The Influence of Miscibility and Micro - structure on the Surface Defects of some Starch Bio – Hybrides

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The paper presents the effects of the miscibility and of the micro-structure on the surface defects of some bio – hybrides based on starch, polyvinyl alcohol (PVOH) and multilayered silicates. At macroscopic level (100μ) the studied starch bio-hybrids seem to be compact materials. If these materials are analysed at a microscopic level (10 μ) depending on their type surface defects like voids, cracks and fractures can be observed. These defects are not a consequence of a poor miscibility, even in case of bio-hybrids that contain untreated silicate. These defects appear because of the bio-hybrids micro-structure. As the new bio – hybrids are probably disorderly ones, it can be estimated that the surface defects appear as a consequence of a poor distribution of the swollen silicate tectoids into the polymeric matrix, possibly as a consequence of the improper melt processing conditions.

Keywords: polyvinyl alcohol, starch, multilayered silicate, surface defects, miscibility, bio-hybrides, micro-structure

Bio-nano-composites represent an emerging group of nano - structured bio - hybrid materials. They can be obtained by the combination of natural and synthetic polymers with inorganic solids. Bio – nano - composites have at least one nanometric scale dimension [1-6]. These bio-hybrids exhibit improved structural and functional properties which are of great interest for different applications [7-31].

Due to the water solubility of the polyvinyl alcohol (PVOH) and to the starch biodegradability, completely degradable packages can be obtained based on these two polymers. However, this task is not an easy one [11 -15].

The obtaining of starch and PVOH based nano-composites was studied considering many aspects [9-19] like: type of clay [11, 14], type of starch [12, 18, 19], type of modifier [16], type of additives [17], water absorption, a.s.o. [14]. Polymeric bio – hybrides can be characterized by methods like: spectroscopy , microscopy, gel permeation chromatography, birefringence [7,9,11,12,14,16,26-28,32-42].

It is well known that composites without surface defects, particularly voids, practically do not exist [20, 21]. If the voids represent more than 5 % of the entire volume, the mechanical properties of the material are lower by 30 % as compared to the properties of the same material without voids. The void content can be calculated with the help of dedicated formulas [21].

Obviously the void content of any material affects its operational properties because it may accelerate the material cracking and fracture, especially under the stress - strain conditions (fig. 1).

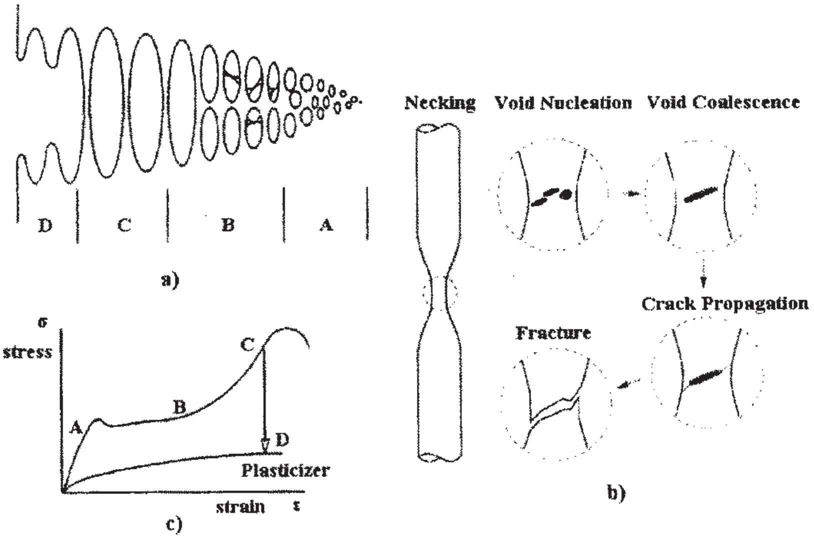

Fig 1 The mechanism of voids, cracks and fracture appearance in semi-crystalline polymers in stress – strain situation (involving neck formation) [22-24]
A – micro- voids ; B – the fibrils formation; C – The fibrils extension; D – The fibrils fracture

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The voids are almost exclusively located nearby the fillers, may exhibit lower (micro-voids) or higher (macro-voids) sizes and represent spaces filled with air around the fillers. These empty spaces depend on the filler shape.

