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Evaluation of Dicumyl Peroxide as a Coupling Agent in Thermoplastic Starch and BioPBS Composites

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DOI: https://doi.org/10.51573/Andes.PPS39.SS.BBB.8

December 2024

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Abstract: To address plastic pollution from fossil fuel polymers, biodegradable alternatives like starch and polybutylene succinate (PBS) are proposed. However, starch is hydrophilic, while PBS and PBSA are hydrophobic. This research investigates the use of dicumyl peroxide (DCP) and tartaric acid (TA) as coupling agents in blends of thermoplastic starch (TPS) and PBS/PBSA, with glycerol as a plasticizer. Different weight/weight compositions of DCP and TA were added to blends in an internal mixer and subsequently compressed molded into films. DCP enhances tensile strength and ductility but increases torque and processing temperature. FTIR analysis show only a physical blend of components and no evidence of chemical interaction. TA reduces torque and tensile strength but increases ductility, with FTIR indicating that TA does not esterify starch but may form new bonds in the PBS carbonyl groups. SEM shows better compatibility in the blends.

Keywords: Thermoplastic Starch, PBS, PBSA, Dicumyl Peroxide, Tartaric Acid, Compatibilization

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Introduction

Several studies have investigated the combination of starch with PBS to obtain a sustainable polymeric material, with comparable mechanical properties and at a low cost [1,2]. However, these two compounds (TPS and PBS) are chemically opposite: starch is a hydrophilic polymer due to the polar groups (hydroxyl and carboxyl), while PBS is a hydrophobic polymer due to the aliphatic units [3]. For that reason, starch and PBS are immiscible and generate blends with low mechanical properties [4].

Therefore, to improve the chemical and mechanical behavior of the starch/PBS blends, different compatibilization mechanisms have been studied. In-situ compatibilization is a mechanism in which the compatibilizing agent is generated during the mixing procedure. Within these strategies, compatibilization with low molecular weight components is favorable due to its low economic and environmental cost [5]. When polymers are blended with peroxides, copolymers could be generated, and cross-linking and branching processes could occur through hydrogen abstraction reactions [5]. Organic peroxides produce free radicals when subjected to an increase in temperature, and in the presence of polymers this could generate a chain reaction: these radicals react with the PBS and starch polymer chains, eliminating a hydrogen atom from each carbon and, thus, generating the union (covalent bond) of monomers between the same or different polymers [6-8].

Furthermore, the use of tartaric acid as a reactive compatibilization agent for blends of starch and biodegradable polymers has been reported. Tartaric acid and other polycarboxylic acids promote esterification and transesterification between starch and PBS, thus increasing their compatibility and mechanical properties [9-11].

In this study, two different approaches were considered regarding TPS/PBS compatibilization: the preparation of a compatibilizer based on (i) DCP and (ii) DCP and TA. To evaluate the effect of the compatibilizers, the incorporation percentages were varied in the blends. In this study, PBS, starch, glycerol, DCP, and TA were processed in an internal mixer and then plastic films were manufactured by compression molding. The processability, morphology, chemical and mechanical properties were studied.

Methodology

Materials

Native cassava starch was obtained from Proyucal. PBS and PBSA were supplied by Mitsubishi Chemical Performance Polymers (MCPP) in references FZ91PM and FD92PM, respectively. Glycerol, 99.5% purity, was obtained from Panreac AppliChem. Dicumyl peroxide with 98% purity was supplied by Alfaesar and 98% tartaric acid was supplied by PanReac AppliChem.

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Experiment Design

DCP Compatibilizer:

Two different factors were considered: type of PBS and relationship between TPS and type of PBS. The levels were: PBS and PBSA, and 60/40, 70/30, 80/20 and 90/10, respectively. The incorporation percentage of DCP was maintained at a constant value of 2% wt respect to the total blend. This value was proposed considering previous work found in literature.

DCP and TA Compatibilizer:

Three different factors were considered: (i) type of PBS, (ii) incorporation of DCP, and (iii) incorporation of TA. The levels correspond to: (i) PBS and PBSA, (ii) 0.5%, 1.0% and 2.0%, and (iii) 1.0%, 2.0% and 5.0%, respectively. The percentage of incorporation of DCP and TA was wt respect to the total blend.

