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PVA/PTFE nanocomposites: Thermal, mechanical, and barrier properties

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In the last 20 years a great scientific and industrial interest has been focused on nanostructured materials [1–2]. In this scientific area a particular interest has been devoted to polymeri-based nanostructured materials [3–8]. They are multiphase systems where one phase (inorganic or organic) is present on the nanometer level.

If well dispersed in the polymeric matrix, the nanometer phase offers a major specific surface area enhancement of the interfacial interactions with the matrix compared to conventional reinforcements, and consequently improves the physical properties of the material [9–16].

In recent years many researchers focused on the introduction of a new class of polymeric commodity nanocomposites and to develop the related technologies to help solving clear user problems [17]. A particular interest is devoted on new polymeric high-performance thermoforming nanocomposites for packaging with enhanced mechanical and barrier properties.

In this communication, results concerning poly(vinyl alcohol) (PVA) filled with polytetrafluoroethylene (PTFE) nanospheres are reported.

PVA polymers are strong, tough materials that can be easily obtained in a variety of molecular weights and they exhibit susceptibility to biodegradation. They are characterized by a low gas and vapor permeability and by a complete transparency. Unfortunately, they also have a poor thermal stability and the gas permeability tends to increase with the increase of moisture. Moreover, tensile strength and Young's modulus decrease with increasing relative humidity. These drawbacks reduce their exploitation in many packaging applications [18]. Finally, another limit in using poly(vinyl alcohol) is that it is generally not melt-processable, since its decomposition temperature is lower than its melting point.

On the other hand, PTFE is an indispensable material for industry because of its unique combination of high thermal, chemical, aging and weather resistance, excellent inertness, low flammability with high purity, and lubricant and dielectric properties.

Recently, Solvay Solexis technology [19] has allowed the preparation of PTFE particles from 10 to 100 nm by utilizing the perfluorinated microemulsion polymerisation with a high conversion latex concentration and relating low surfactant content.

The aim of the present research has been focused on the possibility to improve some PVA properties by filling with PTFE nanoparticles in order to extend its applicability.

PTFE nanoparticles, characterized by a dimensions range from 26 to 30 nm, were furnished in an aqueous dispersion (20 wt%) by Solvay Solexis S.p.A. (MI). It is known that water is also a solvent for PVA, and so nanocomposites preparation was performed in a water solution.

In particular the samples were prepared by adding to a solution previously obtained by dissolving PVA powder and glycerol (30 wt% of PVA phase) in 0.05×10^{-3} m^3 of water at 90 °C under magnetic stirring, a PTFE aqueous dispersion in different amount, obtaining materials with 2, 4 and 6 wt% of nanoreinforcements. Successively the solution-cast films were formed by pouring the aqueous solution onto a plate and subsequent drying at room temperature. The morphological characterisation on the samples and the degree of PTFE nanoparticles dispersion within the polymeric matrix were investigated by a SEM 501 Philips microscope on cryogenically fractured surfaces, see Figs 1–3. From these figures it can be easily observed that a high number of PTFE particles are covered and quite fused to the PVA. In the case of the nanocomposite containing the highest nanofiller amount (6 wt%), some particles are protruding from the surface, but no pullout phenomena are evidenced by the presence of voids.

These observations suggested that the preparation methodology used is able to obtain a homogeneous and fine dispersion of the nanoparticles into polymeric matrix and a good adhesion level.

In fact, it is known that the use of a common solvent often prevents the formation of nanoparticles agglomerates, which naturally occurs, because of a lowering of the polymer viscosity and a consequent improvement of the incorporation of the nanopowders.

The thermal stability of the samples was investigated by thermogravimetric analysis (a Mettler TG 50). The samples were heated, under nitrogen atmosphere, from 40 to 650 °C at a rate of 10 °C/min. The trends of the obtained curves, describing the samples weight loss against the temperature, are reported in Fig. 4.

The presence of PTFE nanoparticles improves the resistance of PVA nanocomposites to degradation

