doi:10.20944/preprints202011.0688.v1

*Article*

# Colour fixation strategies on sustainable polybutylene succinate using biobased itaconic acid

**Lidia G. Quiles[a*], Julio Vidal[b], Debora Puglia[c], Franco Dominici[c], Angel Fernández Cuellod[d], Pere Castell[b*]**

[a] Tecnopackaging, Polígono Industrial Empresarium C/ Romero Nº 12 50720 Zaragoza, Spain.
[b] Fundación Aitiip, Polígono Industrial Empresarium C/ Romero Nº 12 50720 Zaragoza, Spain
[c] Department of Civil and Environmental Engineering, University of Perugia, 05100, Terni, Italy
[d] University of Zaragoza, Escuela de Ingeniería y Arquitectura, Av. María de Luna, 3, 50018 Zaragoza, Spain
* Correspondence: lgarcia@tecnopackaging.com; pere.castell@aitiip.com; Tel.: (+34 976 46 45 44)

**Abstract:** BioPBS is gaining attention in the biodegradable polymer market due to their promising properties such as high biodegradability and processing versatility representing a potential sustainable replacement for fossil oil-based commodities. However, there is still a need to enhance its properties for certain applications, being aesthetical and mechanical properties a challenge. The aim of the present work is to improve these properties by adding selected additives that will confer bioPBS with comparable properties to that of current counterparts such as polypropylene (PP) for specific applications in the automotive and household appliances sectors. A total of thirteen materials have been studied and compared, being twelve biocomposites containing combinations of three different additives: a commercial red colourant, itaconic acid (IA) to enhance colour fixation and zirconia ($ZrO_2$) nanoparticles to maintain at least native PBS mechanical properties. Results show that the combination of IA and the colouring agent tends to slightly yellowish the blend due to the absorbance spectra of IA and also to modify the gloss due to the formation of IA nanocrystals that affects light scattering. In addition, for low amounts of IA (4wt.%), young modulus seems to be kept while elongation at break is even raised. Unexpectedly, a strong aging affect was found after 4 weeks. IA increases the hydrophilic behaviour of the samples and thus seems to accelerate the hydrolisation of the matrix, which is accompanied by an accused disaggregation of phases and an overall softening and rigidization effect. The addition of low amounts of $ZrO_2$ (2wt.%) seems to provide the desired effect for hardening the surface while almost not affecting the other properties; however, higher amounts tends to form aggregates saturating the compounds. As a conclusion, IA might be a good candidate for colour fixing in biobased polymers.

**Keywords:** Biopolymers, Biocomposites, Polybutylene succinate, Itaconic Acid, Zirconium oxide, Colourant, Diazo pigment, Extrusion-compounding, Mechanical properties, Hardness, Colour fixing, Gloss, Aging effect, SEM (Scanning Electron Microscopy), Wettability

## 1. Introduction

Technical biopolymers are becoming increasingly attractive as sustainable and good-performing polymeric materials [1]. One of the most promising biopolymer is the biopolybutylene succinate (bioPBS). BioPBS is an aliphatic polyester synthesised from the polymerization of two biobased building blocks: succinic acid (or dimethyl succinate) and 1,4-butanediol [2,3], all derivable from renewable sources. The materials and products derived from BioPBS are soft, flexible and have become a promising replacement for commodities [4] such as PET, PP and PE as it exhibits nearly comparable mechanical properties [5] to these synthetic plastics for several applications such as packaging, construction applications, houseware, furniture or agriculture [6]. In addition, bioPBS undergoes biodegradation during disposal in compost, moist soil, fresh water and seawater [7] which reduces its potential environmental impacts thus making it a promising candidate to enhance the sustainability of plastic products which is currently demanded by the markets and consumers.

However, a general drawback of biopolymers, among them bioPBS, is that they present poor aesthetic appearance compared to oil-based counterparts. Every thermoplastic material has its own innate colour. A thermoplastic material in its innate color state is referred to as natural. The natural colour of biopolymers usually vary from yellowish, brownish to crude whitish which many times is not the preference by the consumer. Thus, the used of pigments or additives to tailor the appearance of biopolymers is required. BioPBS in terms of colour is a whitish bright matrix. The need to introduce these materials in the market requires the improvement of such property allowing customisation of the final colour.

The term “colorant or colouring agent” denotes a series of coloured substances that affect a material’s appearance. Therefore, the introduction of a colouring agent would increase the attractiveness of the bioplastic and the potential acceptance of the material in more applications. Nevertheless, how the material responds to the colorant is a critical aspect of the overall appearance which also involves gloss and texture. Gloss is used to describe the manner in which a surface reflects light: specular reflection (shiny), diffuse reflection or it can absorb the light (dull). Regarding texture, smooth surfaces reflect light in the specular direction, whereas diffuse reflection dominates in the case of rough surfaces.

Two kinds of colouring agents are usually used to colour plastics: pigments and dyes. Pigments may be either organic or inorganic in structure and are insoluble both during processing of the plastics and in the end product [8,9]. Dyes, on the other hand, are organic molecules that dissolve into the substrate to which they are applied. Azo colorants are the most important class of synthetic dyes and pigments, representing 60 - 80% of all organic colorants [10]. These colorants contain one or more nitrogen-nitrogen double bond (–N=N–) in their chemical structure and may possess other functional groups [11]. They have excellent colouring properties, mainly in the yellow to red range, as well as good lightfastness. Azo colourants are used widely in substrates such as textile fibres, leather, plastics, papers, hair, mineral oils, waxes, foodstuffs, rubbers and paints.

The colorant not only needs to match the desired colour but it shall also satisfy other constraints such as be chemically compatible with the base polymer matrix and be chemically stable. In order to be able to provide a wide pallete of colours, it is important to reach a good colour fixation and gloss, making it long-lasting (durable) and that also does not affect other functional key properties such as hardness or mechanical performance. Other factors influencing colour strength are particle size and dispersion in the plastic matrix.