Film Production:

Starch and BioPBS were dried at 80°C for 5 hours to remove moisture. The mixtures were blended using an internal mixer (CW Brabender 2553 or Brabender PLE 331) at 150°C and 60 rpm for 10 min. The proportion of glycerol used was always 30% wt respect to starch. The test films were compression molded in a Scientific LABTECH Engineering model LP-S-80 press (150°C, preheating of 5 minutes, 5 vents each one 5 seconds, pressure of 15 bars for 1 minute and, finally, pressure of 110 bars for 1 minute).

Characterization

Processability:

This consisted of obtaining torque and temperature data over time during the raw materials blend process. None of the formulations were duplicated. However, consistency was considered based on the evolution of the responses according to the change in composition.

Chemical characterization:

The raw materials and the films obtained were analyzed by Fourier Transform Infrared Spectroscopy (FTIR). For this, a Thermo Scientific Nicolet™ 380 spectrophotometer with an attenuated total reflectance (ATR) accessory and a germanium crystal were used. The spectral range analyzed was 400 to 4000 cm-1 with 32 scans. This test was not replicated.

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Morphology:

A morphology study was carried out on the sampled films obtained through surfaces fractures by Scanning Electron Microscopy (SEM). For this, the films were subjected to cryogenic fracture with liquid nitrogen. Subsequently, the fractured fragments were coated with gold to obtain a conductive material compatible with the instrument. The samples were placed transversely on the LYRA3 TESCAN equipment at 10 kV with magnifications of ×800 and ×3000. No replications of this test were performed.

Mechanical properties:

The films obtained were die cut in modified type V specimens, in accordance with the ASTM D638 standard [12]. These were subjected to tension tests using an INSTRON 3367 universal testing machine following the ASTM D882 standard [12]. The separation between jaws was 25mm and the test speed was established at 12.5mm/min. The thickness of the specimens was measured using a model 549MM micrometer with a resolution of 0.0025mm. For each blend, 6 to 8 replicas were considered.

Results

The thickness of films manufactured by molding compression varied for both compatibilizers evaluated. The average thickness was 0.242mm ± 0.038 mm.

DCP Compatibilizer

Processability Analysis:

All blends present steady state torques between the reference values of the raw materials (6Nm (PBS) or 5Nm (PBSA) and 33Nm (TPS)). For all cases, the addition of DCP generates an increase in torque, related to the increase in the molar mass and viscosity of the blends. This could indicate the copolymers or cross-linkers formation [13].

Similarly, the processing temperatures of the blends fall within the average values of the raw materials. The inclusion of DCP to the formulation results in higher processing temperatures, suggesting a potential reaction between the blend components.

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Fourier Transform Infrared Spectroscopy (FTIR) Analysis:

Considering the hydrogen abstraction mechanism, changes were expected in the signal related to the stretching of the hydrogen atoms in PBS (2880 cm^{-1}) and in the band associated with the OH groups of starch (3000 -3700 cm^{-1}) [14]. The spectra of the TPS/BioPBS blends are a combination of the spectra of the raw materials (TPS and PBS or PBSA). However, despite the addition of DCP, there were no discernible changes in the spectra compared to the control blends. This suggests that there may have been no chemical reaction as proposed in the previous section.

Scanning Electron Microscopy (SEM) Analysis:

The fracture surface images for the samples at x800 magnification are presented in Figure 1. In the case of TPS (a), central voids are observed on a smooth surface, which correspond to the fracture of starch granules with water content [15]. In the case of PBS (b) and PBSA (c), there is a completely smooth matrix in which only the propagation lines are observed.

The morphologies of both the control formulations and those including DCP were observed. In all formulations (d-g), distinct cavities and edges are visible. Upon comparing formulations without DCP to those with DCP, it becomes apparent that there is no improvement in the compatibility of the mixtures, as starch granules and clear phase differentiation remain evident. This indicates that the blends still have compatibility issues.

Mechanical Properties:

For Figure 2(a), it is shown that as the incorporation of TPS increases, the tensile strength of the films simultaneously decreases.