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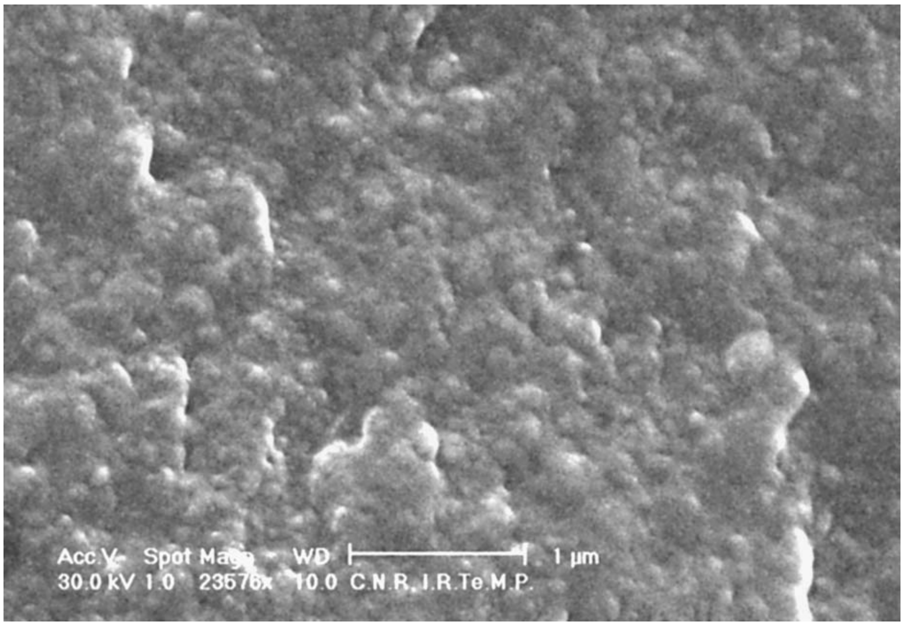

Figure 1 SEM micrograph of PVA/PTFE 2% fractured surface.

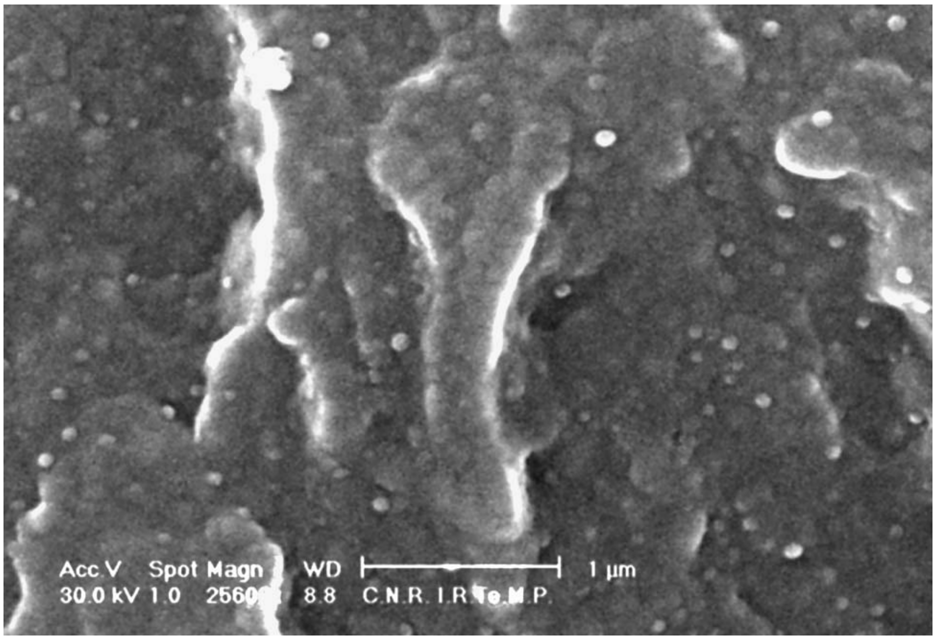

Figure 2 SEM micrograph of PVA/PTFE 4% fractured surface.

especially at temperatures higher than 350 °C. In fact the nanocomposites still gave a residue even at 400 °C for which the remainder ranged between about 30 and 50% depending on the PTFE nanoparticles content, while the PVA homopolymer at that temperature was almost completely degraded. This improved thermal stability can be attributed to a restricted thermal motion of PVA and to the hindered diffusion of volatile decomposition products within the nanocomposite because of homogeneous dispersion of PTFE nanoparticles. This finding is important because it means that these PVA nanocomposites could be used at high temperatures, where normally PVA materials are not employable.

Dumb-bell-shaped specimens were cut from the films according to ASTM D-638 standard and used for mechanical tensile measurements. Stress-strain curves were obtained by an Instron machine (Model 1122) at room temperature and at a cross-head speed, V_t, of 10 mm/min.