Ideally, when a biobased material is conceived, the colourants and additives used in the formulation should come from a bio-based origin [12,13]. Natural pigments and dyes present poor colour fastness and yield compared to synthetic ones [14]. For this reason, it is necessary to introduce a linking agent that enhances compatibility with the polymeric matrix. Most of the natural dyes present hydroxylic groups (-OH) in their structure and for example can be esterified with polycarboxylic acids such as citric acid or itaconic acid (IA) [15]. These, and others such as amino groups, are considered colour helpers. They are known as auxochromes [16], which are able to alter both the intensity and the wavelength of absorbed light influencing the physical-chemical properties of the material while they do not produce colour by themselves. These are many times used as colour fixation chemicals enhancing the overall stability of the coloured part. Among the different linking agents used in polymer science IA has demonstrated good performance in oil-based polymers [17]. Today, IA is exclusively produced by fermentation with carbohydrates by filamentous fungi, mainly Aspergillus terreus [18]. Thus, it has the potential to be produced exclusively from biomass. IA is a fully sustainable industrial building block, an ionic hydrophilic co-monomer, with a myriad of chemical applications due to its structural similarity to acrylic and methacrylic acids [17]. In fact, it presents a viable solution to replace acrylic acid in biodegradable polymers. For example, it is used in the production of lubricants, active agents, dyes, plastics, chemical fibres etc [19]. Other promising uses are unsaturated polyester resins, phosphate-free detergents, and in the food industry [20]. It is stable at acidic, neutral and middle basic conditions at moderate temperatures, so it was considered a good candidate for the extrusion-compounding process in which high temperatures and shear forces are achieved.

However, as it is a component usually used in the formulation of gums/elastomers and latex, one of the drawbacks of using IA in different thermoplastics is the softening effect, which might be accentuated by the organic nature of the diazo pigment. The use of inorganic fillers has been demonstrated to be a good strategy in composites for enhancing mechanical properties [21-25]. Among these fillers, nanoparticles such as $ZrO_2$ have been used in several applications [26,27]. Its natural whitish colour, and its excellent dimensional stability, mechanical and chemical properties, has made Zirconia a highly attractive ceramic material in medical applications such as hip head replacement instead of titanium or alumina prostheses and in particular for prosthodontics [28,29]. Zirconia has also been used to produce hard coatings for plastic surfaces with antifogging, anti-wetting and antistatic properties [30]. Due to this reason, it was decided to add zirconium dioxide to harden bioPBS surface as well as prevent it from losing mechanical properties.

The objective of this study is to develop an enhanced biobased material showing good aesthetical properties in terms of colour fixing while keeping at least the mechanical properties of the original matrix polymer (bioPBS) in order to make it attractive for a plethora of applications in the market such as automotive, householding or furniture. In this research IA has been selected as functional colour helper to better fix and increase the lightfatness of an organic red diazo pigments in bioPBS matrix. To enhance the resulting material mechanical properties $ZrO_2$ was as a reinforcing agent. A complete and detailed characterisation has been conducted using micro and macroscopical techniques such as SEM, wettability, colour change, hardness, and mechanical analysis. Besides, an aging effect was evaluated during the realization of the experimental work and their effects were characterised and compared.

## 2. Materials and Methods

### *2.1 Materials*

The polymer matrix used was a biobased polybutylene succinate BioPBS FZ71 PD which was purchased to Japan Pulp & Paper GmbH (Japan).

The IA 99% pure, was purchased to Sigma Aldrich (Germany). It is a white crystalline powder, unsaturated dicarboxylic acid ($C_5H_6O_4$), in which one carboxyl group is conjugated to the methylene group [31]. It presents a hygroscopic property, and it is odour-free [32,33]. Its melting point is 167–168°C and the boiling point is 268°C [34].

The colouring agent was purchased to NTC SL (Spain) which is an organic red diazo pigment with the commercial code: PR57:1, MDN-1153.

Finally, the Zirconia nanoparticles were kindly provided by TORRECID group (Spain). Zirconia is a crystalline dioxide of zirconium. Its mechanical properties are very similar to those of metals (it has been called ''ceramic steel' [35]). Zirconia crystals can be organized in three different patterns: monoclinic (found at room temperature, under ambient pressure and upon heating up to 1170 °C), tetragonal (between 1170 and 2370 °C), and cubic (above 2370 °C and up to the melting point) [36].

### *2.2 Nano-bio-composites preparation*

Twelve different formulations were prepared by extrusion-compounding with a 26-mm twin-screw Coperion ZSK 26 compounder machine (Germany). Firstly, binary blends were prepared. F2 & F3; F4 and F5&F6. The three additives were introduced in a powder format from a secondary feeder different from the bioPBS main hooper. IA was introduced at the beginning of the barrel while the $ZrO_2$ and the colouring agent at the middle of the barrel. The melted polymer and powders were mixed at a screw speed of 200 rpm; temperature was increased from 160 °C in the feeding zone up to 180 °C at the nozzle. The compounding was extruded through a 2 mm diameter die for a constant output of 15 kg/h. The extrudate was quenched in a water bath at room temperature, dried and cut into pellets. 3 kg of per blend were produced. Ternary and quaternary formulations were produced by re-extruding in a second step using the conditions above. To this end, the colorant and the zirconia were added into bioPBS/IA extruded matrices, by introducing them at the middle of the barrel as for the first extrusion-compounding step. No modifications were required regarding the parameters and conditions of the extrusion process.

**Table 1:** Summary of material formulations based on bioPBS FZ71PD matrix

| Reference | bioPBS matrix | IA | Colourant | $ZrO_2$ |
|---|---|---|---|---|
| F1 | 100% | - | - | - |
| F2 | 96% | 4% | - | - |
| F3 | 90% | 10% | - | - |
| F4 | 96% | - | 4% | - |
| F5 | 98% | - | - | 2% |
| F6 | 96% | - | - | 4% |
| F7 | 94% | - | 4% | 2% |
| F8 | 92% | 4% | 4% | - |
| F9 | 86% | 10% | 4% | - |
| F10 | 94% | 4% | - | 2% |
| F11 | 88% | 10% | - | 2% |
| F12 | 90% | 4% | 4% | 2% |
| F13 | 84% | 10% | 4% | 2% |

Samples were analyzed at week0 (W0), just after their preparation and after aging in ambient conditions at week (W4)

### *2.3 General characterisation methods*

#### *2.3.1 Two types of **specimens** were developed for material characterisation:*

- Injected specimens for mechanical (tensile or dog-bone following ISO 178 standard) and hardness (parallelepiped specimens of 80 x 100 x 4 mm) testing were obtained by injection moulding with a JSW 85 EL II electric injection machine.