The cracked materials contain primary fibrils scattered with voids oriented into the stress direction. The fracture is the creation of new surfaces within a solid especially under stress conditions [25]. In the case of semi – crystalline polymers, the void nucleation and coalescence is a result of necking under stress. The void coalescence and the crack formation are two processes that are simultaneous with the material fibrillation. The crack propagation through the fibrillated material is followed by an initiation of material fracture.

The properties of the filled polymeric materials are determined by the interactions between the fillers and the polymeric matrix. These interactions control the level of the cohesion energy between the matrix and filler and can be of physical nature (Van der Waals, hydrogen bonds, ionic interactions etc.) or based on chemical bonds [29-31]. If the cohesion energy is under a critical value, morphological defects such as voids, cracks and fractures can occur. The cohesion energy can be under a critical value if the miscibility between the blend components is poor or/and because of a poor distribution of the silicate lamellas or of the swollen tectoids into the polymeric matrix as a consequence of the improper melt processing conditions and / or because of all these reasons [15, 36, 37]. If the bonding energy between the silicate lamellas does not overpass a specific critical value then the intercalation with the polymer is not realised and the silicate tectoides maintain their integrity.

The effects of the component miscibility and of the micro-structure on the surface defects of some bio – hybrides based on starch, polyvinyl alcohol (PVOH) and multilayered silicates are studied in this paper.

Experimental part

This paper studies the effect of the component miscibility and of the polymeric bio-hybrids micro-structure upon the surface defects. The studied bio – hybrids are based on starch, polyvinyl alcohol (PVOH) and multilayered silicates.

Materials

Polyvinyl alcohol with hydrolyze degree of 99 , 0.5 – 1.8 % residual polyvinyl acetate, 27 – 33 cP viscosity, 1674 J / kg·K specific heat, vitreous transition at 82 °C, the melting temperature of 255°C, and crystalline content by 30.6% was provided by Du Pont;

Native starch from maize with 13.1% humidity, 2.2 % acidity, 4.9 *p*H, 70°C vitreous transition, 263°C melt temperature, 32% crystalline content was supplied by Sigma-Aldrich.

Silicates: Untreated (bentonite and peruvian Clay) and treated with trimethyldodecadecylammonium silicate (Nanocor I 28) ;

Proper ordinary melt processing additives like plasticizers and stabilizer were used.

Characterization

SEM - The surface defects were analyzed considering the number and the size of voids, cracks, fractures and the shape of the fracture areas. The SEM images were registered on a VEGA TESTAN microscope, at 30 kV. Before the examination at 500X resolution, the samples were cryogenically fractured into liquid nitrogen and then covered with a thin platinum layer. For analysing the surface defects of each studied bio - hybride, the areas of 40 x 40 μm were considered.

FTIR - The FTIR analysis was performed on a DIGILAB Scimitar FT-IR spectrometer, equipped with ZnSe crystal, via the Atenuated Total Reflectance (ATR) method. KBr pellets have been employed. The recording was carried out at 4 cm^{-1} resolution, using the average spectrum resulted from 5 spectra recorded for each compound. The spectrum was processed based on a Grams/32 software;

XRD – The XRD spectra were recorded on a DRON 2.0 diffractometer. Working conditions: step size by 0.03^0 (2 teta), scanning rate = 8 s / step, filter with λ = 1.7921 Å, diffraction range 2 – 15^0 (2 teta).

Results and discusions

At macroscopic level (100μ) the studied bio-hybrids seem to be compact materials. If these materials are analysed at a higher level (10 μ) then, depending on the silicate type, a random number of voids, cracks and fractures can be observed.

While the surface of the blends without silicate is really smooth (fig. 2), the surface of the materials with treated silicate (Nanocor I 28) is relatively homogenous and shows a minor number of voids, cracks and fractures (fig. 3). The surface of the PVOH – starch blends with untreated silicate contains several voids, cracks and fractures (fig. 4 – bio - hybrid with bentonite, fig. 5 – bio-hybrid with Peruvian clay) [15].

