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Deviation from the Theoretical Predictions in the Synthesis of Amphiphilic Block Copolymers in a Wide Range of Compositions Based on Poly(vinyl chloride) by Single Electron Transfer: Degenerative Chain Living Radical Polymerization in Suspension Medium

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ABSTRACT: This work deals with the synthesis of different poly(vinyl chloride) (PVC) based block copolymers, containing poly(hydroxypropyl acrylate) segments having different compositions and molecular weights. These copolymers were synthesized via single electron transfer-degenerative chain living radical polymerization. The block copolymers prepared showed deviations from the theoretical predictions in terms of molecular weight and polydispersity, which were ascribed to the heterogeneous nature of the reaction mixture. The technical problems addressed are important to the establishment of the required technological improvements for the industrial implementation. It has been shown that the control over the composition of the block copolymers is only achieved when the amount of vinyl chloride used in the second step of the polymerization was relatively high. The adhesion performance of these block copolymers in PVC-wood flour composite formulations was studied by assessing the mechanical performance of such composites, when the copolymers were included in the composite formulations. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: poly(vinyl chloride); living polymerization; adhesion; block copolymers; composites

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INTRODUCTION

Controlled/living radical polymerization (CLRP) has received a remarkable interest of the scientific and industrial community due to the possibility of preparing tailor made polymers using a radical process. Several CLRP methods have been reported in the literature[1] with success involving the synthesis of a vast range of monomers with different functionalities. Regarding vinyl chloride (VC), a nonactivated monomer, the CLRP involves the synthesis of poly(vinyl chloride) (PVC) with no structural defects and the presence of active chain ends. Percec et al. developed, for the first time, a polymerization process able to produce PVC with living features.[2,3] The further discovery of the single electron transfer-degenerative chain living radical polymerization (SET-DTLRP),[4] by the same research group, turned the synthesis of activated[5–7] and nonactivated monomers[4,8] possible, using a method that is feasible to be implemented at industrial scale using the existing facilities.[9,10] The SET-DTLRP has also been used with success to prepare PVC-based block copolymers, namely poly(vinyl chloride)-*b*-poly(butyl acrylate)-*b*-poly(vinyl chloride). By controlling the composition and molecular weight of this block copolymer, it is possible to prepare a material with the same mechanical and thermal properties of the conventional flexible PVC that requires use of extractable and sometimes toxic external plasticizers.[11–13]

Understanding the nature of CLRP mechanisms is a critical step to extend these controlled systems to the aqueous media. This trend is extremely important because, at industrial scale, radical polymerization is widely performed in aqueous dispersion systems for environmental and economic reasons. When compared with solution or bulk polymerizations, aqueous dispersion polymerizations have several advantages such as: the absence of volatile organic compounds, better control of the heat transfer, the

Table I. Designing Formulations Used for the Synthesis of Each One of the PVC-*b*-PHPA-*b*-PVC Block Copolymers

Copolymer	$\overline{M_n}$ (PHPA) (kg/mol)	$\overline{M_n}$ (PVC) (kg/mol)	$\overline{M_n}$ (total) (kg/mol)	PVC (wt %)
PHPA23PVC42	23	42	65	64.6
PHPA06PVC09	6	9	15	60.0
PHPA06PVC42	6	42	48	87.5
PHPA03PVC12	3	12	15	80.0
PHPA03PVC42	3	42	45	93.3

possibility of reaching higher molecular weights with higher conversions, and faster polymerization rates.[14] The final aqueous suspension of stable polymer particles is easy to handle and can be used directly as dried polymer after the water removal using technologies known for decades.

The aqueous dispersed environment, in which CLRP operates, influences the polymerization rate, the molecular weight distribution and the "livingness" of the system.[15] The degenerative chain transfer based methods in heterogeneous conditions have low efficiency compared with the same polymerization in bulk, being the molecular weight obtained higher than the theoretical predictions.[16]

This effect was attributed to the slow diffusion of the iodine chain transfer agent from the monomer droplets to the active particles, during polymerization, due to the hydrophobic character of the droplets. Alternatives have been used, by Lansalot et al.[16] and by Butté et al.,[17] to decrease the need for iodine chain transfer agent diffusion to the polymerization locus. By decreasing the internal viscosity and thus increasing the rate of bimolecular exchange between an active macromolecule and dormant one, good control over the polymerization can be achieved. Good control of the aqueous dispersion medium in living radical polymerizations, with degenerative iodine transfer, plays an important role in the synthesis of block copolymers using this technique.[18] Therefore, it is very important to understand the possible deviation to an ideal CLRP system involving the preparation of block copolymers with commercial interest.

The comonomer used in this work for the preparation of PVC based block copolymers was the hydroxypropyl acrylate (HPA), which has a hydroxyl functionality that increases their hydrophilicity. These materials can find important applications as compatibilizers for adhesion promotion of PVC to materials with high degree of hydrophilicity.[19] For example, it is known that the use of compatibility promoters for PVC and wood flour can significantly improve the mechanical performance of PVC-wood flour composites.[20] Preliminary tests have shown that the incorporation of small amounts of PVC-*b*-PHPA-*b*-PVC as a coupling agent in wood-PVC composites can improve the melt mixing and the mechanical performance in such composites.[21] The influence in the poly(hydroxypropyl acrylate) (PHPA) segments in interaction properties relative to those of PVC has been evaluated by Inverse Gas Chromatography and by thermal stability studies.[22] It is expected that the fine control of the block copolymer properties (composition and molecular weight) will open the possibility of tailoring their performance properties. In this work, different copolymerization parameters were varied to understand the course of the polymerization in suspension medium at pilot scale (6.5 L) with the objective of obtaining block copolymers in a wide range of compositions and molecular weights. The adhesion performance of the block copolymers when included in PVC-wood composites was evaluated through tensile testing.

EXPERIMENTAL

Materials

HPA (mixtures of isomers 95%), sodium dithionite ($Na_2S_2O_4$; 85%), sodium bicarbonate ($NaHCO_3$; 99+%), and iodoform (CHI_3; 99%) were purchased from Sigma-Aldrich and used as received. Hydroxypropyl methylcellulose (MF50; 1.86 wt % aqueous solution) and partially hydrolyzed poly(vinyl acetate) (PVA) (3 wt % aqueous solution) were provided by Cires, S.A., Portugal. VC was purchased from Shin-Etsu, Japan.