Temperature profile was increased from 150 °C at the hopper up to 18 at the nozzle with 40rpm. Dosage and filling pressure were varied for each formulation injected. A packing pressure of 35% (55 bar during 20s) was applied. When injecting samples containing IA, temperatures were decreased from 140 °C at the hopper up to 16 at the nozzle and cooling time increased by 10 seconds so that it was cooled enough to be expelled from the mould.

- Circular specimens of 50 mm diameter and 2 mm thick from all the formulations were produced for measuring wettability and colour change. The same processing parameters were considered. The materials were mixed for 120 s at 90 rpm in a co-rotating twin-screw extruder Microcompounder 5 & 15 cc, DSM, using a temperature profile of 120-125-130 °C. Due to the low viscosity of the formulations containing IA, a pressure-time injection moulding profile of 1.0-5; 1.1-15; 1.1-15 in bar-seconds was used. The mould and injection temperatures were set at 30 and 150 °C, respectively.

#### *2.3.2 Measurements*

**Mechanical tests** were conducted under ambient conditions using a Zwick Roell Z 2.5 (Zwick, Germany). At least five specimens per material were tested, according to ISO 178 and ISO 527 methodology.

**Structural properties** were evaluated by scanning electron microscopy (SEM) with a Hitachi S3400N equipment in order to determine the morphology and dispersion. Broken samples coming from mechanical tests were used.

**Hardness,** was measured using a portable hardness tester, METALTEST tester model T500 to verify material hardness with load-cell technology for Vickers, Brinell and Rockwell testing. Rockwell B scale was used for this study.

**Surface properties** of produced materials were evaluated by static contact angle measurements (FTA1000 Analyser (USA). **Wettability** of the surfaces was studied by using the sessile drop method, in air, in contact with HPLC grade water. When a surface is hydrophilic, the drop extends over the material at an angle between 0° and 30°. If the surface of the solid is hydrophobic, the contact angle will be greater than 90°. On surfaces that are very hydrophobic, the angle can be greater than 150° and even close to 180°.

**Colour change** and gloss of samples was investigated by means of a spectrophotometer (CM-2300d Konica Minolta, Japan). Data were acquired by using the SCI 10/D65 method, CIELAB colour variables, as defined by the Commission Internationale de 1'Éclairage (CIE 1995), were used.

Samples were placed on a white standard plate and L*, a*, and b* parameters were determined. L* value ranges from 0 (black) to 100 (white); a* value ranges from -80 (green) to 100 (red); and b* value ranges from -80 (blue) to 70 (yellow). For each sample, 3 measurements were taken at random location. The total colour difference ΔE* between white and the samples was calculated as indicated in Eq. 1:

$$\Delta E* = \sqrt{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2}$$

**Eq. (1)**: Colour-difference formulae

## 3. Results and discussion

### *3.1 Mechanical tests*

The mechanical properties of bio-composite materials are always a compromise between stiffness and toughness which are generally mutually exclusive. The elastic modulus (E) and elongation at break ($\varepsilon_B$) are useful parameters to describe the mechanical behaviour of the developed materials and are closely related to the internal microstructure. The mechanical properties determined from uniaxial tensile tests are summarized in Table 2 and their comparison among the different formulations and aged samples are shown in Figure 1.

