

Behavior of Flexible Poly(vinyl chloride)/Poly(hydroxybutyrate valerate) Blends

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ABSTRACT: Blends of flexible poly(vinyl chloride) (PVC) and a poly(hydroxybutyrate valerate) (PHBV) copolymer were prepared and characterized with different techniques. The tensile strength of PVC did not show a marked reduction at PHBV concentrations up to 50 phr, despite a lack of miscibility between the two polymers. The crystallization of

the PHBV copolymer was markedly hindered by the presence of PVC, as calorimetric results revealed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2102–2107, 2008

Key words: biopolymers; blends; poly(vinyl chloride); (PVC)

INTRODUCTION

Plastics are by far some of the most common materials employed nowadays in almost all fields of human activity. Most commercial plastics are produced in petrochemical plants and derived from oil. Once the service life of the plastics has concluded, they are eventually dumped in landfills, or their energy is recovered in waste incineration plants.

Nowadays, in our society, there is rising concern about carbon dioxide emissions and their likely effects on climate change. In this situation, commercial plastics in waste destined for incineration plants make a direct contribution to carbon dioxide emissions. The substitution of conventional plastics by other biobased and renewable polymers could in part palliate those emissions.

In the literature, the utilization of different renewable polymers has been reported.¹ Two of them are worth mentioning because of their good processability and applicability: poly(lactic acid)s (PLAs) and polyhydroxyalcanoates (PHAs). PLA plastics are obtained through the polymerization of lactic acid produced by the fermentation of biomass, whereas PHAs are directly synthesized with different types of bacteria under certain circumstances. Polyhydroxybutyrate (PHB) and different copolymers with polyhydroxyvalerate [poly(hydroxybutyrate valerate)s

(PHBVs)] can be obtained according to the bacteria and culturing conditions employed. Apart from the renewable aspects of PLA and PHA, both kinds of polymers also present the advantage that certain types of microorganisms present in landfills can successfully degrade them; that is, they are biodegradable.

Unfortunately, nowadays such polymers are more expensive than conventional oil-based plastics. However, the continuous rise of oil prices as well as society's environmental conscience could promote their utilization.

These plastics could be used for certain purposes, but they could also be employed through partial substitution of conventional plastics and blends with them. Thus, Arcana et al.² reported the properties of PHB blends with oxidized polypropylene. Choe et al.³ prepared films by dissolving poly(vinyl chloride) (PVC) and two PHBV copolymers (8 and 18% valerate), Rodrigues et al.⁴ studied the behavior of films containing PHB and poly(ethylene glycol), and Chiu et al.⁵ described the behavior of PHB–poly(vinyl acetate) blends. In all cases, the miscibility of the polymers and its influence on the blend properties are two of the most important factors to bear in mind. In the case of PVC, Choe et al. reported high miscibility and compatibility between PVC and 18% PHBV, in contrast to the 8% copolymer, which showed more limited compatibility.

However, in a large number of applications, PVC formulations also include a plasticizer to impart flexibility to PVC. The aim of this work was the preparation of flexible PVC and PHBV copolymer blends and the study of their morphological, rheological, mechanical, and thermal behavior.

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EXPERIMENTAL

Materials and sample preparation

A commercial PHBV copolymer (12% polyhydroxyvalerate), provided by Goodfellow Corp. (Lille, France), was employed.

The PVC resin Etinox 650 (K (Fickentscher K-value) = 71; Aiscondel S.A.), the plasticizer diisononyl phthalate (BASF Espaniola S.L., Barcelona, Spain), the epoxidized soybean oil Lankroflex E2307 (Akzo Nobel Chemicals S.A., Barcelona, Spain), calcium stearate (Union Derivan S.A., Barcelona, Spain), and the thermal stabilizer Interlite ZP9604 (Akzo Nobel) were employed. The PVC resin, with 60 phr diisononyl phthalate, 5 phr epoxidized soybean oil, 2 phr thermal stabilizer, 1 phr calcium stearate, and different PHBV concentrations, was blended in a high-speed mixer until the PVC absorbed all the plasticizer. After that, dry blends were processed in a Brabender (Halle, Germany) internal mixer at 170°C and then processed at the same temperature in a hot plate press for 10 min under a pressure of 10 atm; 1-mm-thick plastic sheets were obtained.

Methods

Morphological analysis

Samples were introduced into liquid nitrogen and immediately broken. Fractured surfaces were analyzed in a scanning electronic microscope (JSM 840, JEOL, Tokyo, Japan). Images were taken at magnifications of 500× and 5000×.