A conventional PVC suspension polymerization sample, S950 (M_w = 63,000 g/mol, K_{value} = 66, and d_{50} = 168 μm), was provided by Cires, S.A., Portugal. Acetone (technical grade) and tetrahydrofuran (THF; 99.5+%) were purchased from Fisher. Dimethylformamide (99.8+%) was purchased from Fluka. Bubinga wood flour was donated by Distribuição e Produção de Móveis (Portugal) and ground in a cutting mill, Retsch GmbH SM1, with a 500 μm stainless steel trapezium shaped sieve.

Preparation of α,ω-di(iodo)PHPA Macroinitiator

The preparation of the α,ω-di(iodo)PHPA macroinitiator was carried out by the SET-DTLRP of HPA, catalyzed by $Na_2S_2O_4$, in water.[23] The procedure and input material were adjusted according to the scale at which the reaction was performed.

The homopolymerization conditions described below are those used to prepare a PHPA macroinitiator sample with a theoretical molecular weight of 23 kg/mol (sample PHPA23PVC42 in Table I).

The reaction was carried out in a 6.5 L reactor, in a N_2 (5 bar) inert atmosphere, over 6 h, with an agitation speed of 375 rpm. To obtain the synthesis of a macroinitiator with a degree of polymerization (DP) of 180, considering the acrylate monomer conversion to be 90%,[23] the reactor was charged with 5.32 g of CHI_3 (13.5 mmol) in 1.2 L of water at 25°C. Also, 0.4 L of HPA (2.7 mol), 4.71 g of $Na_2S_2O_4$ (27.0 mmol), 4.54 g of $NaHCO_3$ buffer (54.1 mmol), 31.79 g of a 1.86 wt % aqueous solution of MF50, and 45.99 g of a 3 wt % aqueous solution of PVA were added to the reactor.

Synthesis of the Block Copolymer PVC-*b*-PHPA-*b*-PVC by the SET-DTLRP of VC Initiated by the α,ω-di(iodo)PHPA Macroinitiator

The PVC-*b*-PHPA-*b*-PVC block copolymer was synthesized by SET-DTLRP of VC initiated by the α,ω-di(iodo)PHPA macroinitiator[11] and catalyzed by Na_2S_2O4, in water. The procedure described below was carried out to provide a copolymer with a 30 wt % PHPA content. This theoretical design is obtained when the added DP of VC is 875.

At the end of the PHPA homopolymerization, the reactor was opened and charged with 1.5 L of water, 96.59 g of a 3 wt % aqueous solution of PVA, 66.77 g of MF50, 18.84 g of the catalyst $Na_2S_2O_4$ (0.108 mol), 1.65 g of the $NaHCO_3$ buffer (19.6 mmol), and 0.75 L of VC (11.8 mol). VC was charged after the other compounds and vacuum was done inside the reactor. The reaction was undertaken over 24 h in a 6.5 L reactor, at 42°C, with an agitation speed of 750 rpm. The product was left settling for 2 days. The water was removed and the product was dried in an oven at 70°C for 48 h.

Block copolymers of PVC-*b*-PHPA-*b*-PVC with different theoretical compositions and molecular weights were synthesized according to the procedure described above and adjusted according to the design parameters listed in Table I.

Preparation of PVC Wood Composites

The PVC wood composites were produced using as reference the standard ASTM D4703-03 and their preparation was previously described elsewhere.[22] Composites with Bubinga wood flour loading of 20 wt % and different contents of the PVC-*b*-PHPA-*b*-PVC block copolymer were produced by two-roll milling, followed by press molding, at a processing temperature of 170°C.

Characterization Techniques

Scanning Electron Microscopy. The morphology of the materials was investigated using a JEOL JSM-820 Scanning Electron Microscope (SEM). All of the specimens were coated with gold using a Bio-Rad SC500 diode sputter coating unit. The samples were examined over the magnification range from 20× to 1000× using an accelerating voltage of 5 kV.

Fourier Transform Infrared Spectroscopy. Fourier Transform Infrared spectra (FTIR) were obtained using a Nicolet 750 unit, with a Golden Gate attenuated total reflection (ATR) accessory (Specac). The products were analyzed as prepared. The resolution was 4 cm^{-1} and the number of scans was 64.

Chlorine-Atom-Elemental-Analysis. The determination of the chlorine content was performed by Schöninger flask combustion and titration with mercury nitrate. The sample was combusted in a hermetically sealed Schöninger flask, previously filled with oxygen and allowed to stand for 20 to 30 min. Following this period, the basket was placed in the flask and washed with the minimum amount of water. Bromophenol blue and nitric acid solution were added dropwise until a yellow color was achieved. Then, 0.5 mL of nitric acid, 50 mL of ethanol, and diphenylcarbazone indicator were added. Titration to a purple end point was undertaken with the 0.05*M* Hg(II) nitrate solution. A standard determination was carried out on a standard compound of known percentage of chlorine (*p*-chlorobenzoic acid).

Soxhlet Extraction of Block Copolymers. The block copolymer (6 g) was washed in a Soxhlet extraction apparatus for 6 h. Acetone was used as the extractor solvent. The resulting block copolymer was dried in an oven at 70°C until it reached constant weight.

Gas Chromatography-Mass Spectroscopy. A Shimadzu GC-2010 gas chromatograph, equipped with a Shimadzu GCMSQP2010 gas chromatograph mass spectrometer was employed for the analysis of the final solvent obtained by Soxhlet extraction. The operating conditions were as follows: Zebron capillary GC column 30.0 m × 0.25 mm with a film thickness of 0.25 μm, helium carrier gas 1.22 cm^3/min, injector temperature 200°C, interface temperature 250°C, temperature program: 50°C (1 min), 50–250°C (20°C/min), and 250°C (9 min). The total run time was 20 min. The detector voltage was relative to the tuning result. One microliter of the sample solution was injected into the gas chromatograph. Peak spectra were compared to those in the library that was supplied with the instrument.

Collection of the Soluble Fraction in THF. Between 2 and 3 g of copolymer were stirred in 50 mL of THF during 24 h. The solution was then filtered in a poly(vinylidene fluoride) membrane with a porosity equivalent of 0.22 μm. The filtered solution was left in a fume cupboard until complete evaporation of the solvent. The product obtained was then dried in an oven at 50°C, until constant weight was reached.

Gel Permeation Chromatography. The molecular weight and polydispersity (PD) indexes were determined on a Size Exclusion Chromatograph (SEC) equipped with a LC 1120 HPLC (High Performance Liquid Chromatography) pump (Polymer Laboratories, UK), a MIDAS (type 830) auto sampler (Spark Holland, Netherlands), a differential refractive index detector (Shodex, RI-101), a 5.0 μm bead-size guard column (50 × 7.5 mm), and two PL gel 5.0 μm MIXED-C columns (300 × 7.5 mm) in series (Polymer Laboratories, UK). THF was used as the eluent at a flow rate of 1 mL/min at room temperature and toluene was used as a flow rate marker. The SEC system was calibrated with poly(methyl methacrylate) standards (Polymer Laboratories, UK) with molecular weights ranging from 580 to 7,500,000 g/mol.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA 2050 unit, at a heating rate of 10°C/min, under a nitrogen atmosphere, from 30 to 500°C, with the sample weight being between 4 and 5 mg, accurately known.