For the blends with PBS, the inclusion of DCP either maintains or increases the tensile strength. These enhancements range from 36.60% to 47.03% for the 80/20 formulation. However, for the blends with PBSA, the effect of DCP is less clear. In instances where there is an increase in this property, it ranges between 99.54% and 132.96% for the 70/30 blend.

On the other hand, regarding ductility (Figure 2[b]), an expected decrease in elongation was observed with increasing incorporation of BioPBS. This is because the inclusion of BioPBS, while improving tensile strength, typically reduces the material's ductile behavior. The effect of adding DCP to the PBS mixtures is less clear. Increases were observed for the 70/30 (40.38%) and 80/20 (495.22%) mixtures. However, in the case of PBSA, DCP generates higher elongation until fracture in the films, ranging from 25.87% to 238.20%.

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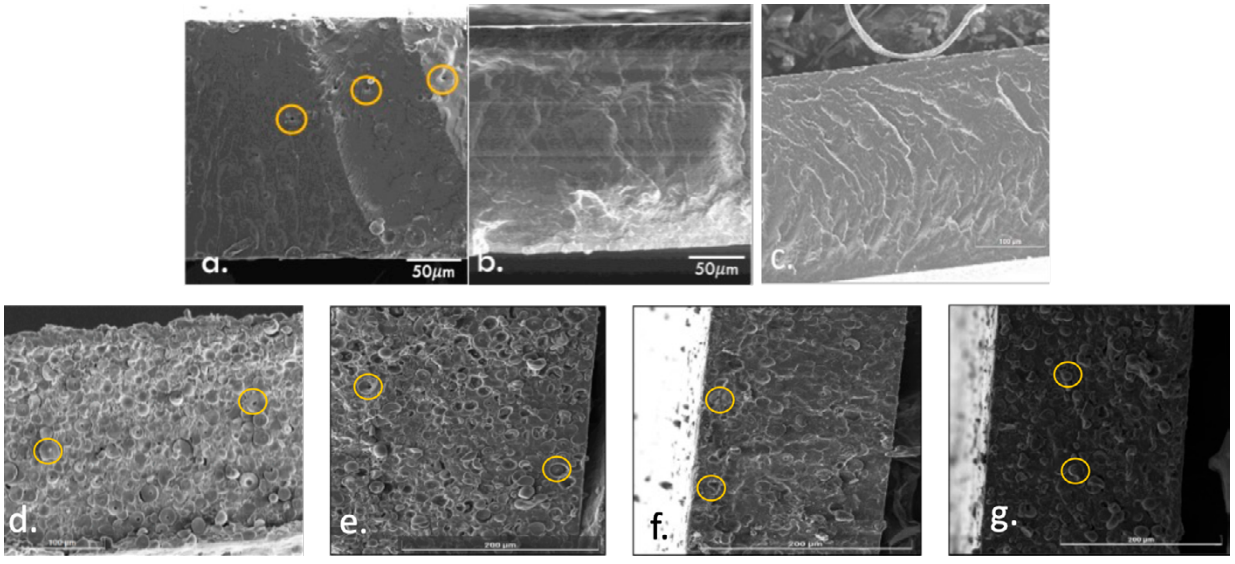

Figure 1. SEM images in x800. (a) TPS, (b) PBS, (c) PBSA, (d) 60TPS40PBS, (e) 60TPS40PBS DCP, (f) 60TPS40PBSA, (g) 60TPS40PBSA DCP.

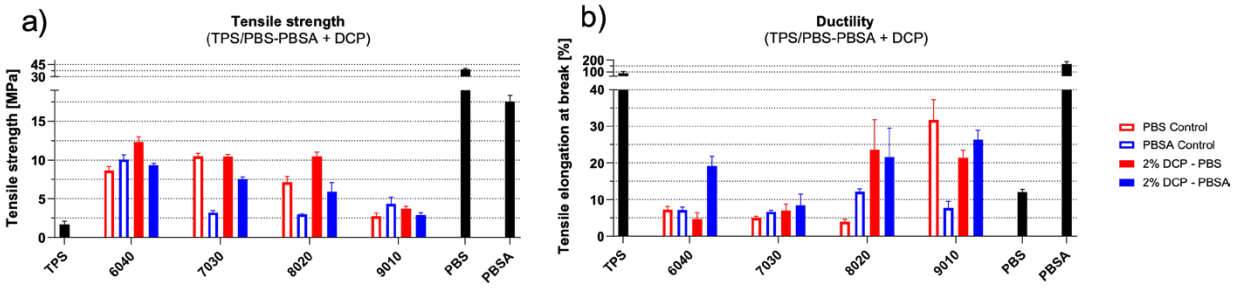

Figure 2. Mechanical properties for films. a) Tensile strength, b) Ductility.

