



# Influence of physical–chemical interactions on the thermal stability and surface properties of poly(vinyl chloride)-*b*-poly(hydroxypropyl acrylate)-*b*-poly(vinyl chloride) block copolymers

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## ARTICLE INFO

### Article history:

Received 14 August 2009

Received in revised form 17 September 2009

Accepted 30 September 2009

Available online 7 October 2009

### Keywords:

Poly(vinyl chloride)

Living radical polymerisation

Block copolymers

Thermal degradation kinetics

Inverse gas chromatography

Interaction parameters

## ABSTRACT

The synthesis of poly(vinyl chloride) (PVC) homopolymers and poly(vinyl chloride)-*b*-poly(hydroxypropyl acrylate)-*b*-poly(vinyl chloride) (PVC-*b*-PHPA-*b*-PVC) block copolymers via a single electron - degenerative transfer mediated living radical polymerisation was carried out on a pilot scale in industrial facilities. The thermal stability of the products was assessed conductimetrically. The block copolymers, that contained a low content of PHPA (below 12 wt.%), showed thermal stability that was approximately three times greater than that of conventional PVC. Inverse gas chromatography study of the copolymers surface showed that there was a decrease in the dispersive component and greater Lewis acidity and basicity constants were observed relative to those of PVC. The thermal stabilisation of PVC when in the presence of PHPA is explained by the interactions between its functional groups and the structures formed during the thermal degradation. The thermal stability and the surface properties of PVC-*b*-PHPA-*b*-PVC were strongly dependent on the molecular weight of the block copolymer. Lewis acid–base interaction parameters were determined and are interpreted as evidence of the PVC-*b*-PHPA-*b*-PVC compatibilising function in PVC-wood flour composites.

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## 1. Introduction

Some PVC copolymers are long-established commercial products. The oldest is the vinyl chloride/vinyl acetate (VC/VAc) random copolymer. However, grafted copolymers, such as with ethylene/vinyl acetate (EVA), are also of commercial interest [1]. The chief properties that result from the presence of a significant proportion of a co-monomer in the vinyl chloride polymer chain are normally similar, but more permanent, to those of additives. The properties of these products include improvements to the weatherability, impact resistance, viscosity control, thermal stability and adhesion to non-plastic surfaces [2].

The discovery of living radical polymerisation (LRP) techniques opened the way for the preparation of well-defined block copolymers by controlling the radical polymerisation reaction [3]. Since more than 80% of PVC is produced by suspension polymerisation, the synthesis of PVC-based copolymers, through LRP in an aqueous environment, is of great interest [4]. Single electron transfer/degenerative chain transfer mediated LRP (SET-DTLRP) [5–8] developed methods have been used in the synthesis of  $\alpha$ - $\omega$ -di(iodo)PVC and  $\alpha$ - $\omega$ -di(iodo)polyacrylates that can be used either for the subsequent functionalisation of their chain ends or as macroinitiators for the synthesis of ABA block copolymers [9,10].

The ability to synthesise PVC block copolymers that contain acrylates, using SET-DTLRP methods, is extremely important. It provides a basis, for the preparation of materials with different morphologies that can be adapted to

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different chemical environments, and with different mechanical properties. A conventional experimental can be used as can an environmental friendly reaction medium. These points make the process attractive from the industrial standpoint [11]. The SET-DTLRP technique has been used to synthesise poly(vinyl chloride)-*b*-poly(hydroxypropyl acrylate)-*b*-poly(vinyl chloride) (PVC-*b*-PHPA-*b*-PVC) on a pilot scale, using common industrial facilities [12].

PHPA has been used as a co-monomer in the hydrophobic/hydrophilic control of copolymeric systems [13,14] and in the creation of hydrogel systems [15]. Hydroxypropyl acrylate (HPA)-related monomers have been used in the synthesis of amphiphilic block copolymers via other LRP methods [16,17]. The inferior mechanical performance of PVC and wood flour composites [18] can be improved by adding small amounts of PVC-*b*-PHPA-*b*-PVC to the composite formulations [12]. PVC-*b*-PHPA-*b*-PVC enables coupling between hydrophobic PVC and hydrophilic wood flour surfaces, due to creation of strong intermolecular forces.