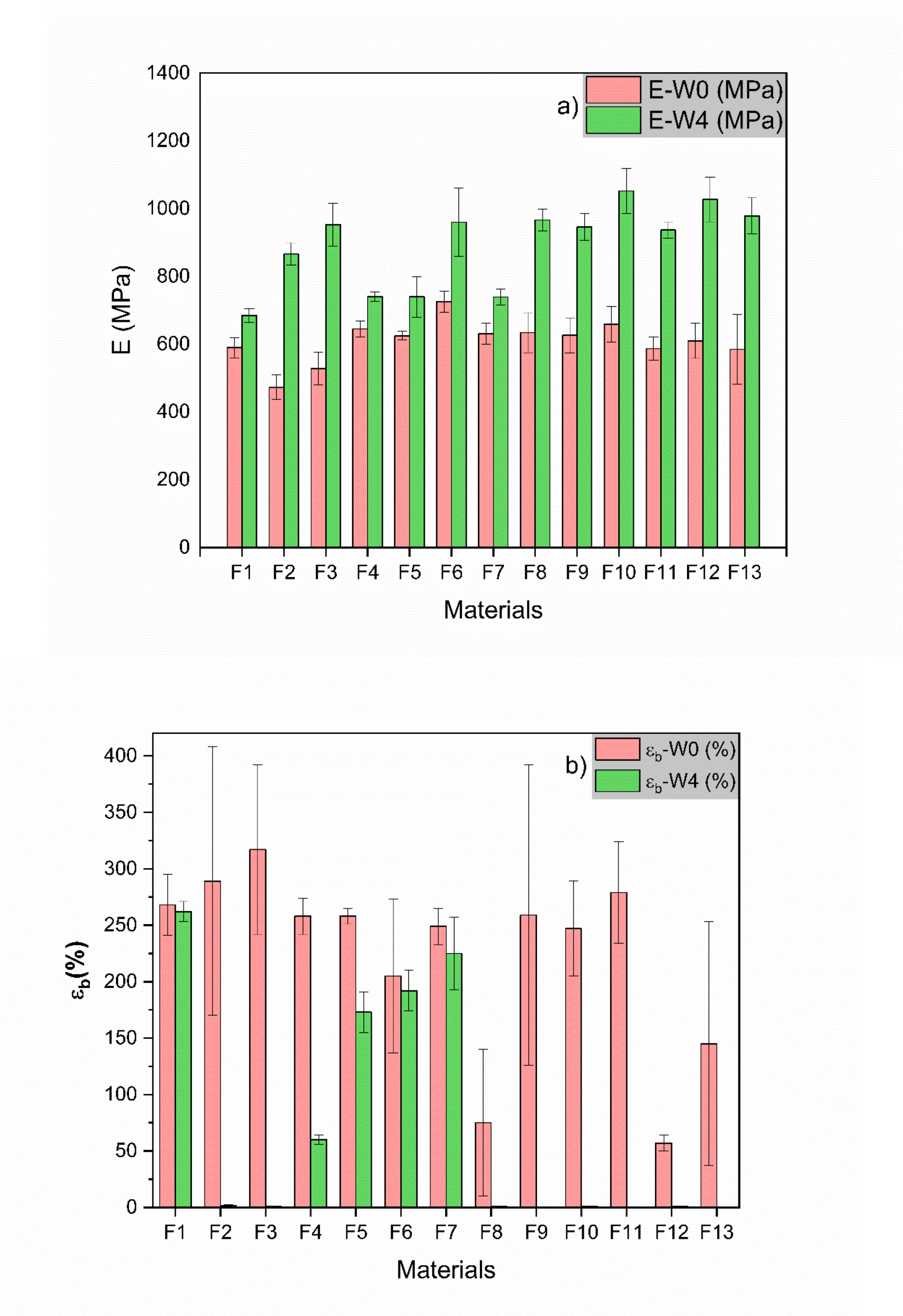

**Fig 1:** Young´s Moduli (a) and Elongation at break values (b) for all specimens evaluated at W0 and W4)

**Table 2:** Mechanical properties under tensile force: modulus [E] and elongation at break [$\varepsilon_B$] for all characterised materials; surface hardness and contact angles measurement (wettability). Measurements done at week 0 (W0) and after 4 weeks aging (W4).

| Material | Young Modulus [MPa] W0 | Young Modulus [MPa] W4 | Elongation at Break [%] W0 | Elongation at Break [%] W4 | Hardness [HRB] W0 | Hardness [HRB] W4 | WCA (°) W0 | WCA (°) W4 |
|---|---|---|---|---|---|---|---|---|
| F1 | 590 ± 30 | 685 ± 20 | 268 ± 27 | 262 ± 9 | 6.2 ± 1.3 | 5.1 ± 0.9 | 76 ± 1 | 69 ± 3 |
| F2 | 473 ± 37 | 866 ± 33 | 289 ± 119 | 1.5 ± 0.8 | 20.6 ± 2.6 | Break | 54 ± 3 | 54 ± 0 |
| F3 | 528 ± 49 | 953 ± 63 | 317 ± 75 | 0.67 ± 0.05 | 5.1 ± 0.4 | Break | 66 ± 3 | 47 ± 3 |
| F4 | 645 ± 24 | 740 ± 14 | 258 ± 16 | 60 ± 4 | 2.6 ± 1.4 | 2 ± 1.3 | 68 ± 3 | 70 ± 3 |
| F5 | 625 ± 13 | 740 ± 60 | 258 ± 7 | 173 ± 18 | 6.6 ± 1.1 | 1.6 ± 0.5 | 75 ± 3 | 66 ± 1 |
| F6 | 726 ± 31 | 960 ± 351 | 205 ± 68 | 192 ± 18 | 4.3 ± 1.3 | 1.1 ± 0.6 | 76 ± 3 | 71 ± 2 |
| F7 | 631 ± 31 | 739 ± 23 | 249 ± 16 | 225 ± 32 | 1.1 ± 0.8 | 1.1 ± 0.8 | 70 ± 3 | 66 ± 3 |
| F8 | 634 ± 59 | 966 ± 32 | 75 ± 65 | 0.88 ± 0.2 | 10.4 ± 1.5 | Break | 63 ± 4 | 56 ± 3 |
| F9 | 626 ± 52 | 946 ± 39 | 259 ± 133 | 0.27 ± 0.01 | 6.4 ± 0.7 | Break | 65 ± 3 | 58 ± 4 |
| F10 | 659 ± 52 | 1052 ± 67 | 247 ± 42 | 0.97 ± 0,4 | 17.4 ± 0.3 | Break | 59 ± 2 | 44 ± 3 |
| F11 | 587 ± 34 | 937 ± 24 | 279 ± 45 | 0.56 ± 0.28 | 5.0 ± 1.2 | Break | 67 ± 2 | 61 ± 3 |
| F12 | 610 ± 52 | 1027 ± 66 | 57 ± 7 | 0.88 ± 0.2 | 10.2 ± 1.6 | Break | 60 ± 3 | 61 ± 3 |
| F13 | 585 ± 103 | 979 ± 53 | 145 ± 108 | 0.3 ± 0.05 | 5.6 ± 0.6 | Break | 60 ± 4 | 59 ± 3 |

### 3.1.1 *Comparative results among formulations at W0 (comparisons among pink columns – Young modulus; and among green columns – elongation at break)*

When IA is added to neat PBS a reduction in the young modulus by 11% for F2 and by 26% for F3 is observed while an increase in the elongation at break by 8% for F2 and by 18% for F3 is found. Thus, IA seems to induce a plastizing effect which is in coherence with Kirimura et al [34] who explained the use of this component in rubber-like polymers due to its excellent strength and flexibility, making the PBS tougher. This result is also aligned with Krishnan et al [37], who used IA to design an aliphatic copolyester elastomer that was used as PLA toughener.

The addition of the colourant (F4) as well as low amounts of $ZrO_2$ (F5) slightly augments the young modulus, while the material stiffness is considerable risen by 23% when a 4 wt.% of $ZrO_2$ is incorporated (F6). On the one hand, Zirconia affects in the elongation at break and an overall fall can be observed (F6 decreases a 24%). Nevertheless, the data dispersion is broad what indicates the appearance of agglomerates producing a stress concentrating effect favouring a premature rupture [38]. All in all, this decrease is noticeably found for 4 wt.% of $ZrO_2$, which is a quite positive result for such a high content of zirconium if compared with other similar studies using it as reinforcement agent in polymers. For example, Mishra T.K. et al [39] found the same decrease in the elongation at break for PEEK/$ZrO_2$ compounds with just a 1wt%. On the other hand, when the colourant is incorporated to PBS (F4) elongation at break values remain almost unchanged. Consequently, the colourant appears to be better dispersed and integrated than the $ZrO_2$ probably due to its organic nature which is more compatible with the blend.