DCP and TA Compatibilizer

Processability Analysis:

For all formulations, the inclusion of tartaric acid reduces the torque in steady state, with the 5% TA group presenting the lowest torque, even reaching values lower than the torque of the control sample that does not include DCP. This result indicates that the processing of mixtures with 5% TA, independent of the DCP incorporation level, are easier to process than the pure TPS and PBS or PBSA mixture. In contrast, by increasing the percentage of DCP incorporation, the torques always increase; so in terms of processability it is recommended to use the lowest DCP level.

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In relation to the processing temperatures, higher percentages of DCP lead to increased maximum temperatures within each % TA group. This may be related to the formation of free radicals at high temperature. Regarding the amount of TA, it is evident that at higher % TA the maximum temperatures decrease, reaching values below the control mixture.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis:

Figures 3(a) and 3(c) show that maintaining the DCP composition, increasing the % TA increases the signal intensity. Likewise (Figures 3[b] and 3[d]), by leaving the TA constant and increasing the DCP composition, the signal intensity will also increase. This indicates that neither the DCP nor the TA reacted with the OH groups of the starch. That is, the TA is not functionalizing the starch through esterification. However, although the addition of DCP and TA always generates higher signal intensities, the magnitude of the effect of the incorporation percentage is different for the PBS and the PBSA.

Now, in Figure 4(a) and 4(c) we see that by leaving the % DCP constant, increases in TA generate a decrease in the intensity of the OH groups of the PBS. For both the formulations with PBS and PBSA, the higher the % TA, the more significant the decrease in peak intensity. Now, by leaving the TA constant and increasing the amount of DCP, it is evident that the peak related to the OH groups is also reduced. In this case, the largest drops in intensity are also presented with the highest percentages of DCP.

Based on literature review, when TA is introduced into polyesters/starch blends, the anticipated outcome is the heightened intensity of peaks at 1712 cm-1, which correlates with the esterification process [16]. On the contrary, the absence of heightened intensity in this signal suggests that TA did not facilitate esterification of TPS. However, the observed decrease in signal intensity suggests that the carbonyl group bonds of PBS were substituted by new bonds.

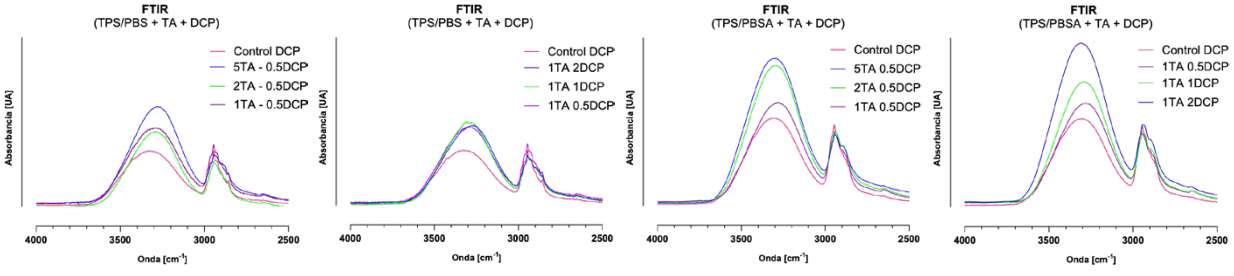

Figure 3. FTIR spectrum between 2600 and 4000 cm^{-1}. (a)(b) formulations with PBS, and (c)(d) formulations with PBSA.

