for Blend film (0.2 ratio PEI) annealed at RT, cryosectioned and stained for 5 min with RuO₄.

indicated the presence of a lower amount of amines in the interparticle spaces, compared to PEI-7.7 ratio blend.

In order to confirm the presence of amines on the interparticle spaces, the TEM images of component-0 has also been analysed (Fig. S.4 in the Supplementary information). In that case it was seen that films were homogenous and there was not presence of any honeycomb structure as the one seen in Fig. 8. Therefore, this image supported the presence of amines moieties in the interparticle spaces of Blend film and moreover the formation of this honeycomb structure due to the crosslinking reaction of between C-1 and C-2 particles, which could hinder the interdiffusion of polymer chains between adjacent particles.

3.3. Mechanical properties

The effect of crosslinking and interdiffusion has also been studied by measuring the mechanical strength of films annealed 3 days at RT or with an extra annealing at 60 °C for another day. Fig. 10 presents the mechanical properties of a non-crosslinked film (C-0), of the Blend containing 0.2 amine to AAEMA ratio in C-2 and of the Blend containing

7.7 ratio.

For the non-crosslinked C-0 film, the mechanical properties did not significantly vary when the film was annealed at RT or at 60 °C. Fig. 7 showed that the interdiffusion was just slightly further increased when annealing the non-crosslinked film at 60 °C, which could be the reason for the slightly higher elongation (from 6 to 7 %) at break for the annealed film. However, annealing at 60 °C had a significant effect on the films including the crosslinking PEI moiety attached to C-2. The Young's modulus of the films increased significantly (modulus increased from 54 (±5) MPa to 206 (±10) MPa) when annealing the films at 60 °C. As shown previously by FTIR and rheological measurements, full crosslinking was only achieved after annealing the films at 60 °C for 24 h, which would be the reason for the increase of the Young's modulus and decrease of the elongation at break of the films annealed at those conditions. Furthermore, a significant effect of the amount of PEI used to produce C-2 can also be detected. 0.2 ratio of amine/AAEMA produces some crosslinking points between polymer particles, producing stronger films (modulus increased from 11 (±3) MPa to 32 (±5) MPa) than non-crosslinked C-0 film, but 7.7 ratio increases even more the strength of the films. Therefore, the higher interdiffusion between particles produced in 0.2 PEI film cannot compensate the higher crosslinking degree of 7.7 PEI film.

If we compare these mechanical properties with the ones obtained with HDMA instead of with PEI, it can be seen that the mechanical properties have been greatly improved by the PEI containing multiple amine groups, and therefore favouring a more 3D crosslinking network (Fig. S.5 in Supplementary information).

Therefore, taking into consideration the crosslinking and the interdiffusion studies carried out, it seems that the crosslinking reaction is occurring on the shell and it is occurring before interdiffusion of the polymer chains between particles to produce a strong film (Fig. 11).

4. Conclusions

Interparticle crosslinking has been used in this study to produce strong coatings out of waterborne latexes. Latex particles functionalized with acetoacetoxy moieties have been blended with latex particles functionalized by the amine moieties provided by polyethyleneimine. Therefore, the reacting species were linked to different particles and not solubilized in the aqueous phase. It has been proved by FTIR and rheological measurements that once the two-pot-one-pack latex is cast, crosslinking reactions between amine and acetoacetoxy moieties start to occur at room temperature, but they evolve very slowly at this temperature, needing one month to get full crosslinking. However, annealing at 60 °C speeds up the crosslinking reactions, being completed

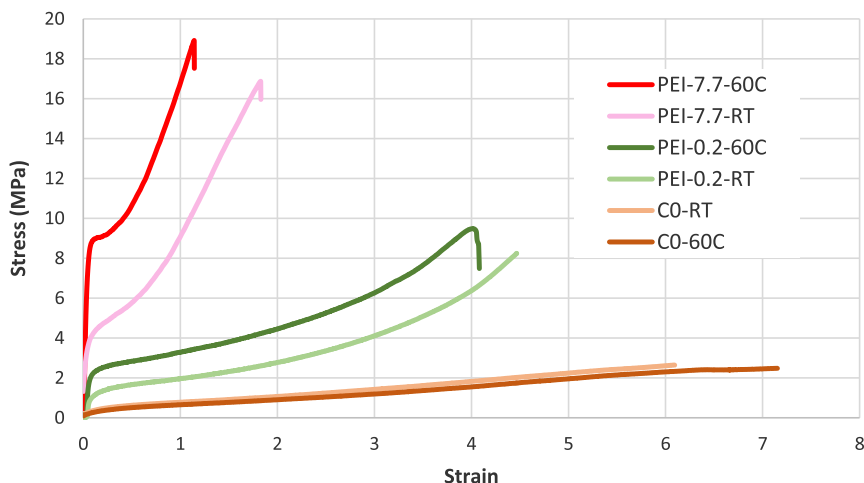


Fig. 10. Comparison of tensile test for Blend films prepared at room temperature and 60 °C.

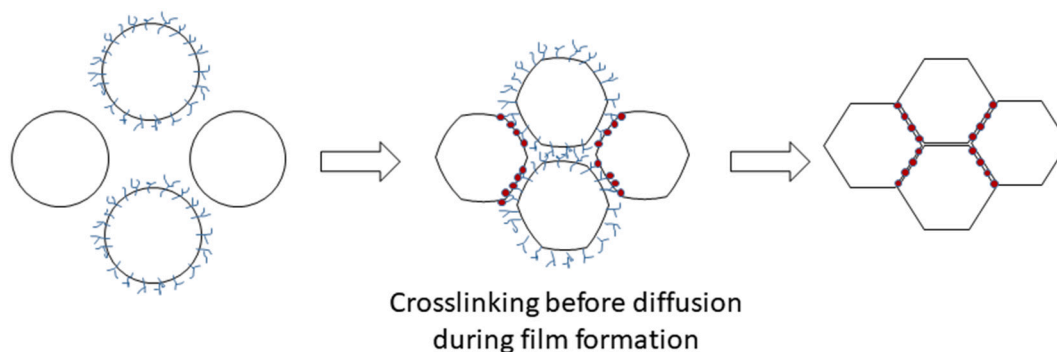


Fig. 11. Film formation route for polymers presenting interparticle crosslinking reactions.

after 24 h. On the other hand, PEF experiments have shown that the interdiffusion between particles is negligible when crosslinking between particles occur at high amine concentration on the surface of the particles. Nevertheless, the lack of interdiffusion did not prevent from obtaining strong films for the highest crosslinked Blend film. In fact, the crosslinked Blend in which more interdiffusion was obtained at the expense of reducing the crosslinking density, by including a lower amount of amine moieties in component-2, did not present so high mechanical properties.

CRediT authorship contribution statement

Sheraz Tariq: Investigation, Formal analysis, Writing – original draft. **Lourdes Irusta:** Writing – review & editing, Data curation, Formal analysis. **Mercedes Fernández:** Writing – review & editing. **Maria Paulis:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2022.107292>.

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