Ternary formulations (F5, F6, F8, F9, F10, F11) and quaternary blends (F12, F14), lead to a complex mechanical behaviour in which the rigidity of the materials is kept or even scarcely increased when compared to neat PBS. The combination of these additives induce a remarkable fall in the elongation at break respect to neat PBS. The most prominent decrease is found for F8 by 72% and F12 by 79%, closely followed by F13. Both formulations are complex blends combining a 4% wt.% of IA and colourant. The high scattering of the data, confirms a lack of integration between the IA, the matrix and the additives, probably forming regions of high and low IA concentration peaks; and the formation of zirconia and colourant aggregates with insufficient dispersion (a result that has been corroborated with SEM micrographs).

### 3.1.2 *Comparative results of same formulations between W0 and W4 (aging effect)*

All plastic materials suffer from aging with time. They tend to recrystallize as the polymer chains end their ordering. The plastic gets stiffer and in a long-term becomes brittle. Kimble et al [40], studied aging in PLLA/PBS blends including annealing and creep studies. As conclusion, blends with high content of PBS tend to decrease its Mw with time produced by degradation and showing and embrittlement of samples. Thus, their results also highlighted the importance of appropriate storage conditions for ductility retention. In this study, the Young Modulus of neat PBS increased by 16% (F1) after 4 weeks. The elongation at break was maintained, what indicated the good integrity of the material and, apparently, an absence of degradation.

Remarkable was the effect of the IA. In F2 and F3 samples, the Young Modulus rised by 80%, which clearly indicate the rigidization effect. The blends lose their toughness and become very brittle. A drop in the elongation at break by more than 98% was observed in all the formulations containing IA.

When adding the colourant (F4) and a 2wt.% of $ZrO_2$ (F5) the material became a 15% stiffer in both cases while when increasing the addition of $ZrO_2$ by 4wt% (F6) the Young modulus doubled by reaching a 32% higher value. Stiffness and toughness are usually compromised properties, and we can find a reduction in elongation at break by 6% for F6 and by 33% for F5. This results drawn a better dispersion of $ZrO_2$ for F6 rather than F5. The colourant also seems to highly affect this property, falling by 77% (F4), what may indicate a disaggregation of the organic phases with time what weaknesses the interphase between the colourant and the additive.

When ternary and quaternary blends are studied (F8-F13), we can observe a rise in the young modulus between a 60 and a 70 % as expected and practically an absent of elongation at break, effect induced by IA.

### *3.2 Hardness*

#### *3.2.1 Hardness results at W0*

The highest value on hardness is found for F2 (4 wt.% IA), which multiplies almost by four the hardness value for neat PBS, while for F3 (10 wt.%) it decreases a 18 % down neat PBS value. Probably a 10 wt.% IA has saturated the blend and shows a lack of miscibility among the two phases (PBS and IA). The shear forces or thermodynamics produced during the compounding process might not have been enough to disperse and homogenise the components which seems not to be compatible and tends to form separated phases inside the blend. Moreover, as these phases are distinct, the IA apparently seems to crystallize into the surface of the injected specimen. Looking to the SEM micrographs we can observe the IA crystals, thus when the indenter finds a high concentration of IA in the surface it founds a fragile and brittle point.

When looking to F4, PBS containing the colourant, which is a soft pigment, the overall hardness of the blend decreases by 58%, but when characterising F5 and F6, we can find a hardening effect by 6 % for the 2 wt% of Zirconia. However, when adding a 4 wt.% of zirconia, hardness descends by 31 %, probably due to a saturation of the blend accompanied by the apparition of agglomerates. High surface energy of nanoparticles is prone to induce the formation of nanoparticles aggregation [41]. Thus, phase separation often takes place owing to the great differences in the properties of polymer and inorganic materials.

When combining the colourant and the $ZrO_2$ (F7), there is negative synergistic effect, decreasing the hardness value by 82 %, while the combination of any of them with the 4 wt.% IA induce a positive synergy in which the IA domains the behaviour of the complex blends (F8 by 68 %, F10 by 181 % and F12 by 65 %). However, with a 10 wt.% IA added instead, it still domains the blend keeping similar values to those found for F3.

#### *3.2.2 Hardness results at W4*

When hardness was measured at W4, authors found a clear embrittlement of the samples. Especially in those containing IA (F2, F3 & F8-F13), to which was no possible to repeat the characterisation test. The specimens broke when the indenter penetrated the sample, even some of the samples experiment a ductile fracture just when they were manipulated.

### *3.3 Structural properties (SEM)*

Surface morphology of the developed formulations was studied by using scanning electron microscope (SEM). Micrographs of representative specimens are shown in Figure 2.