The surface aspect of the bio – hybrids with or without silicate depends on the affinity between the polymeric matrix and the silicate galleries. This affinity is controlled by the silicate gallery treatments and the silicate concentration. At low concentrations (max. 3 % silicate), the surfaces are more homogenous and have a few voids

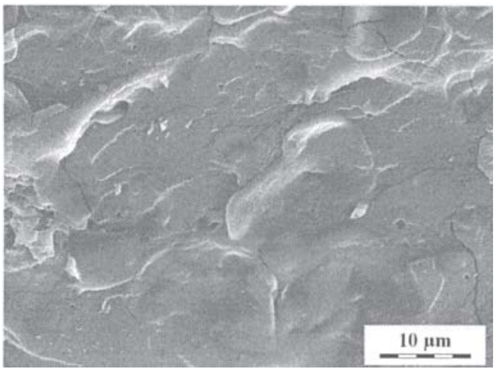

Fig. 2. SEM image of cryo-fractured surfaces of the blend of 1/ 1 PVOH - starch at 500 X resolution

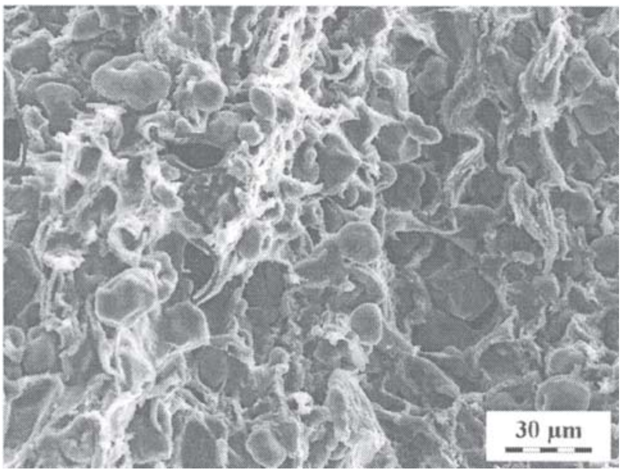

Fig. 3. SEM image of cryo-fractured surfaces of the blend of PVOH with starch and 3 % Nanocor I 28 at 500X resolution

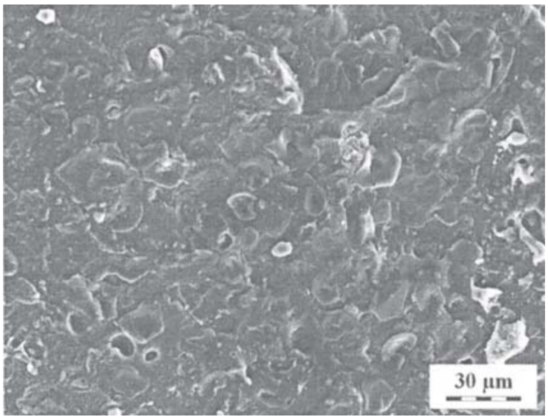

Fig. 4. SEM image of cryo-fractured surfaces of the blend of PVOH with starch and 3 % bentonite at 500X resolution

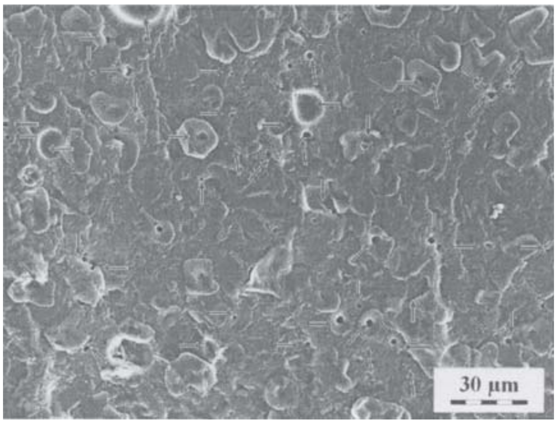

Fig. 5. SEM image of cryo-fractured surfaces of the PVOH – starch blends with 3 % peruvian clay at 500X resolution

or cracks if the silicate has been treated, and they have more defects if the silicate has not been treated. With concentrations higher than 3 %, the surfaces become non-homogenous and have frequent voids or/ and fractures, especially if the silicate was not treated [15].

The possibility to study the relationship among the bio-hybrid miscibility and the level of the cohesion between the bio-hybrid components is given by the FTIR spectroscopy [32]. The way in which the FTIR spectrum is affected may give information about the presence of specific interactions between the functionalities of the polymer and the other blend components. A change of the FTIR spectrum is therefore a qualitative criterion of miscibility. The nature of the information obtained by FTIR spectroscopy, as well as the confidence which may be placed in such conclusions, highly depend on the magnitude of the spectral changes being observed. The main FTIR spectral changes which can prove the blend component miscibility are: the gross / small changes and the significant spectral shifts [33, 34].