Water Absorption Tests. PVC and the block copolymer in powdery form were used as films. These were prepared by casting 0.2 g of the sample in 10 mL of THF. The films were then left in a fume cupboard for 1 week. The films and the samples in a "rubbery" form were accurately weighed and immersed in distilled water at room temperature for 72 h. The samples were carefully dried using soft paper tissue and weighing was undertaken immediately.

RESULTS AND DISCUSSION

The formation of the block copolymers can be investigated on the basis of an evaluation of their morphology (physical structure) and by the determination of their chemical composition. Comparison of the properties of the PHPA macroinitiator with those of the final block copolymer allows one to correlate the influence of the design conditions, for each specific copolymer, with the progress of the copolymerization reaction.

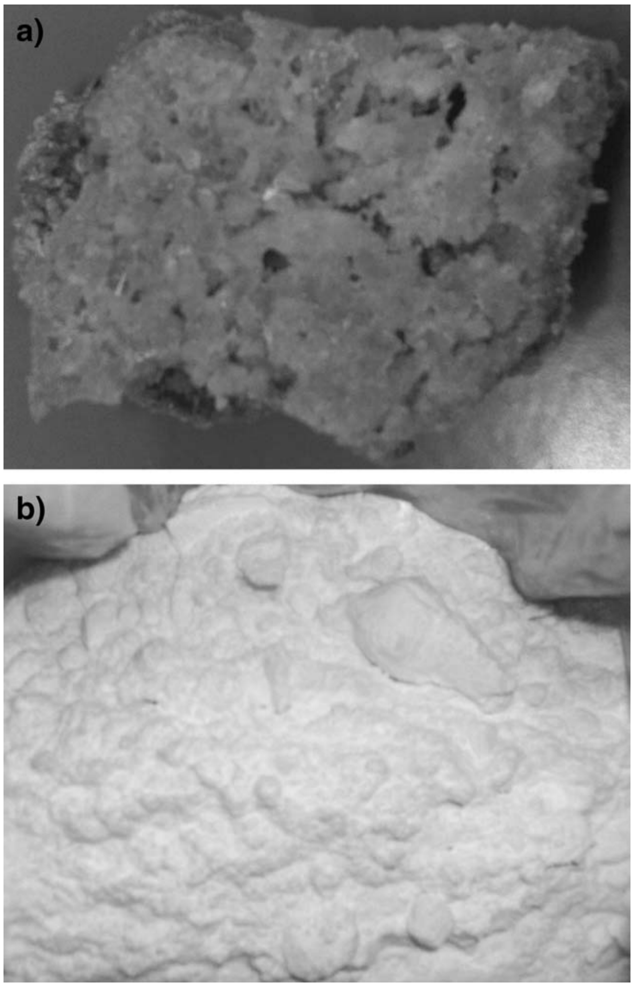

Figure 1. Photographs of block copolymers PHPA23PVC42 (a) and PHPA03PVC42 (b), as produced.

Morphology

All the synthesized block copolymers listed in Table I were found to be in a "rubbery" form [see exemplificative PHPA23PVC42 in Figure 1(a)], the exception being the copolymer identified as PHPA03PVC42 [Figure 1(b)]. This copolymer was obtained in a white powdery form, which is the typical morphology of conventional PVC products. The macroscale images of a rubbery block copolymer and a powdery copolymer are shown in Figure 1.

The differences in morphology suggest that there are significant differences in the composition between the rubbery block copolymers and the powdery block copolymer, with an evident larger homogeneity in the white powdery block copolymer.

Figure 2 shows the SEM micrographs of samples PHPA23PVC42 and PHPA03PVC42. The "rubbery" copolymer PHPA23PVC42 has a morphology that resembles that of PVC suspension grains stuck together because of the "rubbery" nature of PHPA, while the PHPA03PVC42 product has a different appearance. This result suggests that high VC content in the reaction mixture (see Table I) contributes to the disruption of the rubbery structure of the PHPA segments. The small, but still present, connection between certain grains in PHPA03PVC42 in relation to the PVC homopolymer can be attributed to the relatively strong association between the particles, due to the existence of hydrogen bonding within the PHPA segments of the block copolymer.

For the block copolymer with the white powdery form (PHPA03PVC42), the VC conversion is expected to be greater than that obtained for the rubbery products, since more reaction sites would be available after the disruption of the PHPA macroinitiator rubbery structure. As shown in other CLRP systems,[15] alteration of the way in which the different components interact in the aqueous dispersed medium may strongly affect the conversion of the monomer and, thus, the composition and molecular weight of the final product.

Chemical Structure

The variation from the "rubbery" form (PHPA06PVC42) to the powdery form (PHPA03PVC42) suggests that the change in the theoretical weight fraction of PHPA from 12.5 to 6.7 wt % (see Table I) may have led to great differences in the structure of the reaction suspension medium and, thus to the composition of the resulting product. Figure 3 presents the FTIR spectra for the

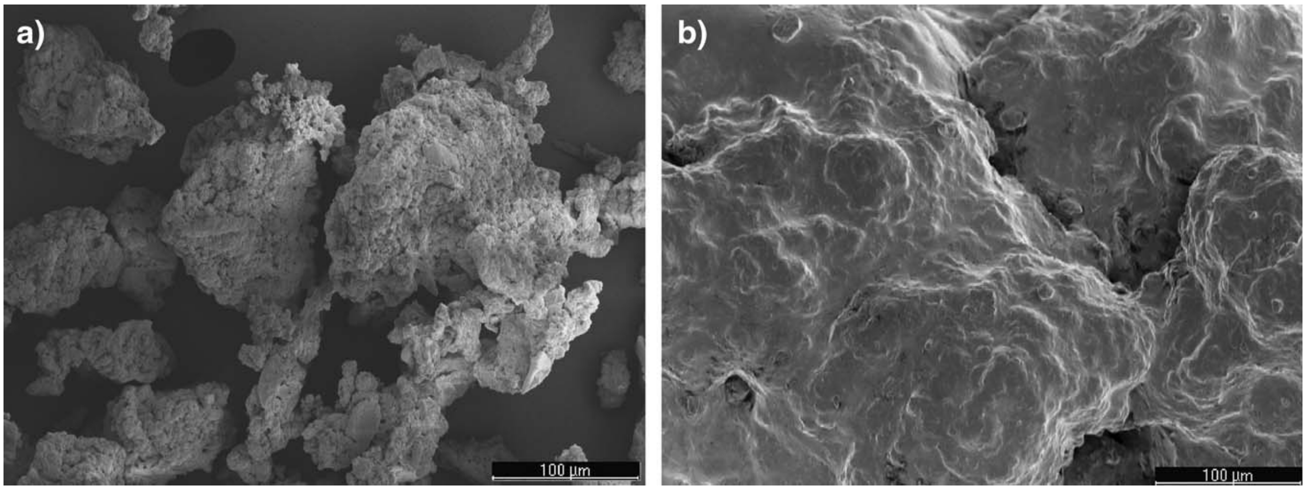

Figure 2. SEM images of block copolymers PHPA23PVC42 (a) and PHPA03PVC42 (b), as produced.