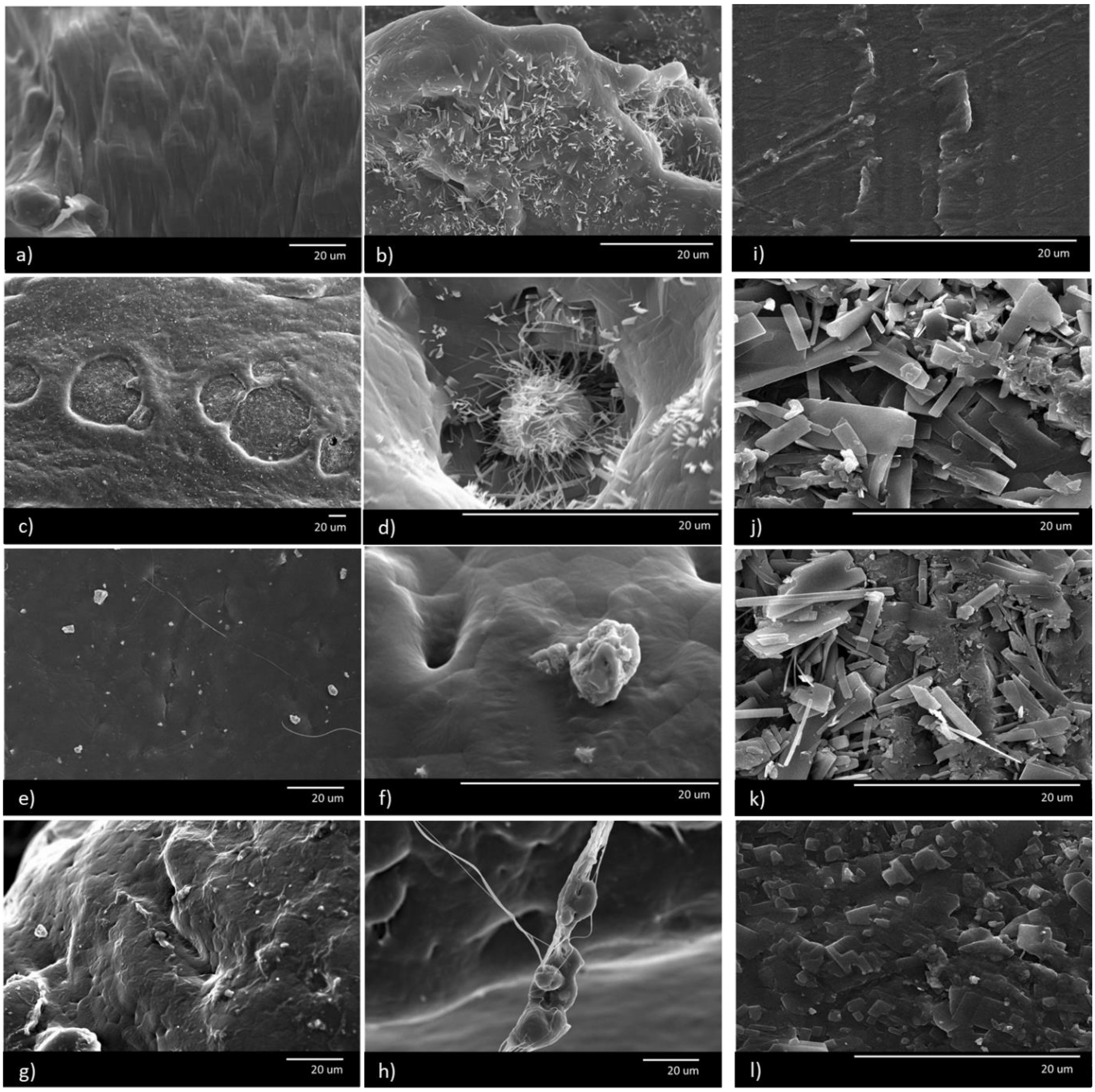

**Fig 2:** SEM – W0 (left – *a,c,e,g*- and central –*b,d,f,h*- columns) & W4 (right column –*i,j,k,l*-). a): F1; b): F3; c): F9; d): F13; e) & f): F5; g) & h): F4; i):F1; j): F3; k): F9; l) F10.

### *3.3.1 Structural results at W0*

The micrographs confirmed the tendencies observed in the mechanical and hardness results. IA crystallizes in form of rectangular nanocrystals. It clearly manifests a special phase morphology constituted by the disperse phase of IA. These nanocrystals are found to group themselves in a heterogeneous way showing a lack of compatibility between the IA and the PBS (b,c). The IA nanocrystals are found to migrate to the surface of the part. Authors observed this phenomena: either over time outside to the external surface (j or k are taken from the border perimeter), or within internal created surfaces such as for example in bubbles or defects generated during the injection process of the specimen (d). Therefore, we find a highly reinforced material at the surface level, but as it is not miscible, it is not well integrated, and a very accused separation of the phases is produced.

Apparently, the pigment, being highly organic, experiments a good interfacial bonding with the polymer (g, h). $ZrO_2$ seems to be well dispersed although a few aggregates can be found (e, f). When ternary and quaternary blends are studied, those containing IA nanocrystals tends to allocate surrounding the colorant aggregates. This effect can be explained probably due to the combination of the polar-apolar performance of both materials which generates a complex interface inducing a low adherence with the polymeric matrix, PBS. The IA is an acid what means that the hydrogen on the OH group can easily be removed, leaving an anion. Both the colourant pigment as well as $ZrO_2$, may act as a salt to the IA favouring the attraction between them (d). These aggregates have a stress concentrating effect which reduces the toughness of the material favouring a premature breaking, what explains the mechanical behaviour found.

### *3.3.2 Structural results at W4*

Finally, a change in the type of fracture can be observed between W0 and W4. At W0 the fracture surface evidence a ductile behaviour (a), while at W4 a more fragile surface is found showing a flat fracture surface of the polymer accompanied by some striations (i), in which polymeric chains have had the time to rearrange. So does IA, which is unstable in the blend and migrates to the surface of the specimen, seeking the state of minimum energy (j, k, l). Thus, it can be confirmed that the materials suffer from aging which induces a rigidization mechanism and that it is clearly intensified with the addition of IA.

## *3.4 Hydrophobicity / Wettability*

Wettability results are included in Table 2. The range WCA values for our bioPBS systems vary between 44º and 76º.

### *3.4.1 Structural results at W0*

The presence of IA in binary systems reduces WCA when compared with neat PBS (F1), this phenomenon is more pronounced in F2 than in F3 making the material more hydrophilic. It is also found a slight reduction in the WCA when colourant is added (F4) while the presence of $ZrO_2$ does not change the WCA value of reference PBS matrix (F5, F6). Mizuno et al [42], showed the same tendency as with IA when introduced grafted Acrylic Acid into PBS to study and control the biodegradability of this aliphatic polyester. His study demonstrates that a more hydrophilic surface had a considerable impact in the biodegradation of the PBS and thus it negatively affects the mechanical and structural properties.

In the samples where IA was combined with $ZrO_2$ (F10, F11 systems), the WCA seems to be influenced only by the presence of IA and the contact angle values are similar to the values recorded for PBS/IA binary systems.

The addition of $ZrO_2$ (F7) does not change the values of F4, influenced by the colourant pigment, as already noted in the case of ternary systems. The presence of IA reduces the values of F4, so the decrease in wettability in presence of IA is confirmed even in coloured samples (F8, F9). Moreover, as lately explained, coloured samples suffer from cleavage of the labile groups of the red pigment, thus accelerating even more these degradation process what is also translated in a more hydrophilic surface.

Including $ZrO_2$ in F12 and F13 systems only slightly changes the WCA values, when compared to ternary systems having IA but without $ZrO_2$ (F8, F9).

### *3.4.2 Structural results at W4*

An overall decrease on WCA was observed comparing the values obtained for PBS samples at W0 and at W4, making the matrix material more hydrophilic with time as a result of material degradation. According to Mizuno et al, wettability together with the stereochemistry, the flexibility of molecular chains and the crystallinity, have been found to be decisive factors in the biodegradability of PBS [42]. Our results show the natural effect of conjugating the natural biodegradation process of PBS synergistically speed up by the acid transfer of IA to the PBS matrix.