The “gross spectral changes” describe newly appeared spectral features or changes in the intensity by over 50 %. The “significant spectral shifts” describe the case when the same features are present in the spectra, but they have been shifted by more than a half height of the absorption peak, or have changed their intensity by more than 30 %. The “small spectral shifts” are shifts of < 10 cm^{-1} in the characteristic absorption peaks of the polymers used as a probe of the miscibility and polymer interactions. Generally, in assessing miscibility, the smaller the perturbation in the spectrum, the greater is the possibility of making mistakes.

The analysis of the spectra presented in figures 6, 7 demonstrates that the FTIR spectroscopy of the bio - hybrids based on PVOH, starch and Nanocor I28 renders as evident gross, significant and also small spectral changes as well as spectral shifts [35] in the following frequency ranges:

- 3600 cm^{-1} – 3000 cm^{-1} with the maximum at 47 cm^{-1} which defines the hydrogen bonds established between the O–H bonds. This maximum of absorption is displaced by 47 cm^{-1} as against the maximum of the two individual polymers from this range;
- 2920 cm^{-1} and 2854 cm^{-1}, which are displaced by 2 – 4 cm^{-1} as compared to the values observed in the case of silicate;
- 1800 – 1500 cm^{-1} can be linked to the absorbed water by the PVOH–starch–silicate bio-hybrids, because all the components are highly hydrophilic. Due to the width of this band one may appreciate that this compound is more hygroscopic than the two polymers. An increased hygroscopic characteristic can be determined by the presence of the silicate;
- 1500 – 1190 cm^{-1} associated with new secondary intermolecular forces between the bio - hybrids components, and with a higher crystallinity as compared with the individual components;
- 1190 – 970 cm^{-1}, associated with saccharide blends and an amorphous zone results in new secondary valence interactions between the components.

Based on the considered FTIR spectral changes it can be estimated that high miscibility does exist between the components of the bio-hybrids with Nanocor I 28 or bentonite. It can also be observed that the shape of the

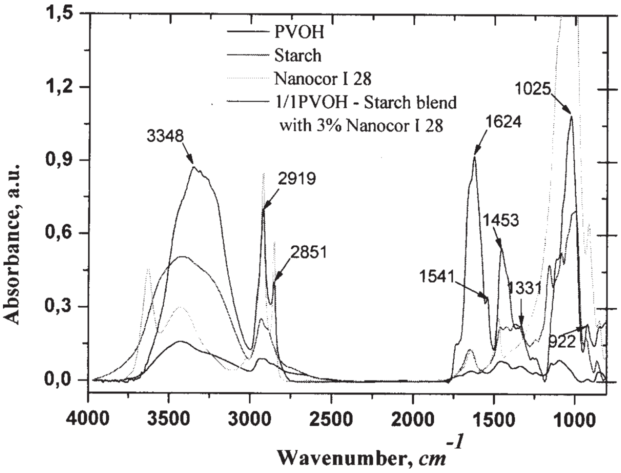

Fig. 6. The FTIR spectra of 50 % PVOH – 50 % starch – 3 % Nanocor I 28 blend

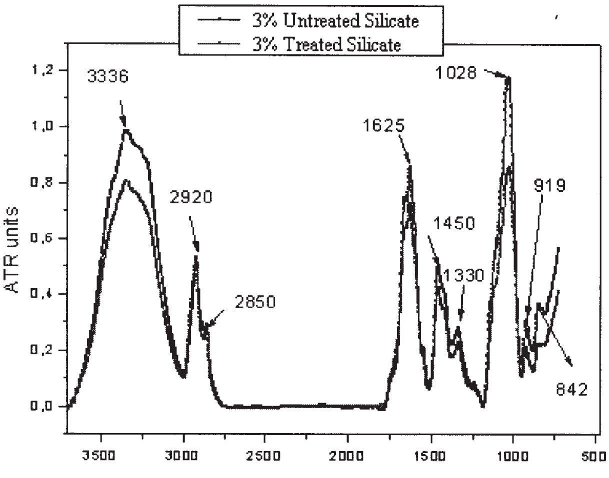

Fig. 7. FTIR spectra of byo-hybrides based on treated silicate and untreated silicate