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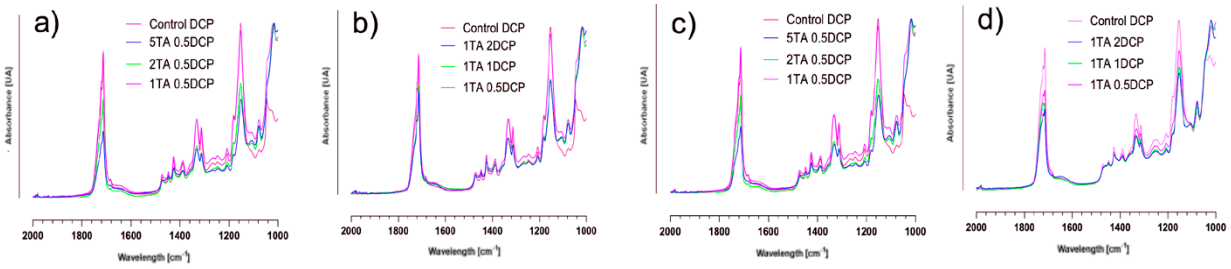

Figure 4. FTIR spectrum between 1000 and 2000 cm^{-1}. (a)(b) formulations with PBS, and (c)(d) formulations with PBSA.

Scanning Electron Microscopy (SEM) Analysis:

Figure 5 shows that the simultaneous incorporation of TA and DCP, as opposed to the exclusive incorporation of DCP, has a positive effect on the morphology of the fracture surfaces of the films. Films with TA and DCP have a considerable reduction in cavities or holes, and their surface is noticeably smoother. By increasing the percentage of TA, the interfacial adhesion between TPS and BioPBS improves. Additionally, an increase in the percentage of DCP in the blends produces the same effect. These changes indicate a better interaction between TPS and BioPBS, so TA and DCP would have the desired effect: promoting the compatibility of the polymers. Considering the above, it is expected to have a positive effect on the mechanical properties of the material, especially on ductility, since this property is related to imperfections. As the amount of starch granules and/or cavities is reduced, the transfer of stress in the material would then increase, thus facilitating ductility.

In some images (Figure 5[f-k]), it is possible to distinguish some darker and irregular regions on the surface of the sample (indicated by the arrows in yellow). These regions could indicate that the material has fractured or cracked or could be related to the presence of a second phase.

By contrasting with literature, it is possible to relate the morphology of the films as co-continued morphology. In this, there is the simultaneous presence of at least two continuous three-dimensional structures within the same volume [17]. However, considering that it is a 3D network morphology, SEM images are not conclusive and other tests are necessary, such as confocal microscopy, dynamic mechanical analysis (DMA) or solvent extraction.

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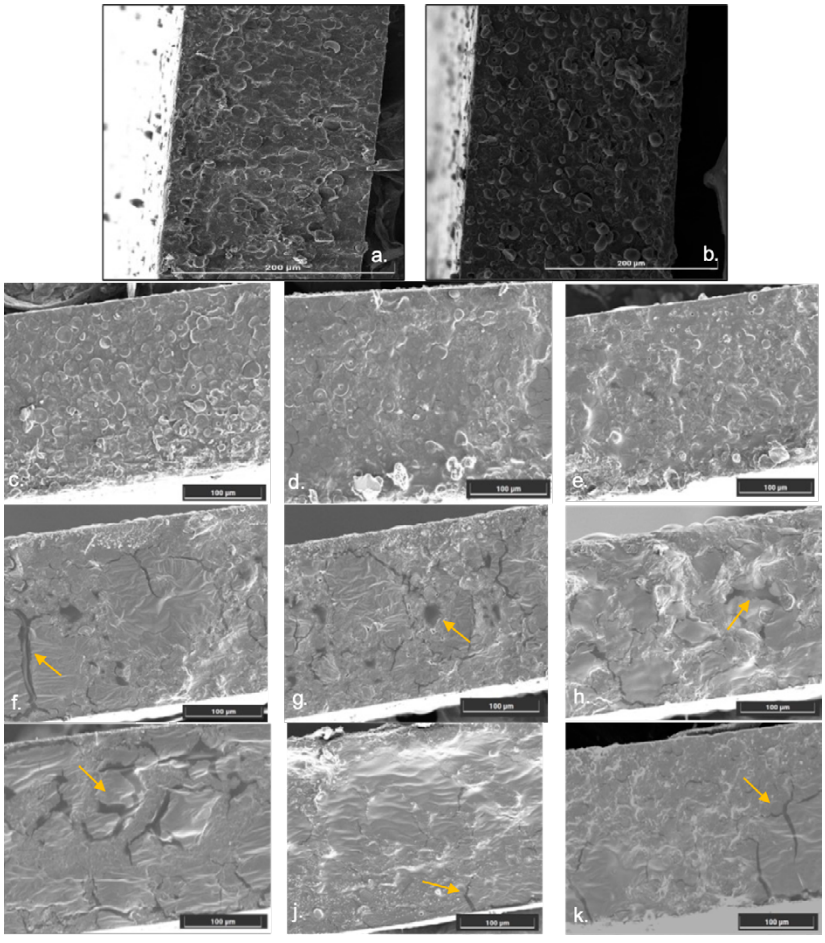