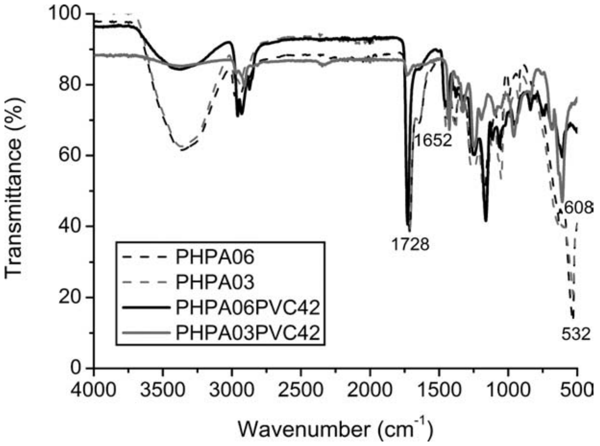

Figure 3. FTIR spectra of products PHPA03PVC42, PHPA06PVC42, and their macroinitiators PHPA03 and PHPA06, respectively.

products PHPA06PVC42 and PHPA03PVC42 and their respective macroinitiators, PHPA06, and PHPA03.

The two macroinitiators, PHPA06, and PHPA03, show very similar FTIR spectra, since both of the macroinitiators correspond to the same product in composition (PHPA homopolymer). The only difference between these macroinitiator samples is their molecular weights. The addition of VC at the second stage of the copolymerization reaction leads to differences in the composition that can be seen on the FTIR spectra of the products. The incorporation of PVC segments, with addition of VC in the second stage of the copolymerization, is shown by the presence of the C—Cl stretching at 608 cm^{-1}.[24] The greater peak obtained for the C—Cl stretching for PHPA03PVC42 suggests a greater content of PVC segments in the PHPA03PVC42 block copolymer than in PHPA06PVC42.

Two other differences that are indicative of the progress of the copolymerization reaction can be highlighted from consideration of the FTIR spectra, presented in Figure 3. The first concerns the disappearance of the C=C stretching peak at 1652 cm^{-1},[25] which shows that any unreacted HPA monomer possibly present at the end of the first stage of the PVC-*b*-PHPA-*b*-PVC copolymerization would react during the second copolymerization stage. Polymerization studies concerning methacrylate monomers that contain hydroxyl groups[26] have shown that the conversion of this type of monomer decreases if a considerable degree of gelation is present. When VC is added, at the second stage of PVC-*b*-PHPA-*b*-PVC block copolymerization, the tendency toward the disruption of the PHPA gel structure allows some of the "trapped-in PHPA structure" residual HPA monomer to be polymerized at this new stage. Thus, the addition of VC to the copolymerization system decreases the gelation degree of the PHPA macroinitiator and leads to an increase in the HPA conversion. The second difference concerns the disappearance of the C-I vibration peak at 532 cm^{-1},[27] after the second stage of the copolymerization has been completed. This effect can be related to the lower fraction of iodine-active chain ends on the final copolymerization products, when compared to that of the macroinitiator products, due to an increase in the molecular weight. The peak at 1727 cm^{-1}, assigned to the carbonyl (C=O) stretching[28] in the PHPA units, is greatly evidenced in the copolymer PHPA06PVC42. The block copolymer PHPA03PVC42 shows a much smaller peak at the carbonyl stretching frequency and greater evidence of the C—Cl, stretching is given by PHPA03PVC42. These FTIR-ATR results qualitatively[29] suggest that PVC has the major block segment fraction in PHPA03PVC42, whereas PHPA has the major block segment fraction in PHPA06PVC42. The greater content of the PVC segments can be used to explain why the morphology is closer to that of PVC homopolymer for the sample PHPA03PVC42. As expected, the "rubbery" copolymers, whose morphology is closer to that of PHPA homopolymer, are rich in PHPA segments.

The amount of PVC incorporation was estimated assuming that all chlorine atoms (determined by Elemental Analysis) present in the copolymer were from PVC segments. Table II gives the quantity of PVC that was incorporated in the block copolymers, as produced.

These results confirm that the white powdery copolymer (PHPA03PVC42) is the one with a greater content of PVC segments and it is the only one with a PVC incorporation that is close to the theoretical value (shown in Table I). All the other copolymers are richer in PHPA segments and gave a level of PVC incorporation that was lower than the theoretical value.

These results could be derived, on a qualitative basis, from the morphology and FTIR studies. When the block copolymer was obtained in a "rubbery" form, significant differences between the theoretical design and the experimental compositions were found. This can be related to the influence of the physical interactions that are undergone during the copolymerization process. These physical interactions vary depending on the chemical composition of the reaction medium. A greater ratio of VC charge compared to the amount of macroinitiator that is present at the end of the first copolymerization stage) strongly favors the provision of homogeneity in the reaction medium, by breaking the PHPA "rubbery" structure. An increase in the homogeneity of the reaction medium leads to compositions that are closer to the theoretical values.