Mechanical properties

Specimens were prepared as follows: the plastic sheets, obtained by compression molding, were cut to samples with the standard shape for tensile strength tests. The prepared specimens were 1 mm thick with a neck 35 mm long and 4.5 mm wide. The ultimate tensile strength (UTS) and elongation at break were measured in an Instron (Cerdanyola, Barcelona, Spain) 4411 extensometer with an extension rate of 25 mm/min and an initial distance between grips of 22 mm.

Thermal analysis

Samples of around 10 mg were analyzed in a Perkin-Elmer, (USA) Pyris 6 differential scanning calorimeter with the temperature program described later with a nitrogen flow of 20 mL/min.

Rheological analysis

Plastic disks were prepared through the cutting of samples obtained by compression molding. Then, they were placed between the 20-mm-diameter par-

allel plates of an ARES rheometer (TA Instruments, USA). The complex viscosities of the samples were determined with frequency sweep tests at 180°C with an oscillation amplitude low enough to ensure a linear viscoelastic regime (1% of target strain).

RESULTS AND DISCUSSION

Morphological analysis

Figure 1 shows photographs of fractured samples taken in a scanning electron microscope. A fracture with one unique phase was observed for plasticized PVC [Fig. 1(a)] and the sample with 20 phr PHBV [Fig. 1(b)]. However, at higher PHBV concentrations (40 and 50 phr), small droplets approximately 1 μm in diameter were present [Fig. 1(g)], indicating a lack of miscibility between the two polymers; this was similar to conclusions drawn by Choe et al.,³ who reported some immiscibility between a PHBV copolymer (8% valerate) and rigid PVC.

Thermal analysis

On the one hand, flexible PVC is an amorphous polymer, the glass-transition temperature of which is below room temperature; in this case, the glass transition, determined by differential scanning calorimetry (DSC; the temperature program was -80 to 90°C at 10°C/min), is -37.4°C. On the other hand, PHBV is a crystalline polymer, the glass transition of which occurs around 50°C (it can be observed only by the magnification of this temperature range in Fig. 2), and it melts in the range of 130–160°C (Fig. 2). When the molten copolymer is cooled at 5°C/min, its crystallization takes place around 100°C. The calorimetric curve obtained during heating did not present a single pattern but instead presented a double peak; this was similar to results reported by Furukawa et al.⁶ The presence of different polymorphisms of PHBV crystals could justify the presence of two melting peaks.

In any case, calorimetric curves of binary blends of PHBV and PVC in the temperature range of 40–200°C should reflect only the characteristic processes of PHBV (melting or crystallization and glass transition) because plasticized PVC is an amorphous polymer, the glass transition of which is below 0°C. Any modification of the pattern of processes associated with PHBV should be a result of the interactions and miscibility of the two polymers. Because the glass transition of PHBV takes place according to a weak signal in comparison to melting or crystallization, we have focused the study on the latter processes.

As can be observed in Figure 3, to monitor PHBV melting and crystallization, different heating and cooling runs at 10 and 5°C/min, respectively, were performed between 40 and 200°C.