## *3.5 Colour Properties*

**Table 3:** Colour coordinates and Gloss of PBS based systems at W0 and W4

| *Material Formulations* | *L** | *a** | *b** | *ΔE** | *Gloss (°)* |
|---|---|---|---|---|---|
| **White Control** | 99.47 ± 0.00 | -0.08 ± 0.01 | -0.08 ± 0.01 | - | 121 ± 0 |
| **F1 – W0** | 85.80 ± 0.26 | -1.22 ± 0.03 | -1.04 ± 0.08 | 13.75 ± 0.26 | 78 ± 4 |

| | | | | | |
|---|---|---|---|---|---|
| **F1 – W4** | 86.05 ± 0.43 | -1.05 ± 0.03 | -1.60 ± 0.08 | 13.54 ± 0.43 | 72 ± 1 |
| **F2 – W0** | 86.84 ± 0.13 | -1.34 ± 0.04 | 3.53 ± 0.08 | 13.20 ± 0.13 | 72 ± 2 |
| **F2 – W4** | 87.34 ± 0.23 | -1.07 ± 0.02 | 3.02 ± 0.19 | 12.56 ± 0.25 | 53 ± 3 |
| **F3 – W0** | 84.01 ± 0.06 | -2.27 ± 0.02 | 9.92 ± 0.10 | 18.54 ± 0.06 | 63 ± 2 |
| **F3 – W4** | 84.37 ± 0.21 | -1.68 ± 0.14 | 8.08 ± 0.06 | 17.23 ± 0.23 | 17 ± 2 |
| **F4 – W0** | 35.09 ± 0.09 | 36.71 ± 0.26 | 16.06 ± 0.12 | 75.89 ± 0.08 | 77 ± 3 |
| **F4 – W4** | 34.84 ± 0.12 | 35.72 ± 0.17 | 15.39 ± 0.15 | 75.49 ± 0.18 | 77 ± 4 |
| **F5 – W0** | 86.43 ± 0.07 | -0.41 ± 0.03 | 8.97 ± 0.05 | 15.87 ± 0.04 | 70 ± 2 |
| **F5 – W4** | 86.50 ± 0.15 | -0.46 ± 0.01 | 8.41 ± 0.13 | 15.51 ± 0.06 | 71 ± 4 |
| **F6 – W0** | 88.34 ± 0.06 | 0.77 ± 0.03 | 13.29 ± 0.12 | 17.42 ± 0.09 | 68 ± 3 |
| **F6 – W4** | 88.41 ± 0.10 | 0.73 ± 0.05 | 13.07 ± 0.10 | 17.20 ± 0.11 | 75 ± 2 |
| **F7 – W0** | 39.30 ± 0.39 | 44.58 ± 0.12 | 12.51 ± 0.20 | 75.99 ± 0.30 | 66 ± 3 |
| **F7 – W4** | 39.01 ± 0.23 | 43.73 ± 0.17 | 11.60 ± 0.27 | 75.57 ± 0.32 | 60 ± 3 |
| **F8 – W0** | 36.18 ± 0.09 | 40.28 ± 0.65 | 15.7 ± 0.24 | 76.72 ± 0.38 | 66 ± 3 |
| **F8 – W4** | 36.04 ± 0.36 | 40.81 ± 0.99 | 15.43 ± 0.22 | 77.05 ± 0.40 | 8 ± 2 |
| **F9 – W0** | 34.88 ± 0.14 | 38.34 ± 0.38 | 15.39 ± 0.33 | 76.73 ± 0.20 | 66 ± 3 |
| **F9 – W4** | 34.78 ± 0.51 | 39.33 ± 1.03 | 15.38 ± 0.41 | 77.32 ± 1.03 | 11 ± 2 |
| **F10 – W0** | 87.62 ± 0.34 | -0.56 ± 0.04 | 11.55 ± 0.20 | 16.62 ± 0.25 | 71 ± 3 |
| **F10 – W4** | 88.05 ± 0.13 | -0.78 ± 0.04 | 10.83 ± 0.40 | 15.81 ± 0.33 | 26 ± 1 |
| **F11 – W0** | 85.44 ± 0.26 | -0.46 ± 0.02 | 11.38 ± 0.07 | 18.12 ± 0.19 | 61 ± 3 |
| **F11 – W4** | 85.82 ± 0.10 | -0.44 ± 0.05 | 10.56 ± 0.10 | 17.31 ± 0.13 | 29 ± 3 |
| **F12 – W0** | 38.25 ± 0.60 | 40.30 ± 0.13 | 12.70 ± 0.28 | 74.44 ± 0.52 | 63 ± 3 |
| **F12 – W4** | 37.84 ± 0.52 | 42.11 ± 0.46 | 12.83 ± 0.13 | 75.79 ± 0.42 | 5 ± 1 |
| **F13 – W0** | 38.88 ± 0.11 | 42.90 ± 0.11 | 12.98 ± 0.11 | 75.42 ± 0.11 | 67 ± 2 |
| **F13 – W4** | 38.89 ± 0.29 | 44.20 ± 0.21 | 13.03 ± 0.20 | 76.17 ± 0.34 | 8 ± 1 |

### *3.5.1 Colour results at W0*

On the one hand, IA (F2, F3), reduces the parameter *a* (a bit greener) and it also induces an increase in parameter *b* (more yellow), so the samples tend to have yellowish coloration (shift to warm tones). The absorbance range for red colour in UV-VIS spectra is about the 600 to 700 nm [43], while the natural absorbance peak for IA locates at 200-205 nm [44]. Therefore the logic combination tends to move the overall material spectra to lower wavelength absorbance spectra, moving down first to yellowish and then to greenish values. The gloss of PBS_IA binary systems decreases as the IA concentration increases probably due to the formation of nanocrystals which scatter the light in a number of different directions than the original matrix.

On the other hand, the presence of $ZrO_2$ in PBS (F5, F6) causes an increase in *L*, *a* and b parameters, due to its opaque white colour. It can be observed that $ZrO_2$ whitens the specimens and decreases also the gloss of the material. This drop in gloss values may be produced by the roughening effect induced in the matrix structure by the $ZrO_2$ agglomerates.