Table II presents the weight loss values, obtained from TGA analysis undertaken up to 170°C. These results show that there was a weight loss below the copolymer thermal degradation, related to the evaporation of the residual HPA monomer, retained in the final product by hydrogen bonding.[28] Thus, the weight loss up to 170°C can be used in an attempt to estimate the amount of residual HPA that was present in each of the

Table II. PVC Incorporation in the Block Copolymers, as Produced

Block copolymer	PVC (wt %)	Weight loss (wt %) at 170°C
PHPA23PVC42	14.4	7.3
PHPA06PVC09	27.7	5.6
PHPA06PVC42	39.8	4.3
PHPA03PVC12	38.6	13.9
PHPA03PVC42	93.2	0.5

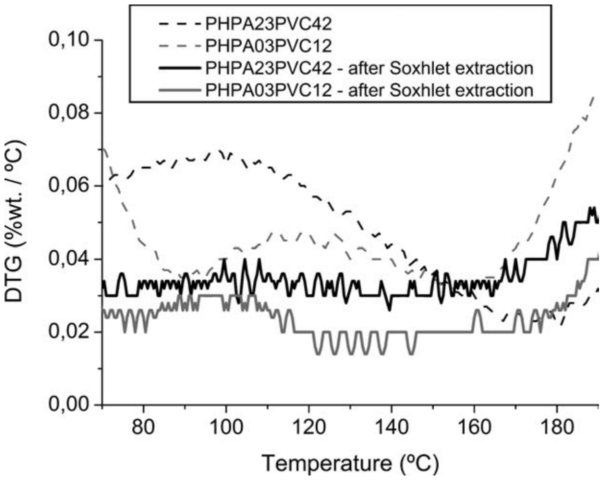

Figure 4. DTG for block copolymers PHPA23PVC42 and PHPA03PVC12, as produced and after being subjected to Soxhlet extraction in acetone.

block copolymers, as produced, excluding possible weight losses that might be due to the initial stages of thermal degradation of PVC and/or PHPA segments.[30] The weight loss percentages suggest that the white powdery block copolymer, PHPA03PVC42, does not contain residual monomer. This was as expected, since the PHPA segments would be present in this copolymer at a very low content and, therefore, the HPA retention by hydrogen bonding would be expected to be minimal. For the efficient exploitation of the "rubbery" block copolymers that were synthesized in this work, the residual HPA monomer needed to be removed. Additionally, the study of the extractable products from the block copolymer structure can provide more information concerning the copolymerization process.

Monomer Removal from the "Rubbery" Block Copolymers

If PVC-*b*-PHPA-*b*-PVC block copolymers are intended to be used as part of PVC formulations to be processed, to achieve specific properties that can not be provided by the PVC homopolymer alone, then the freed of acrylate residual monomer is not only important environmentally,[31] but also from the formulation processing standpoint. The commonly used PVC processing temperatures are in the range of 170–210°C.[32] It is important to guarantee that the present HPA is not evaporating and causing a vapor phase formed at these temperatures.

Acetone-soluble residual monomer and other extractable products were removed by Soxhlet extraction. The extraction process was stopped when the HPA monomer concentration in the extractor solvent reached a consistent level, monitored by the GC-MS technique.

The presence and evaporation of residual HPA monomer in "rubbery" PVC-*b*-PHPA-*b*-PVC can be determined using the TGA. The rate at which the weight loss changes with temperature can be measured by plotting the derivative of the TGA curve (DTG curve). Figure 4 presents the DTG curves for two "rubbery" block copolymer samples, PHPA23PVC42 and PHPA03PVC12, before and after the Soxhlet extraction process.

As expected, after being submitted to the Soxhlet extraction, the rate of weight loss of the block copolymer is strongly reduced and the product stabilized below the temperatures at which PVC thermal degradation occurs,[33] in this case, at a temperature of around 160°C. The temperature of 160°C divides the DTG curves in two sections. Below such temperature, the peaks obtained in the DTG curves are attributed to the evaporation of residual monomer. Above 160°C, the increase in the derivative of the thermogravimetric curve is related to the onset of weight loss due to dehydrochlorination of PVC segments.[34] For this reason, all the DTG curves increase greatly once the onset of weight loss is reached. These results confirm an evidence of a higher degree of purity of the block copolymer, having an improved thermal stability, which makes them commercially more attractive and suitable for use in typical PVC formulations.

Influence of the Reaction Formulation on the Product Composition

The "rubbery" block copolymers, after being cleansed of extractable acetone soluble products, were characterized to establish the influence of the polymerization conditions on the final composition and on the structure of the block copolymers.

Estimation of the extent of PVC incorporation in the cleaned block copolymers, using chlorine-atom-elemental-analysis can give an approximation of the amount of PVC that was incorporated into the block copolymer molecules during the copolymerization reaction. This approach assumes that most of the residues, by-products, and oligomers were removed in the Soxhlet extraction.

Based on the chlorine-atom-elemental-analysis results, the PVC incorporation in the block copolymers was determined. Figure 5 shows how the level of PVC that was incorporated into the copolymer varies with the theoretical content of PVC.

The results show that only when the copolymer is designed to have a very high content of PVC segments, it is possible to incorporate the desired amount of PVC segments in the PVC-*b*-PHPA-*b*-PVC block copolymer. If the copolymer was designed to have PVC content in the block copolymer of 60 wt %, only a very small amount of PVC (below 10 wt %) was actually

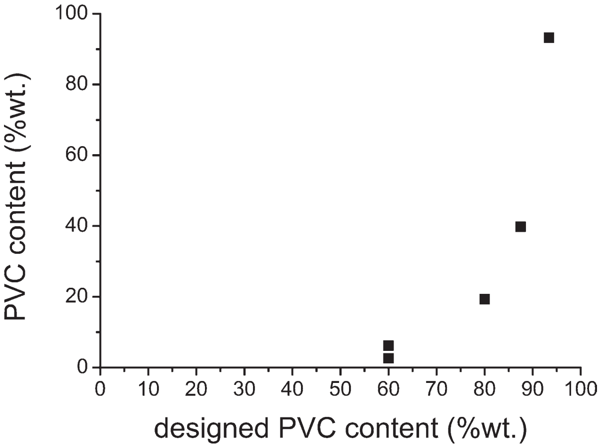

Figure 5. PVC incorporation in the block copolymer as a function of the designed PVC content.

incorporated. Above that theoretical content, the VC conversion grew exponentially with the designed value.

The theoretical calculations of the PVC content are based on the assumption that the system behaves homogeneously, without any restriction on the reaction system of mass and heat transfer, making all the active chain ends accessible with the same probability of reaction. The typical "rubbery" structure of PHPA, due to strong hydrogen bonding interactions,[35] turn the reaction mixture very different from the ideal conditions. In the synthesis of the block copolymers in suspension aqueous medium via CLRP, the comonomer conversion can decrease greatly if the comonomer can not physically interact with the macroinitiator.[36] Furthermore, in CLRP with polyacrylates, the trapping of the intermediates leads to low conversions.[37] The addition of a hydrophobic comonomer, such as VC, favors the disruption of the PHPA gel network. A greater amount of VC, charged into the reactor, can decrease the interaction between the macroinitiator PHPA units.