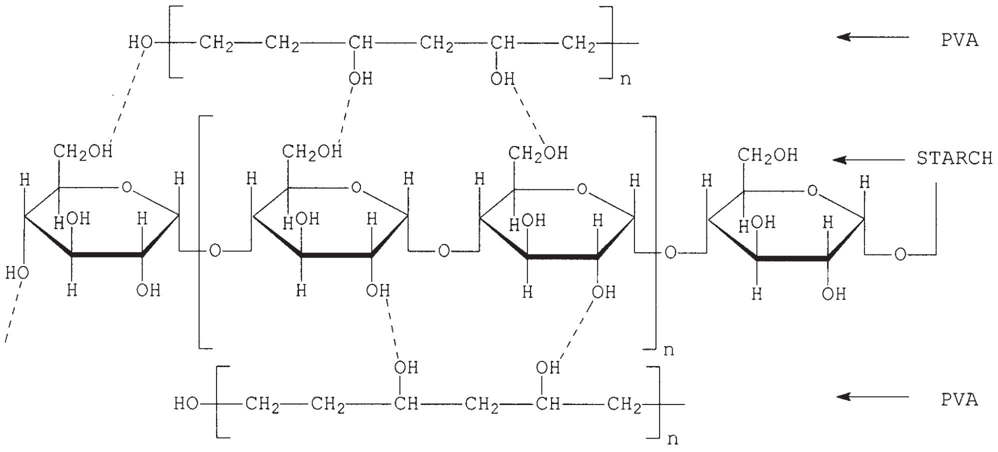

Fig. 8. Possible hydrogen bonds between the macromolecular chains of PVOH and starch established after the the polymer destructuration

Table 1

THE COMPARISON OF THE XRD DIFFRACTOGRAMES OF THE LAYERED SILICATES WITH THOSE OF THE BIO - HYBRIDES PVOH - STARCH - LAYERED SILICATES [39]

PVOH – starch with:	No. of the diffraction peaks Bio – hybride / silicate	Shifted degree of the diffraction angle, ^{0} Peak no.1/2	Galleries swelling size Å	Diffraction peaks intensity, Bio - hybrides / silicate Counts/s /counts / s Peak no.1/2	Type of the resulted bio - hybrides
Nanocor I 28	2 / 2	1,83 / 2,18	20	1. 20/60 2. 40/150	Intercalated
Bentonite	1 / 1	3,80	7,88	50/100	Intercalated

spectrum of bio - hybrids that contain un-treated silicate is almost the same with the shape in the spectrum of materials with treated silicate. The differences lie in the fact that the specific peaks of material with treated silicate are higher and / or tighter than the peaks in bio – hybrids with un-treated silicate. These changes prove that the component miscibility from the bio - hybrid with un-treated silicate is lower, and that the differences between the two situations are not significant.

All the above results demonstrate that the hydrogen bonds between the PVOH chains and the starch were broken and new bonds were established, this time between PVOH and starch, and possibly the silicate, when the exfoliation and the dispersion of the resulted lamellas has been reached (fig. 8).

Under these circumstances, it can be concluded that the surface defects of the new bio – hybrids based on starch are not a consequence of the poor miscibility between the components, even in the case of the bio – hybrids with un-treated silicate.

Transmission electron microscopy (TEM) and X ray diffraction (XRD) especially by small angle have been extensively used in the characterization of polymer nanocomposite micro – structure [38].

The transmission microscopy allows a qualitative understanding of the various phases of the matrix distribution. The XRD gives information about the micro – structure if the following bio - hybrid diffraction characteristics are compared with those of the silicates: number of the diffraction peaks, shifted degree of the diffraction peaks, diffraction peak intensity, silicate galleries swollen degree. In the XRD diffractograme a fully exfoliated system is characterized by the absence of the diffraction peaks in the 1.5 – 10^0 range ($1.5\,^0 \le 2\theta \le 10\,^0$) which corresponds to a d-spacing of at least 6 nm [38-41].