Generally speaking, the mechanical performances of polymer composites are strongly correlated to the reached interfacial strength between the matrix and the reinforcing phase. If the interface between the two components is good, the external load will be transferred from the polymer matrix to the reinforcement through the interface and the mechanical performances of the composite increase. On the contrary, if the interface it not strong enough, it will become a break point of the material and the mechanical behavior will be poor. The same concept can be applied in the case of nanocomposites. In our case, as can be seen from the values reported in Table I, the PVA/PTFE nanocomposites have shown

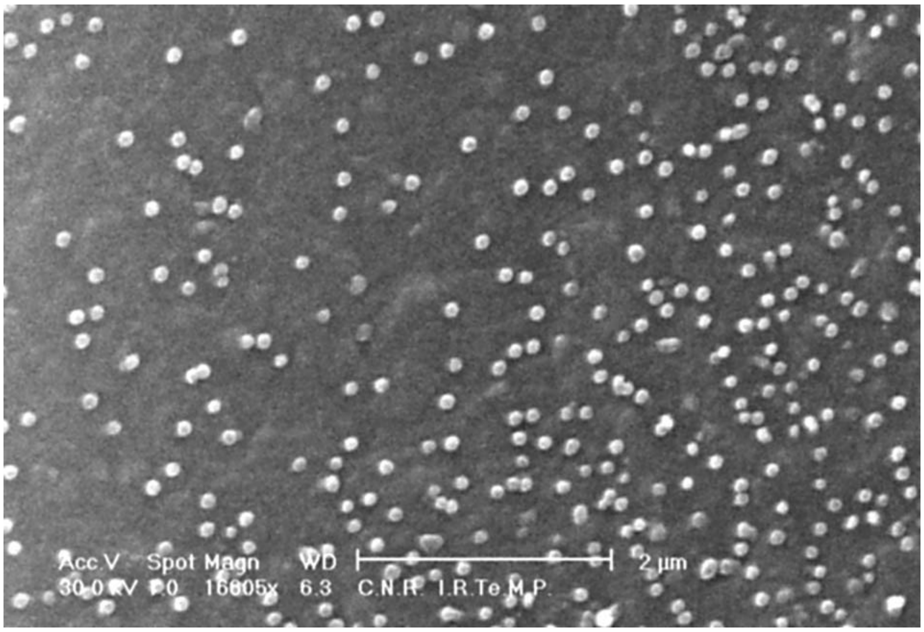

Figure 3 SEM micrograph of PVA/PTFE 6% fractured surface.

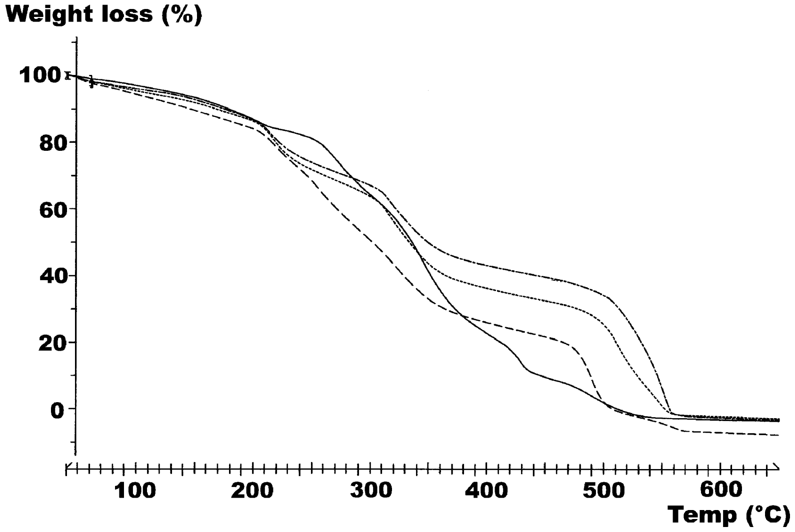

Figure 4 TGA analysis: ____ PVA, _ _ _ PVA/PTFE 2%, ... PVA/PTFE 4%, ._._. PVA/PTFE 6%.

an increase of Young's modulus with respect to that found for PVA homopolymer.

As a consequence of this modulus increasing, the mechanical parameters of break (strain and strength) present lower values than the PVA matrix. Moreover, the PTFE addition produces a strong increase of the toughness (80–90% with 6% of nanoparticles). These results can be explained on the basis of nanofiller nature and properties and of the homogeneous nanopowder distribution reached.

As is well known because of their small dimensions, nanocomposites could have superior physical and mechanical properties compared to those of conventional microcomposites and thus simultaneous strong increase both of modulus and impact strength are not surprising. Similar cases in the literature were already observed and discussed [20]. In these systems nanoparticles functionalization was a key step in order to obtain their homogeneous dispersion and to improve mechanical parameters.

As also shown, our nanomaterials presented strong improvements of moduli and impact properties by adding PTFE nanopowder in the PVA matrix. These results probably are still due to the good dispersion and interface realized as already evidenced from the morphological analysis.