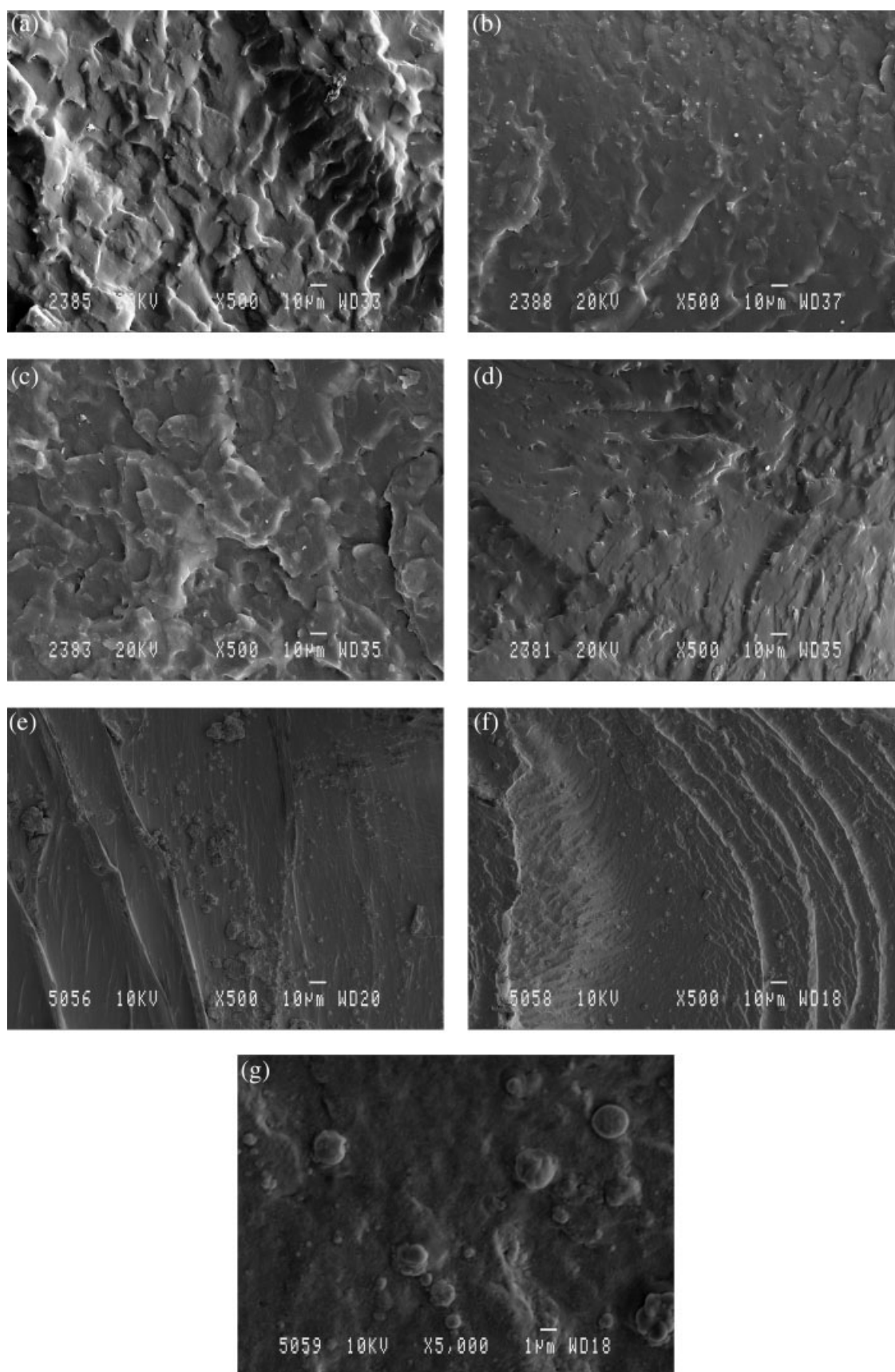


Figure 1 Microphotographs of plasticized PVC with: (a) 0, (b) 5, (c) 10, (d) 20, (e) 40, (f) 50, and (g) 50 phr PHBV (magnified).

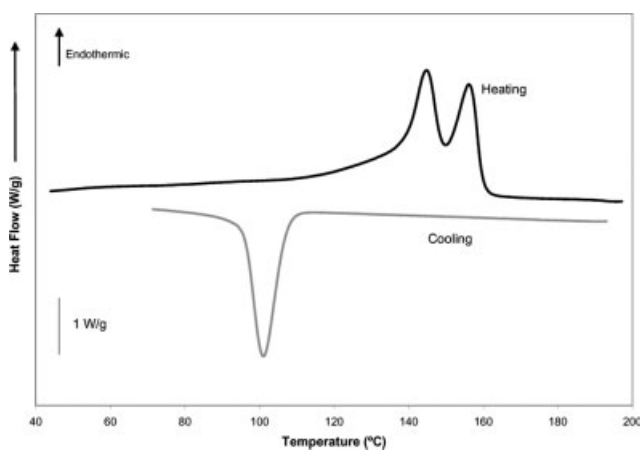


Figure 2 DSC curves for the pure PHBV at a heating rate of 10°C/min and a cooling rate of 5°C/min.

At low concentrations of PHBV, a remarkable process can be observed, probably because in the melt, molecular chains of the two polymers are interacting in a certain way, hindering PHBV crystallization, at the same time that the dilution effect of PHBV in plasticized PVC can make good observation of the melting or crystallization peaks difficult. At 10 phr PHBV, a weak endothermic peak can be observed (ca. 135°C); because of its low intensity, it is not possible to assess whether it is attributable to the presence of PHBV or a baseline modification.