For the ternary systems F10 and F11 that combines IA and $ZrO_2$, the *L* parameter increases when compared to F2 and F3 (IA based). Again, this effect may be produced because of the presence of $ZrO_2$. The gloss of F10 and F11 systems does not change if compared to binary F5 and F6 ($ZrO_2$ binary systems) and F2 and F3 formulations. Thus, we can confirm that there is no sum of the effects of fillers in terms of gloss.

The presence of the 4wt% colourant determines a considerable variation of the color parameters induced by the red color of the pigment. The combined species formed in the samples absorbs and attenuates the light [45]. The *L* parameter decreases when compared to the value recorded for PBS (what makes darker the material), *a* and *b* increases as expected following the red color scale. The addition of this red pigment does not change the values of the gloss (F4). The presence of $ZrO_2$ in F7, F8 and F12 samples causes *L* and *a* parameters to increase while *b* to decrease (bluish) respect to F4, which we consider now as the sample of control. The presence of IA and $ZrO_2$ in F12 and F13 system reduces gloss and no combined effect of the two fillers is revealed.

### *3.5.2 Colour results at W4*

After 4 weeks a considerable reduction of gloss parameter was recorded in all PBS based samples containing IA. The same behavior was also found when colourant was added. Moreover, a synergistic effect appeared when both additives are combined. The azo bond, which is known to be the most labile portion of an azo colourant, can readily undergo cleavage photochemical degradation [46]. Both, the effect of the cleavage in the polymer structure and the formation and regrouping of IA nanocrystals vary the manner in which the surface reflects light. The internal structure of the material becomes rougher and gloss is dominated by a diffuse reflection.

Only for PBS samples with $ZrO_2$ (F5 and F6) the gloss tends to increase with time. However, any combination of $ZrO_2$ either with IA or colourant or both, is dominated by the other two, obtaining fully dull gloss samples.

## 5. Conclusions

The present work demonstrates an industrial technology to produce biobased composites with enhanced colouring properties trough extrusion-compounding of complex blends. A methodology thought to design a biobased material with enhanced and ad-hoc aesthetical properties while maintaining the natural polymer performance. To this end, a diazo red colourant has been added to a bioPBS matrix. In order to increase the colour fixing, IA has been used with the aim of acting as compatibility agent between the matrix and the pigment as its structure is quite similar to acrylic acid, looking for a similar behaviour as in paints formulations. Lastly, as IA was also modifying other fundamental properties of bioPBS, $ZrO_2$ nanoparticles which have a similar natural colour as the bioPBS matrix, were incorporated to avoid decreasing stiffness and hardness. Besides, an aging effect was observed during the realization of the experimental work and their effects were characterised and compared (week 0 and week 4).

Regarding the mechanical properties, at W0 the addition of colourant and low amounts of $ZrO_2$ makes the material stiffer while it almost does not affect the elongation at break, making the material tough and ductile. The addition of IA provokes the desired effect as it maintains or even increase the young modulus (26% for 10wt% IA) while increasing the elongation at break (18% for 10wt% IA). Concerning hardness, it is reduced by the addition of the diazo pigment, as expected, while it is increased by the Zirconia at low loads. Combinations of colourant and $ZrO_2$ are found to produce a negative synergistic effect, decreasing by 82% the hardness value. In contrast, for low amounts of IA, hardness value is multiplied almost by four times, while higher amounts tend to soft the blend. Complex blends combining the colourant, $ZrO_2$ and IA shows a dominant behaviour induced by IA.

At W4, a prominent embrittlement is found due to an aging effect. A drop in the elongation at break by more than 98% can be observed in all the formulations containing IA, while the Young modulus rises by 60% to 70% showing a rigidization effect. This behaviour is accompanied by a softening of all samples being outstanding for those blends containing IA, losing their plastic deformation capacity. These loss in mechanical and hardness properties was corroborated by SEM and wettability results. When SEM micrographs were studied, IA nanocrystals were found to group themselves in a heterogeneous way showing a lack of compatibility between the IA and the matrix and a very accused separation of the phases. In addition, WCA results, showed a tendency to become the material more hydrophilic when IA was incorporated inducing biodegradability (hydrolysing effect with the water of the environment) and thus accelerating the degradation of the material.

Our findings on colour fixing show that, on the one hand, IA has an absorbance range somewhat lower than the red spectrum, so the material tends to slightly yellow the matrix; and, on the other hand, the high formation of IA nanocrystals shown by SEM micrographs, produces such a variation in the structure of the material that it modifies the way of scattering and absorbing light and decreases the gloss of the blend which is translated into a more matte finish. This effect is accentuated with time. $ZrO_2$ by itself increments the gloss of the material with time, but in ternary systems IA governs the overall behaviour.

To sum up, the use of IA might be a good candidate to be used as colour fixation agent. However, coupling techniques such as the use of reactive polymers (grafting to with i.e. peroxide initiators) or the use of compatibilizers (grafting from with i.e. amphiphilic structures) of IA with the PBS matrix should be further explored as these could favour the compatibility of the materials, therefore increasing their miscibility and avoiding the quick undesirable aging effect found on the materials (nor separation of phases, nor accelerated biodegradation), which would also affect the colour fastening and keep the gloss. These coupling techniques may be industrialised through adapted extrusion-compounding processes, as for example reactive extrusion (REX). Moreover, due to the natural absorbance ranges of IA, it would be a recommended strategy to be used for yellow to blue colourant pigments.

**Author Contributions:** L.G-Q. Conceived the work, carried out the preparation of the materials and the mechanical experimental work, contributed to the scientific discussion and wrote the manuscript.; J.V. collaborated in the hardness measurements; F.D. carried out the WCA measurements; D.P. performed the colour measurements and collaborated in the description of colour results; A.F. contributed to scientific discussion and reviewed the manuscript; P.C. designed the methodology, contributed in the interpretation of results and scientific discussion, got funding and reviewed the manuscript.

**Funding:** This research was funded by the Government of Aragón (DGA) under the project T08_17R 614 (I+AITIIP).

**Acknowledgments:** The authors acknowledge TORRECID for kindly provide the zirconia used for this research.

**Conflicts of Interest:** “The authors declare no conflict of interest.”

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