The thermal degradation of PVC involves the sequential loss of hydrogen chloride molecules, accompanied by the generation of conjugated polyene sequences [19,20]. Studies in blends of PVC with a range of poly(methyl methacrylate)s (PMMA)s have shown a dependency of the PVC thermal stability on the methacrylate chemical structure [21]. Studies in PVC/EVA blends have related the availability of acetate groups to the capture of protons released during the dehydrochlorination, preventing the auto-catalytic effect [22].

Inverse gas chromatography (IGC) is a method that can be used to examine the surface characteristics of solids [23]. IGC has been of great interest to the evaluation of interaction parameters for the different components in PVC formulations [24,25] and the surface energy and Lewis acid–base behaviour of PVC-based materials [26–28]. The tensile strength of cellulosic fibre composites that contained PVC has been correlated with the acid–base parameters, determined by IGC, of each main component of the composite [29].

The addition of low contents (3.5 wt.%) of PVC-*b*-PHPA-*b*-PVC, rich in PHPA ( $\approx 90$  wt.%), can enhance the performance properties of PVC and wood flour composites [12]. This work concerns a study of the influence of low contents of PHPA, in the block copolymer, on the thermal stability of the copolymers and on its surface properties. PVC-*b*-PHPA-*b*-PVC copolymers, rich in PVC, are attractive for use in traditional PVC manufacturing and processing technology, especially when the PHPA content is low and yet sufficient to create the desired physical properties.

## 2. Experimental

### 2.1. Materials

Different PVC suspension polymerisation grades were provided by Cires, S.A. (Estarreja, Portugal). These samples are identified as *S* (meaning suspension) followed by the degree of polymerisation: 700, 950, or 1200. Pine wood

flour, Fibreton<sup>®</sup>40, was supplied by WTL International (Bosley, United Kingdom).

Hydroxypropyl acrylate (mixture of isomers, 95%), sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) (85%), sodium bicarbonate ( $\text{NaHCO}_3$ ) (99+%), and iodoform ( $\text{CHI}_3$ ) (99%) were purchased from Sigma–Aldrich and used as received. Hydroxypropyl methylcellulose (MF50) (1.86 wt.% aqueous solution) and the partially hydrolysed poly(vinyl alcohol) (PVA) (3 wt.% aqueous solution) were provided by Cires, S.A., Portugal. Vinyl chloride (VC) was purchased from ShinEtsu, Japan.

### 2.2. Synthesis of PVC-*b*-PHPA-*b*-PVC

The block copolymer was prepared in a two steps reaction. The first step was the synthesis of PHPA. The reactor was charged with the compounds in the respective amounts that are presented in Table 1. For each batch, the recipe was adjusted to the desired degree of polymerisation of PHPA (DP1). The recipe presented in Table 1 is designed to give synthesis of a macroinitiator with degree of polymerisation (DP) of 23, considering that the HPA conversion is 90% [30], in a copolymer containing 6.7 wt.% of PHPA. The volume of HPA that was charged into the reactor depended also on the fraction of PHPA that was required in the final copolymer, since a second charge was to be added, i.e. the amount depended on the volume with which the reactor was charged at the second stage. The reaction was undertaken in a inert atmosphere, nitrogen (5 bar), over 6 h, at 25 °C, with an agitation speed of 375 rpm.

Then, an aliquot sample was taken. The reactor was opened and charged with the recipe presented in Table 1 (PVC-*b*-PHPA-*b*-PVC stage). The theoretical design, given as an example above, is met when the added DP of VC is 672 (DP2). VC was charged after the other compounds and a vacuum was achieved inside the reactor. The reaction was undertaken over 20 h, at 42 °C, and with an agitation speed of 750 rpm.

This last stage made it possible for the completion of the synthesis of the copolymer PVC-*b*-PHPA-*b*-PVC to be realised. The product was left settling for two days. The water was removed and the product dried in an oven at 70 °C for 48 h. Then the product was rinsed with distilled water, until the washing water had shown no variation in its conductivity. Note that, reaction residues (catalyst and buffer) are ionic. Thus, their presence in the washing water can be detected by conductimetry.

### 2.3. Standard characterisation of synthesised materials

#### 2.3.1. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra were obtained with a Spectrum-One FT-IR Spectrometer (Perkin-Elmer) using an attenuated reflectance accessory, containing a diamond crystal. The products were analysed as prepared and the number of scans was 100.

#### 2.3.2. *K*-value determination

Samples of  $0.500 \pm 0.0005$  g of the product were weighed and added to 100 mL volumetric flasks. The flasks were filled with 80 mL of cyclohexanone and carefully stir-

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