At 20 phr PHBV, a small endothermic peak around 140°C can already be detected and logically attributed to the presence of PHBV, which keeps its identity and has crystallized. Although scanning electron microscopy (SEM) pictures have not revealed the presence of PHBV not incorporated into the PVC phase, DSC has revealed that it exists, although in a low concentration in view of the low intensity of the peak.

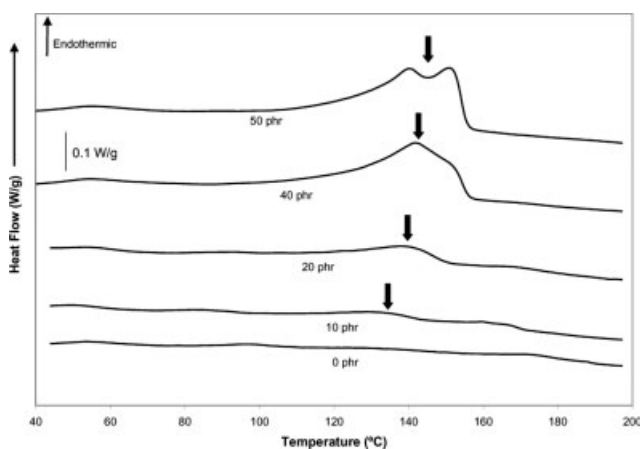


Figure 3 DSC curves for the PVC samples with different PHBV concentrations at a heating rate of 10°C/min.

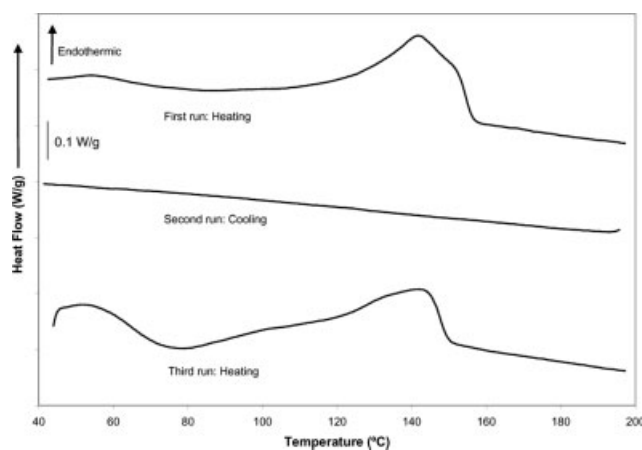


Figure 4 DSC curves for the 40-phr PHBV sample (heating rate = 10°C/min and cooling rate = 5°C/min).

At higher PHBV concentrations (40 and 50 phr), the observed behavior is more marked, and the presence of PHBV is clear, in good agreement with SEM pictures, which have already revealed its presence.

Concerning cooling runs, it is worth mentioning that at 5°C/min, no process due to PHBV crystallization, like that shown in Figure 2 for pure PHBV, can be observed in any formulation; only a straight line, the shape of which is marked only by the baseline, can be observed (as an example, in Fig. 4 the behavior of the 40 phr PHBV formulation is illustrated). However, a new heating step reveals again an endothermic peak attributable to PHBV melting. Nevertheless, a deeper inspection of the data reveals that before the melting peak, an exothermic process seems to occur. This could be due to a molecular rearrangement or cold crystallization, as Hatakeyama and Quinn⁷ described. It is obvious that during the cooling step, PHBV does not have time enough to crystallize. Although the melting and crystallization of pure PHBV were readily monitored by DSC under the employed heating and cooling conditions, the presence of PVC hinders PHBV crystallization. This indicates that although PHBV is segregated, according to the SEM pictures, they present in the molten state a certain degree of miscibility.

To check this possibility, that is, the fact that PHBV cannot crystallize because of very fast quenching, a different temperature program was applied to a 40 phr PHBV sample. It was heated at 10°C/min from 40 to 200°C; then, it was cooled from 200 to 70°C, and an isothermal run was applied.