According to our own results concerning the study of PVOH - starch bio – hybrids, the degree of intercalation of the two polymers with the layered silicate is increased if NaMMT is used or if the multilayered silicate is intercalated with ammonium ions that contain small radicals (like Nanocor I 28) [36]. The bio – hybrids with NaMMT seem to

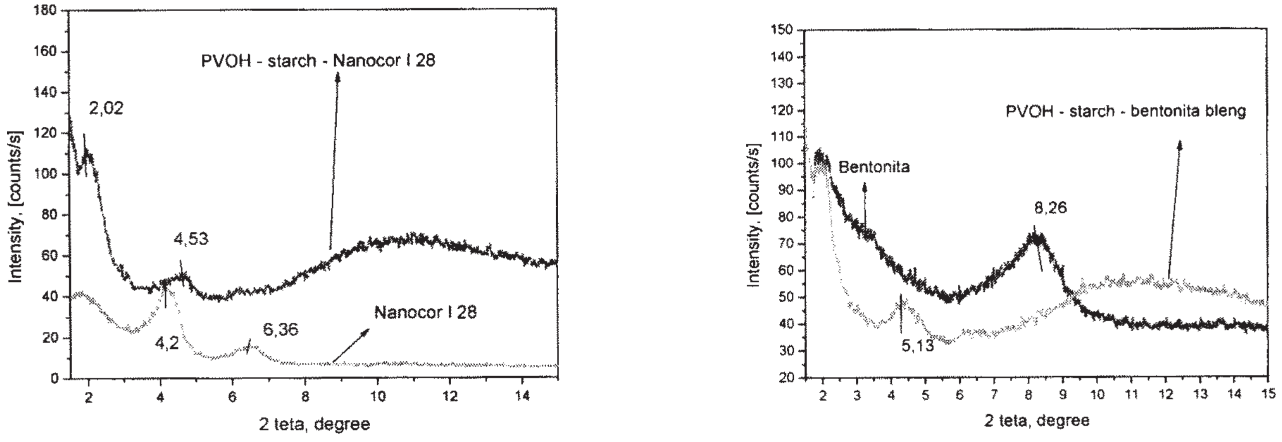

Fig. 9. The XRD diffractogrames of the PVOV – starch bio-hybride with Nanocor I 28 (a) and bentonite (b) [39]

a)

b)

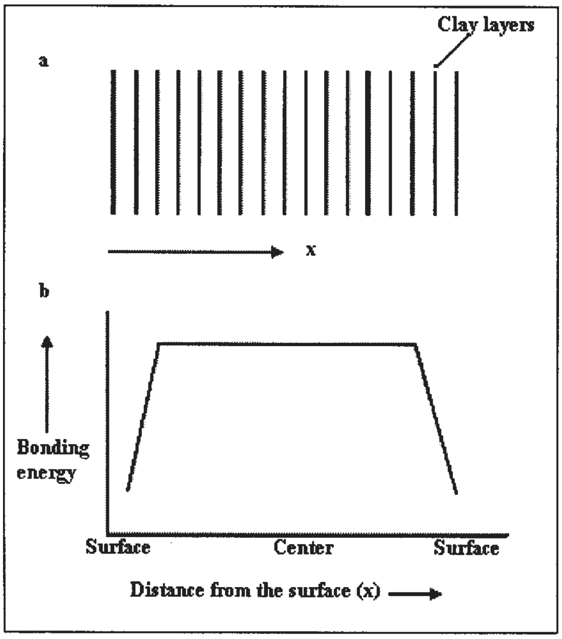

Fig. 10. The relationship between the ionic bonding of the layers in the silicate tectoid (a) and (b) Variation of the bonding energy along the thickeness of the tectoid [36]