As discussed above, the PTFE nanoparticles used without any coating agent are able to disperse themselves in the matrix generating a good interfacial adhesion as well. This can be explained by the polymeric nature of PTFE particles that is organic, and then compatible with the polymeric matrix. Moreover, their homogeneous dispersion was also possible owing to the high

TABLE I Tensile properties of PVA and PVA-based nanocomposites

Sample	Young's modulus (MPa)	% Strain at break	Stress at break (MPa)	Toughness (MPa)
PVA	112	410	16	20
PVA/ PTFE 2%	138	308	9.5	26
PVA/ PTFE 4%	149	270	10	36
PVA/ PTFE 6%	151	250	10	38

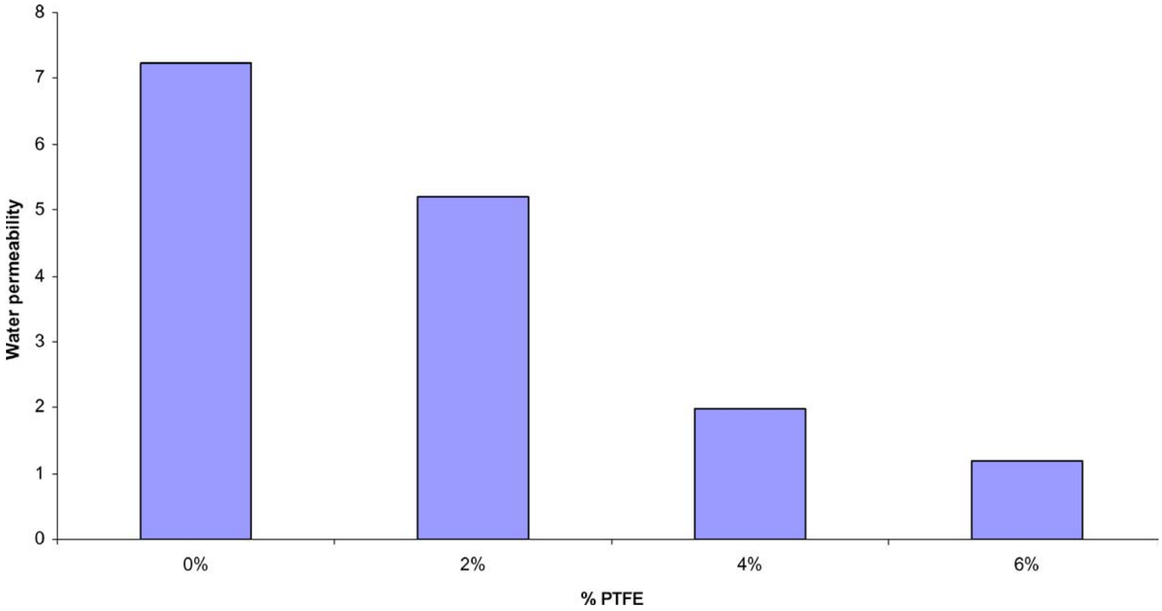

Figure 5 Influence of PTFE amount on PVA water permeability (10^{-4} g/m^2 s atm).

specific autolubrificant characteristic of PTFE material that allows to gain a low degree of clustering among the nanoparticles.

Finally, measurements of water permeability according to ASTM E 96-80 method were performed in order to investigate if the presence of PTFE nanoparticles can influence positively the water permeability of PVA. Samples, with thickness and weight checked, were fixed on standard cups previously filled with distilled water. The weighed cups were put in a chamber having a temperature and relative humidity control device at 40 °C and 55% RH. After 24 hr their weight was recorded. Moreover, the films were reweighed to determine the amount of water absorbed during the experiment.

This test outlined the strong influence on the barrier properties of PVA due to PTFE nanoparticles presence. In Fig. 5 the water permeability values of PVA-based materials filled with the PTFE powders are reported.

It is easy to note that the presence of nanoparticles strongly influences the water permeability. For example, in the case of PVA/PTFE 6% sample the permeability is reduced of more that 80% passing by 7.24×10^{-4} value for PVA to 1.2×10^{-4} g/m^2 s atm for PVA/PTFE 6%.

These results can be explained on the basis of the following:

- The unique and unexpected properties of polymer-based nanocomposites are strictly correlated to the enormous specific surface of the nanoparticles and consequently to the large potential interfacial region.
- A homogeneous distribution of nanoparticles will provide a coating on the polymer surface avoiding an easy penetration of water (permeant). Thus, if the coating is thick, it is more difficult for the water molecules to penetrate owing to a long "tortuous path" that they have to cover.

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