The obtained results are shown in Figure 5. The melting peak is relatively different from that of Figure 4; the previous thermal history has a marked influence on the amounts and types of crystals that form and, consequently, on the melting process monitored by the DSC curve. On the other hand, it is also possible to observe that the crystallization of

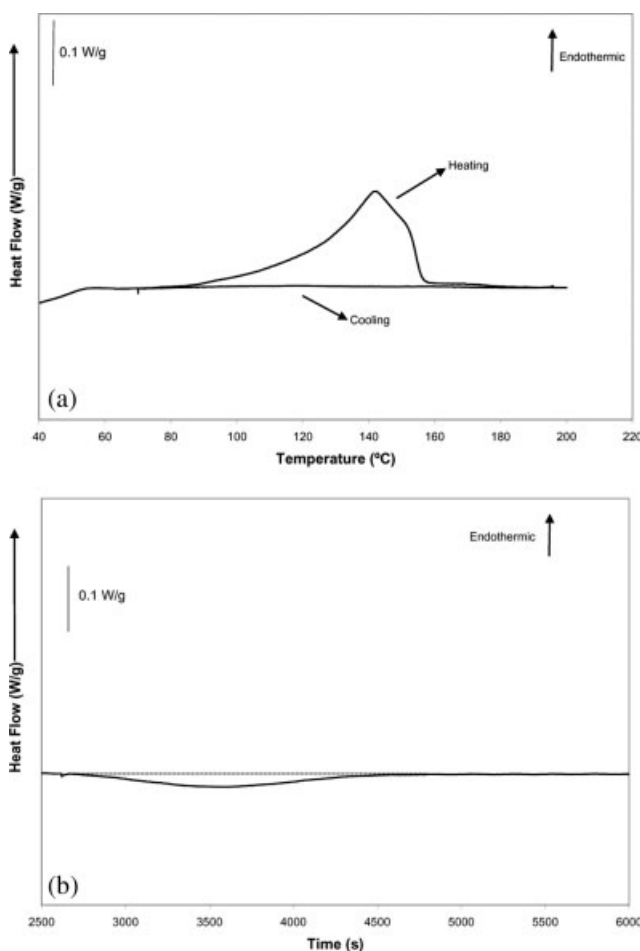


Figure 5 Different DSC runs for the 40-phr PHBV: (a) heating at 10°C/min and cooling at 5°C/min and (b) isothermal at 70°C.

PHBV occurred during the isothermal run at 70°C following a slow process.

All in all, the cooling rate is a relevant factor to keep in mind for these kinds of polymeric blends because their properties, in general terms, can be markedly influenced by the amounts and types of crystals generated, which are at the same time determined by this factor.

Rheological properties

Complex viscosity curves of different samples are presented in Figure 6. The presence of PHBV, the viscosity of which is much lower than that of the PVC formulation, tends to reduce the melt viscosity of the blends. Although this is logical, reasonable, and expectable behavior, it is worth mentioning that the lower viscosity of the PHBV copolymer (probably because this copolymer has a lower average molecular weight) could bring about the opposite effect under other circumstances. For example, clear and marked immiscibility between the same PHBV copolymer and polypropylene provoked an increase⁸

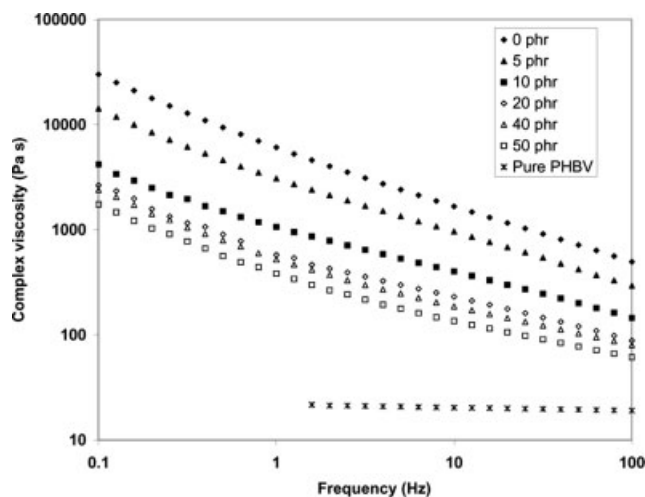


Figure 6 Complex viscosity versus oscillation frequency for different PVC-PHBV formulations.

in the viscosity of polypropylene at low shear rates, as reported in general terms in the literature for immiscible blends.⁹

Then, although the viscosity of the PHBV copolymer is lower, a progressive reduction of the viscosity does not necessarily occur, and very likely this is the reason for the saturating effect contemplated in Figure 7. When PHBV concentrations up to 10 phr are employed, the melt viscosity decreases; PHBV and PVC seem to be highly miscible at this temperature, and the effect of PHBV is similar to the effect that a lubricant could bring about, that is, a reduction of the viscosity. When the PHBV concentration is increased again, a further decrease in viscosity can be expected. However, the viscosity seems to reach a limiting value; this indicates that PHBV is not being incorporated anymore into the melt, or if it is being incorporated to a lesser extent, the increase in the viscosity produced by the presence of a immiscible