According to Coelho et al.[11] studies using a poly(*n*-butyl acrylate) (PBA) macroinitiator, the SET-DTLRP copolymerization of VC can be divided in four stages. The first stage is the induction period, which is attributed to the time necessary for the VC droplets to dissolve the macroinitiator. The second stage may occur between 3 and 17% of conversion. This stage is related to the activation of the iodine chain ends, which leads to an increase in the radical concentration and, thus, to a higher rate of copolymerization. In the third period, the suspension phase is formed, and the resulting increase in the viscosity leads to a decreasing rate of copolymerization. At last, in the fourth stage, after 24 h of VC copolymerization with the macroinitiator, the VC conversion reaches a limit.

The description of the kinetic mechanism of VC copolymerization with a polyacrylate macroinitiator, via the SET-DTLRP method, can be related to the VC conversion values that are obtained during the formation of the PVC-*b*-PHPA-*b*-PVC block copolymers. As shown in Figure 5, these values are strongly dependent on the theoretical PVC content for the copolymer. The very low values that are obtained when the copolymer is designed to have a PVC content of 60 wt % indicate that the copolymerization does not leave the induction period for these copolymers. The amount of VC monomer that is charged into the reactor does not seem to be enough to dissolve the macroinitiator. Thus, the reaction proceeds to an extremely small extent. If the amount of VC that is charged into the reactor is then increased to 80 wt %, the VC conversion can slightly increase to around 20 wt %. This change is attributed to a slight increase in the dissolution fraction of the PHPA macroinitiator by the VC droplets. The dissolution of the PHPA macroinitiator increases the probability of reaction with the SET-DTLRP intermediates, increasing the amount of active iodine chain ends and, therefore, the degree of copolymerization with the VC monomer.

The partial activation of the iodine chain ends means that there is no control of the molecular weight of the copolymer at these stages. Two reasons can be put forward for this. First, only a small fraction of iodine chain ends that could be activated is actually activated. Second, as shown by the VC conversion levels obtained, most of the VC droplets may never find an active iodine chain end with which to react with. According to Figure 5, when the copolymer is designed to have a PVC content of 87.5 wt %, (PHPA06PVC42), a great increase in the concentration of active iodine chain ends seems to occur. In addition, their availability for reaction with the VC droplets seems to increase. The value of nearly 50% of VC conversion (incorporation of around 40 wt % instead of 87.5%) means that the copolymerization took place to a significant extent. The "rubbery" form of the copolymer obtained and the final VC conversion show that some restrictions on the mass transfer process were still present during the copolymerization. This explains the low conversion obtained. Finally, at a theoretical PVC content of 93.3 wt %, the amount of PVC that is actually incorporated into the final copolymer is approximately the same as that for which it was designed. At this stage, the amount of VC charged into the reactor, relative to the amount of PHPA macroinitiator that was already present in the reactor, was enough to break totally the PHPA "rubbery" structure. This allowed the creation of a homogeneous suspension phase and the copolymerization to proceed as designed. Coelho et al.[11] have shown that a smaller amount of VC monomer, charged into the reactor, leads to longer induction periods and lower conversions at the end of the copolymerization. In their work, the macroinitiator used was the PBA. When PHPA is used as a macroinitiator, the effect of the amount of VC charged into the reactor becomes even more relevant. This is due to the presence of stronger interactions between the PHPA units (hydrogen bonding) than those existent when the macroinitiator is PBA. The set of results presented shows clearly the importance of the mixture properties in the fate of the CLRP in heterogeneous conditions.

Fractionation of the Block Copolymers

Block copolymers commonly present molecular weight heterogeneity and compositional heterogeneity. Homopolymers or copolymers with different architectures may arise as a result of incomplete coupling during intermediate reaction steps. Fractionation is a powerful tool that is used to separate copolymer fractions according to their molecular weight and/or their chemical composition.[38]

When the amount of VC charged into the reactor is insufficient to satisfy fully the "rubbery" structure, the SET-DTLRP intermediates become more difficult to access. This naturally leads to significant compositional and molecular weight heterogeneities. The macroinitiator molecules that do not have their iodine chains ends activated, during the copolymerization process, remain as PHPA homopolymers. Moreover, the heterogeneous suspension system does not allow the molecules to grow uniformly, leading to gross differences in the molecular weight of the copolymerized molecules.

The PHPA macroinitiator was insoluble in THF, one of the most powerful solvents for PVC.[39] The THF route to fractionation was undertaken on the washed block copolymer samples to avoid interference that occurs with acetone extractable products. Table III presents the fraction, which was solubilized in THF for each of the synthesized block copolymers.

Table III. Soluble Fraction for Each of the Synthesized Block Copolymers

Block copolymer	Soluble fraction (wt%)
PHPA23PVC42	7.0
PHPA06PVC09	8.6
PHPA06PVC42	11.9
PHPA03PVC12	25.5
PHPA03PVC42	75.0

The block copolymers in the "rubbery" form have a very low solubility in THF. This can be related to the fact that these copolymers are rich in PHPA, whose homopolymer is insoluble in THF. A greater insoluble fraction is expected in block copolymers with greater contents in PHPA, since more "rubbery" segments are available to form an insoluble gel structure.[40] The existence of both a soluble fraction and a non-soluble fraction may also be an indication of the compositional heterogeneity that is present in the products obtained. The chemical composition of the solubilized fractions was compared with the original copolymers using the FTIR and the chlorine elemental analysis techniques.

Figure 6 presents the FTIR spectra of samples PHPA06PVC09 and PHPA03PVC42, their soluble fractions and the macroinitiator PHPA06 for comparison. The FTIR spectra presented in Figure 6 show that the composition of the sample PHPA03PVC42, solubilized in THF, is close to the original block copolymer. The hydroxyl peak and the carbonyl peak are still present in the soluble fraction. Since the PHPA homopolymer is not soluble in THF, the solubility of the PHPA units is attributed to its incorporation as block segments of the PVC-*b*-PHPA-*b*-PVC block copolymer. In conventional PVC-based materials, any insoluble fraction of PVC products is commonly attributed to a crosslinked fraction, which can occur chemically due to the presence of specific comonomers.[41] Since PHPA units have strong hydrogen bonding association, it can be expected that the insoluble fraction corresponds to copolymer molecules that are physically crosslinked. Acrylates that are used in block copolymers having thermoplastic elastomer properties, very often have a physically crosslinked state.[42]

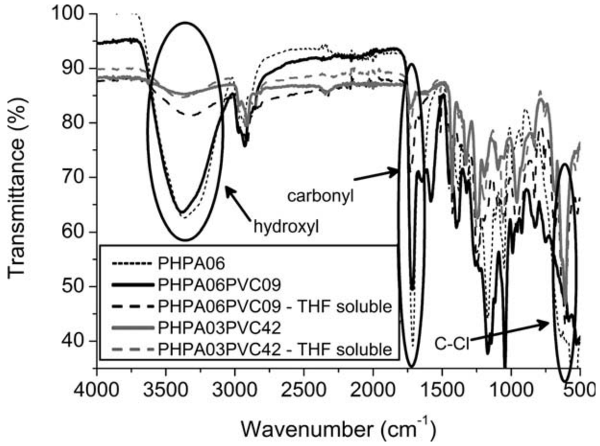

Figure 6. FTIR spectra of samples PHPA06PVC09 and PHPA03PVC42, their soluble fractions and of the macroinitiator PHPA06.