Figure 5. SEM images in x800. (a) Control, (b) DCP Control, (c) 1TA 0.5DCP, (d) 1TA 1DCP, (e) 1TA 2DCP, (f) 2TA 0.5DCP, (g) 2TA 1DCP, (h) 2TA 2DCP, (i) 5TA 0.5DCP, (j) 5TA 1DCP, (k) 5TA 2DCP.

Mechanical Properties:

For tensile strength (Figure 6[a]), as the percentage of TA incorporation increases, this mechanical property decreases. The effect of the DCP variation is not so clear. When comparing the tensile strength values obtained for the formulations with DCP+TA with respect to their control values, it is evident that there is an increase in the property using both compatibilizers only for the group of formulations with PBS. This increase is 11.06% for the 1TA-0.5DCP mixture and 7.17% for the 1TA-1DCP mixture.

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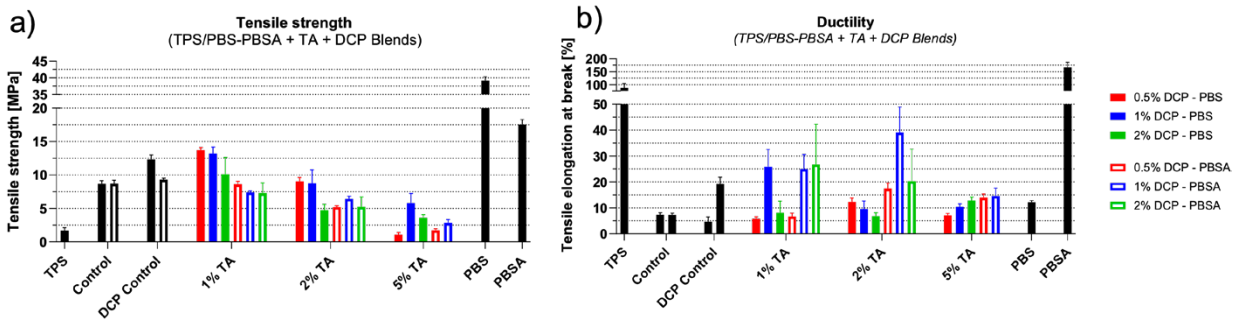

Figure 6. Mechanical properties for films. (a) Tensile strength, (b) Ductility.

In contrast, the results obtained for the ductility of the films (Figure 6[b]) are not conclusive. This is because it is not possible to identify a clear trend for the variations in %T A nor % DCP. The mixtures with PBS increase or at least maintain ductility compared to their control with only DCP, which does not occur with the PBSA group. However, when comparing formulations with PBS and formulations with PBSA, the latter has higher elongation values until fracture.

Conclusion

The use of compatibilization agents DCP and DCP+TA improved the tensile strength and ductility of the material. DCP increases torque and processing temperatures but enhances tensile strength and ductility, especially in mixtures with PBS (12.34 MPa) and PBSA (26.40%) with respect to their control blends without compatibilizer, respectively. However, SEM and FTIR analyses show no improved compatibility or chemical reaction between components. Adding DCP and TA simultaneously modifies processing conditions: TA decreases torque and temperature, while DCP increases them. Increased TA decreases tensile strength, especially in PBS formulations, but the effect of DCP on tensile strength is inconclusive. Ductility showed no clear trend. SEM suggests better compatibility for the blends, and FTIR indicates that TA is not esterifying starch, however, bonds of carbonyl groups in PBS could have been replaced by new bonds.

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