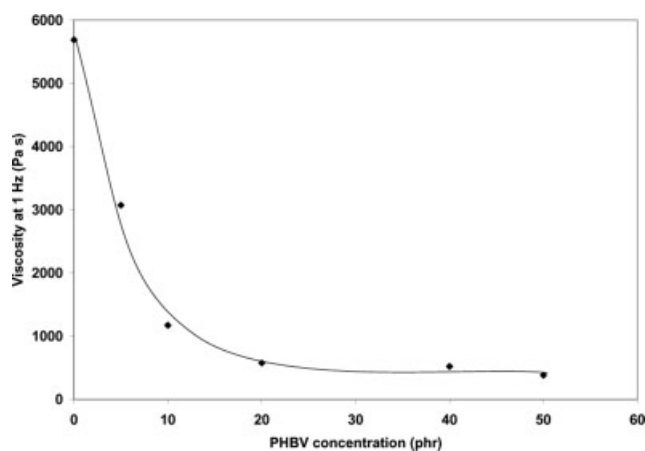


Figure 7 Complex viscosity at 1 Hz for different PHBV concentrations.

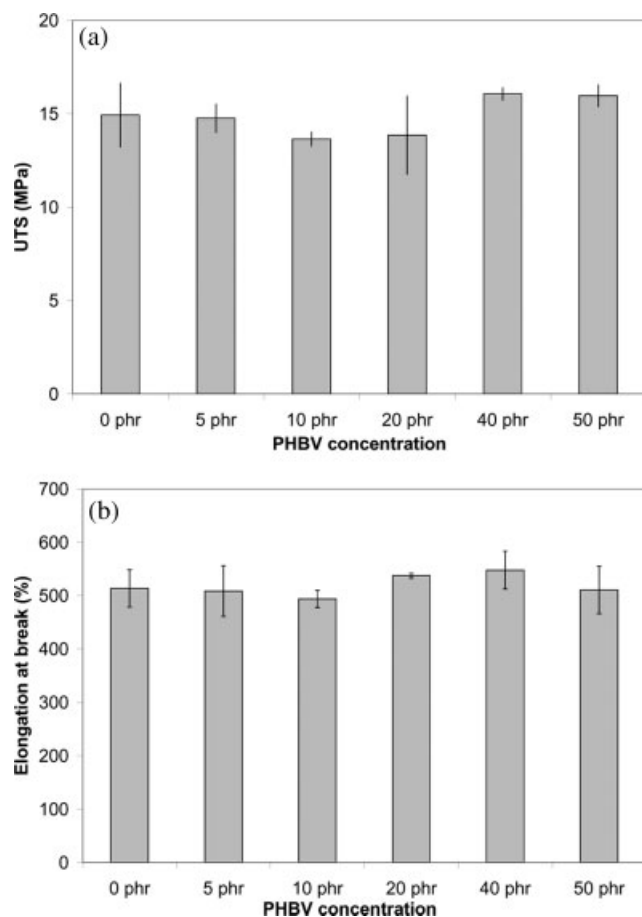


Figure 8 (a) UTS and (b) elongation at break of the PVC samples.

fraction of PHBV compensates for the decrease produced by such incorporation.

Mechanical properties

In Figure 8, it is possible to observe the mechanical properties at room temperature of different blends; under the conditions employed, the determination of the mechanical properties of the pure copolymer was not possible because of the brittleness of the samples obtained. Although in previous sections partial immiscibility between PHBV and PVC was found, such immiscibility apparently does not

involve a clear effect on the tensile strength in view of the UTS and elongation at break results. It is possible to state that even when two phases are evident at 40 and 50 phr PHBV and a decrease in the mechanical properties can be expected, both phases should show good cohesion, so that even in the 50 phr formulation, the UTS and tensile strength are relatively similar to those of pure PVC formulations.

CONCLUSIONS

In this work, the behavior of PVC–PHBV blends has been analyzed with different techniques (microscopy, calorimetry, rheology, and mechanical property measurements). The results have permitted us to conclude that blends with up to 50 phr PHBV are processable and that even when PHBV and PVC are segregated, the tensile strength is similar to that of the pure PVC formulation.

A calorimetric analysis has revealed that PHBV crystallization, when PVC is present, is much slower than pure PHBV crystallization; the blend properties (e.g., mechanical and optical properties) can consequently be affected by the cooling rate experienced by the blend.

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