Table IV. Numerical Molecular Weight Obtained by GPC Technique for the Soluble Fraction

Sample	PVC (wt %), theoretical	$\overline{M_n}$ (kg/mol)	PD
PHPA23PVC42	64.6	144.4	1.43
PHPA06PVC09	60.0	166.5	1.62
PHPA06PVC42	87.5	83.4	1.97
PHPA03PVC12	80.0	27.1	2.14
PHPA03PVC42	93.3	43.3	2.18

The presence of hydrogen bonding in the PHPA units enhances this physical crosslinking. Therefore, it is expected that the presence of PHPA segments lead to an insoluble fraction in significant amounts even in the block copolymer richer in PVC. For example, although the block copolymer PHPA03PVC42 has only 6.8 wt % of PHPA segments, the insoluble fraction represents 25 wt % of the block copolymer.

The FTIR spectrum of the soluble fraction of PHPA06PVC09, presented in Figure 6, confirms that PHPA segments can be dissolved when they are part of the PVC-*b*-PHPA-*b*-PVC block copolymer. In fact, if one compares the FTIR spectrum of PHPA06PVC09 with that of PHPA03PVC42 it can be concluded that the composition of the THF-soluble fraction of the "rubbery" block copolymer, PHPA06PVC09, is extremely similar to the composition of the powdery block copolymer PHPA03PVC42. When the rubbery physical structure is present during the copolymerization reaction, the suspension phase is heterogeneous. However, a fraction of the PHPA iodine chain ends that can still be activated can react with the VC monomer droplets in a similar way to that occurring when the suspension phase is completely homogeneous (as occurs in the PHPA03PVC42 copolymerization). Even at a low conversion, block copolymer synthesis in "rubbery" structures can give rise to a product (soluble fraction) with a composition similar to that obtained with a homogeneous suspension phase, as shown in the spectra presented in Figure 6.

From the chlorine-atom-elemental-analysis of sample PHPA03PVC12, the amount of chlorine is 40.3%. Using this value, the PVC segments percentage in the soluble fraction can be estimated as 71 wt %. This value is close to the designed value for this block copolymer (80 wt %), confirming that the reaction of the PHPA macroinitiator molecules, which are actually activated by the SET-DTLRP intermediates, with the VC droplets, may lead to copolymer molecules with compositions that are close to the designed values.

The solubility in THF of a specific fraction of the block copolymers allowed the numerical molecular weight determination of those fractions to be determined by Gel Permeation Chromatography (GPC). Table IV shows the determined number average molecular weight and the PD for the soluble fractions of each of the block copolymers in study.

The molecular weight of those samples that were designed to have a lower PVC content is greater than the expected considering the theoretical predictions. In fact, if only a small number of sites of the macroinitiator were available for reaction with the VC monomer, one would expect that the VC that was charged into the reactor would react at this small number of active iodine chain ends, leading to very high molecular weights. On increasing the amount of VC into the reactor, more iodine chains ends become available to react with the VC monomer. Thus, the increase in the molecular weight (compared to the desired value) is not as great as in the copolymerizations that were designed to yield products with a lower content in PVC. In the reaction design that led to a homogeneous suspension phase, the numerical molecular weight became very close to the designed value, highlighting the control over copolymerization. The lower values obtained for the PD, when the copolymer was designed to have lower PVC content can be explained by a lower variety of molecular growths. This effect may be related to the lower availability and greater similarity of the reaction sites for copolymerization.

A homogeneous suspension phase could only be achieved when the block copolymer was designed to have a very high content of PVC (93.3 wt %). Moreover, only with this reaction-product composition it was possible to obtain a block copolymer, in high purity and with a molecular weight that was close to the design requirements.

Inclusion of PVC-*b*-PHPA-*b*-PVC Block Copolymers in PVC-Wood Flour Composites

The major objective of the synthesis of the PVC-*b*-PHPA-*b*-PVC was to include this block copolymer in PVC-wood flour composites, since such copolymer can enhance the mechanical performance of the composites.[21] The poor mechanical performance of PVC and wood flour composites is usually attributed to the natural incompatibility between the hydrophilic wood flour and the hydrophobic thermoplastic.[43] The use of a PVC-based hydrophilic product would, therefore, improve the interfacial adhesion between the wood flour and the PVC. The new product can act as a physical compatibilizer for both parts. The hydrophilicity of the synthesized block copolymers was assessed by measuring the water absorption and the influence on the mechanical strength, when included in PVC-wood flour composites, from tensile testing experiments.

Hydrophilic polymer networks usually swell to a high degree in water due to their great affinity for water.[44] Hydrogels can be formed by the copolymerization of vinyl monomers that contain hydrophilic side groups, with multifunctional vinyl monomers. By manipulating the chemistry of the hydrophilic segments in the copolymers, hydrogels may be tailored to exhibit specific properties.[45] Acrylate monomers, containing the hydroxyl functionality, have been used in the creation of superabsorbent hydrogel copolymers.[46,47] The addition of PVC to hydrophilic polymers can decrease the water absorption of such polymers. Moreover, PVC is usually combined with hydrophilic polymers to improve their dimensional stability and swelling (which is greatly reduced by the addition of small amounts of PVC) properties.[48]

The water absorption of the synthesized block copolymers, of a macroinitiator sample (PHPA03) and a PVC (commercial sample) reference sample (S950) was determined and the obtained results are presented in Table V.