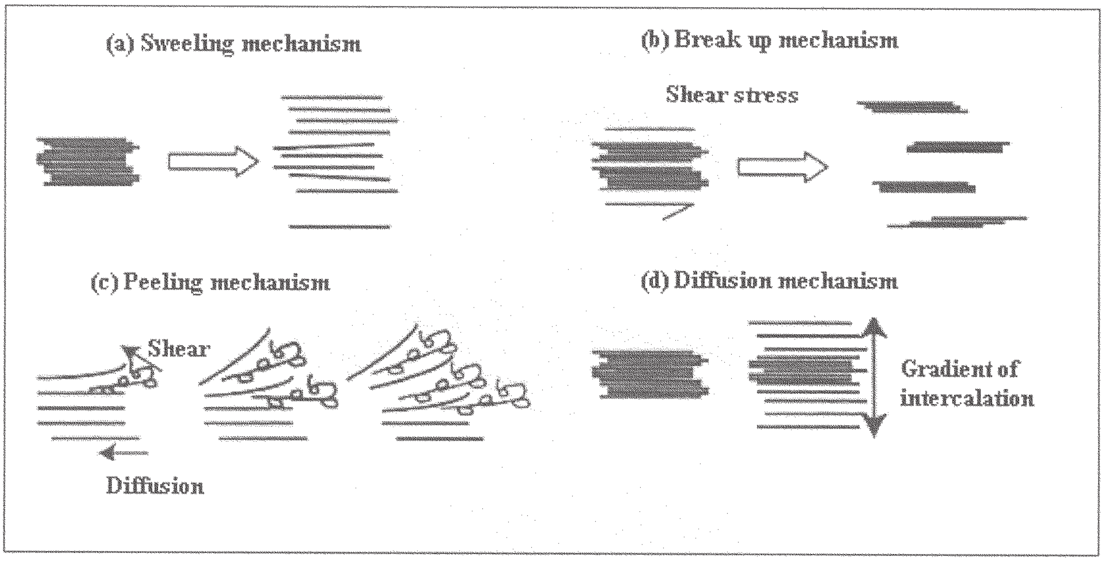

Fig. 11. The possible mechanisms of polymer / layered silicate intercalation [37]

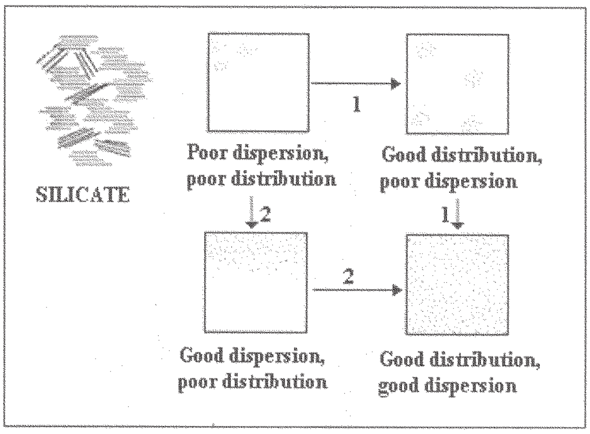

Fig. 12. The dispersion and distribution of the multilayered silicate through a polymeric matrix[37]

be exfoliated and those with Nanocor I 28, Nanocor I33, Cloisite 15 A or bentonite are of an intercalated type (fig. 9, table 1). If the bio – hybrid is reinforced with Cloisite 93A micro-composites can be obtained [42].

Considering that the new bio – hybrids are probably intercalated nanocomposites one can estimate that a reason of the surface defects of the studied bio – hybrids can be the poor distribution of the silicate tectoides into the polymeric matrix. The melt shear stress was probably too small to surpass the bonding energy between the silicate lamellas (fig. 10) and to start the swelling and /or breaking up and / or peeling mechanism that determines the tectoides delamination (fig. 11). In such situation it is possible that evenly the distribution of the tectoides into the polymeric matrix to be a disordered one (fig. 12). This hypothesis seems to be sustain by other own results [12] according to which, certain among studied bio – hybrids based on PVOH, starch and untreated silicate melt un-homogeneously (considering the shape of the melting peaks). The poor dispersion of the tectoids into lamellas and distribution of the tectoides into the polymeric matrix can be a consequence of the obtaining of the bio – hybrids into improper melt processing conditions.

All the aspects concerning the degree of structural order in the new starch and PVOH based bio – hybrids will be presented in a future paper.

Conclusions

The effects of the component miscibility and of the bio-hybrides micro-structure on the surface defects of some bio – hybrides based on starch, polyvinyl alcohol (PVOH) and multilayered silicates are presented. The surface defects, miscibility and micro – structure were estimated based on SEM, FTIR, and XRD techniques.

At macroscopic level (100 μ) the studied bio-hybrides seems to be compact materials. If these materials are analysed at higher level (10 μ) then dependeing of type, a random number of surface defects like voids, cracks and fractures can be observed.

The FTIR spectra of the new bio - hybrides are entirely different than that of the individual polymers, reason that can be considered a proof for the miscibility between bio - hybride components. The surface defects of the new bio – hybrids based on PVOH and starch are not a consequence of a poor miscibility between the blend components, even in case of the materials that contain un-treated silicate.

Taking into account that according to the XRD diffractogrames the new bio – hybrids are intercalated nanocomposites can be assess that the reasons of the surface defects are the poor distribution of the silicate tectoids into the polymeric matrix, probably because of the melt processing into un-proper conditions.

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