Table V. Water Absorption of PVC, PHPA, and Different PVC-*b*-PHPA-*b*-PVC Block Copolymers

Sample	PVC (wt %)	Water absorption (wt %)
PHPA06	0.0	110.5 ± 14.5
PHPA23PVC42	14.4	54.3 ± 6.0
PHPA06PVC09	27.7	39.5 ± 6.8
PHPA06PVC42	39.8	90.4 ± 9.2
PHPA03PVC12	38.6	85.9 ± 5.1
PHPA03PVC42	93.2	8.0 ± 1.0
PVC (S950)	100.0	2.8 ± 0.7

The incorporation of the block PVC segments in the chains ends of PHPA, forming an ABA block copolymer, decreases the water absorption capacity, in relation to that of the PHPA homopolymer. This is attributed to a decrease in the hydrophilicity, when the PVC segments are included. As indicated by the results listed in Table V, by increasing the PVC incorporation in the block copolymer, for specific ranges of PVC segments content (for example, from PHPA06PVC09 to PHPA06PVC42), the water absorption increases again. This may be explained by the fact that even in the case of an increasing content of a more hydrophilic comonomer, the water absorption can decrease if a change in the morphology makes it difficult for the penetration of the water molecules to occur through the copolymer structure.[49] When PVC was incorporated in the copolymer structure, there was a decrease in the smoothness of the typical PHPA "rubbery" structure. This is due to the formation of globules (typical of the PVC granule structure) at the surface. Thus, the water absorption decreases when small amounts of PVC are incorporated, due to an increase in the copolymer hydrophobicity. However, for greater PVC incorporation levels, the water absorption may increase again, due to an increase of the globular (and therefore porous) morphology of the copolymer toward powdery morphology (PHPA03PVC42). The greater water absorption of the white powdery form block copolymer (PHPA03PVC42), when compared with that of a PVC reference sample (S950), shows that the presence of 6.7 wt % of PHPA block segments in the PHPA03PVC42 is enough to increase the hydrophilicity, in relation to that of the PVC homopolymer.

Tensile strength data for the composites that were obtained for different contents of PVC-*b*-PHPA-*b*-PVC are presented in Figure 7 as a function of the PHPA segments in the overall composite composition. The loss in the tensile strength, caused by the addition of wood flour to the PVC, can be almost completely recovered when the PVC-*b*-PHPA-*b*-PVC block copolymer is added to the formulation. This improvement is only relevant for specific loadings of the block copolymer (between 2.0 and 2.5 wt %) and is attributed to hydrogen bonding interactions between the PHPA units of the block copolymer and the wood flour. With greater contents of the block copolymer, there is a reduction of the tensile strength of the composites. The strong hydrogen bonding associations between the PHPA units

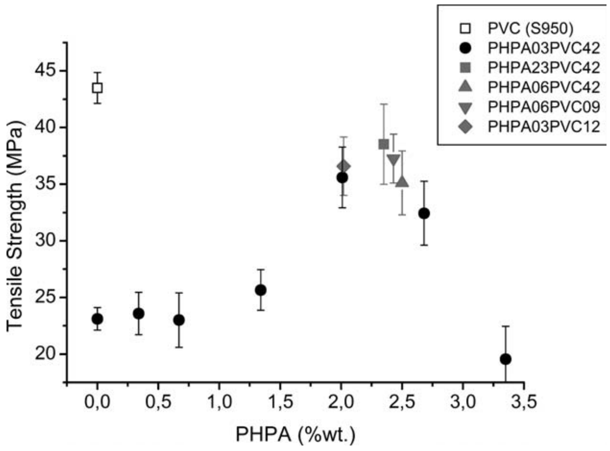

Figure 7. Tensile strength of the composites depending on the PHPA units content in the overall formulations of PVC and Bubinga wood flour composites (20 wt % loading of wood flour).

may increase the degree of incompatibility between the block copolymer and the PVC matrix, leading to a deterioration of the mechanical performance of the composite when greater contents of PVC-*b*-PHPA-*b*-PVC are used.[21] The inclusion of the "rubbery" block copolymers leads to similar increases in the tensile strength of the composites for similar PHPA segments contents in the overall formulation. This shows that the improvement in the tensile strength of PVC-wood flour composites is mainly due to the incorporation of specific loadings of PHPA segments in the formulation.

Since the improvement in the mechanical performance is only dependent on the quantity of the PHPA segments that are available and since that amount is relatively low, the use of PVC-*b*-PHPA-*b*-PVC block copolymers that are rich in PVC is desirable. The great differences in the way that PVC and the PHPA segments physically interact leads to a tendency toward heterogeneity.

The results obtained show that if the white powdery block copolymer that was prepared in this work (rich in PVC) is used in PVC-wood flour composites, then increased compatibility between the PVC and the wood flour can be achieved. The extent of this increase is similar to that obtained with the "rubbery," rich in PHPA, copolymers.

A block copolymer that has a low content of PHPA has the advantage of providing a product with physical properties that are very close to those of PVC homopolymers. The similarity of the properties of the copolymer to the PVC physical properties makes it possible to use the common polymerization, handling, and processing technologies in the manufacturing of products containing this copolymer. The facile easy inclusion of the PHPA segments at the polymerization stage (as obtained in the synthesis of PHPA03PVC42) reduces the heterogeneity problems that are encountered during the processing of products including PVC and PHPA, due to the physical incompatibility of these segments. The presence of the PHPA segments is of great interest for applications in which a PVC-based material, with some degree of hydrophilicity, is required.

CONCLUSIONS

The use of different designer formulations for the synthesis of PVC-*b*-PHPA-*b*-PVC block copolymers allows one to conclude that the final morphology of the copolymer was strongly dependent on the amount of VC monomer that was charged into the reactor for the copolymerization reaction. The increase in the theoretical PVC content from 87.5 to 93.3 wt % was sufficient to change the product from a rubbery to a powdery form. Furthermore, the VC conversion greatly increased with the theoretical content of PVC. The number of PVC segments that became incorporated in the block copolymer increased exponentially with the theoretical content. These values could only be matched in the powdery block copolymer (93.3 wt %).

In the "rubbery" block copolymers, the low availability of reaction sites, during the copolymerization of VC, resulted in a heterogeneous product that combined the residual HPA monomer, by-products, and oligomers, PHPA homopolymer macroinitiator and the PVC-*b*-PHPA-*b*-PVC block copolymer product.

Analysis that were undertaken on the THF-soluble fraction has shown that the molecular weight of such block copolymer fractions was greater, in relation to the theoretical values, for those copolymerization reactions in which lesser reaction sites were available for reaction with the VC monomer. The water absorption of the PVC-*b*-PHPA-*b*-PVC block copolymers increased with increased PHPA segments content (consequence of greater hydrophilicity) and with the greater degree of porosity of the structure. The tensile performance analysis of PVC-wood flour composites, containing different block copolymer designs at different loadings, indicated that changes in the composites' tensile strength were only relevant for specific loadings of the block copolymer. The inclusion of the block copolymer in the composites could give recovery of some of the PVC tensile strength that was lost due to the presence of the wood flour. However, for very high block copolymer contents, the tensile strength became even worse than that of composites that did not contain a coupling agent due to increased mixture heterogeneity.

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