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Influence of Processing Method and Components Molecular Structure on the Phase Behaviour of Polyethylenes/Dye Blends

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Summary: The phase dispersion of terthiophene alkyl derivatives on different polyethylene matrices was investigated. The PE affinity toward dichroic dyes with different structure, the effect of blending process and the influence of a polyolefinic compatibilizer on the homogeneity of host-guest blends were comparatively investigated by calorimetry, DSC and SEM analyses. For these purposes, polyethylenes with different molecular weights and densities and EVAc were used as host matrices. The polymeric compatibilizer was prepared by radical functionalization of a commercial low density polyethylene. The dichroic nature of the guest phase allowed to perform UV-Vis measurements in polarized light on oriented blend film samples. The dyes affinity toward PE is one of the key factor in obtaining oriented polyolefinic films with high optical performances for several applications.

Keywords: dichroic blend films properties; melt-processing; phase dispersions; polyolefinic blends; solution-casting

Introduction

Multicomponent polymeric materials based on conventional polyolefins and polar polymers or guest aromatic molecules present a great importance because they allow the optimization of their properties compared with the isolated components. For this purpose, the miscibility and the phase behaviour of polymer blends have received much attention due to the difficulty to obtain materials with good phase dispersion. It has been demonstrated that phase separations phenomena lead to materials with poor mechanical,[1] electronic[2] and optical[3] properties. In this work the phase and the dispersion behaviour of blends based on guest dichroic functionalized terthiophene dyes and host polyethylenes were studied by varying the structure

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of the guest molecule and the type of blending process utilizing different processable polyolefinic matrices. In addition, in order to reduce the interfacial tension[4] between the components of the blend and to improve consequently their phase dispersion, the effect of a polyolefinic compatibilizer on the phase behaviour of these systems was investigated. The functionalization of polyolefins with polar monomers seems to be the favourite route to prepare polymeric compatibilizers due to the good availability of the materials and the extensive knowledge of the process. Indeed, it was demonstrated that functionalization degrees of about 2 mol-% of modified olefinic polymers positively affect the dispersion of the two phases of incompatible polymer blends leading to materials with better properties and performances.[5] The dispersion behaviour of host-guest materials were analyzed by calorimetry, differential scanning calorimetry (DSC) and microscopy. In addition, due to the dichroic nature of the guest chromophores,[6] the homogeneity of the blends prepared was also investigated by UV-Vis spectroscopy in polarized light, monitoring the anisotropic behaviour of the binary blend films after tensile deformation at high temperature. The key property to characterise the molecular orientation in such systems is the dichroic ratio[7] (R) defined by the equation $R = A_{//}/A_{\perp}$, where A is the respective absorbance and the subscripts // and ⊥ denote, respectively, the direction parallel or perpendicular to the drawing direction. These results were discussed and used for the preparation of dye/polyolefin blends with specific thermo-mechanical properties and suitable optical performances for applications as linear polarizers.

Experimental

Apparatus and Methods

^{1}H- and ^{13}C-NMR spectra were recorded by a Varian Gemini-200 MHz spectrometer on 5-10% $CDCl_3$ (99.6+ atom % D, Aldrich) solutions. NMR spectra were recorded at 20°C and the chemical shifts were assigned in ppm using solvent signal as reference. FT-IR spectra were recorded by a Perkin-Elmer Spectrum One spectrophotometer by deposition of a drop of liquid between two KBr windows or on dispersions in KBr. Mass spectra were recorded with a Varian Saturn 2000 connected to a gas-chromatograph Varian 3800, on solutions of diethyl ether. The melting points were accomplished by a Reichert Polyvar optical microscope with crossed polarizers, equipped with a programmable Mettler FP 52 hot stage. Elementary analyses were made by microanalysis laboratories at the Faculty of Pharmacy, University of Pisa. Optical absorption studies were carried out in dioxane ($5\cdot10^{-5}$ M) solutions with a Jasco 7850 UV-Vis spectrophotometer or on polymer films in polarized light with the same instrument, fitted with Sterling Optics UV linear polarizer, or with a Perkin-Elmer Lambda 900, fitted with Glan-Thomson polarizers. Differential scanning calorimetry (DSC) analysis were performed by a Perkin-Elmer DSC7 calorimeter equipped with a CCA7 cooling device. The calibration was carried out by using Mercury (m.p. –38.4°C) and Indium (m.p. 156.2°C) standards for low-temperature scans and Indium and Zinc (m.p. 419.5°C) for high-temperature ones. Heating and cooling thermograms were carried out at standard rate of 10°C/min. The Scanning Electron Microscopy (SEM) analysis was performed with a Jeol 5600-LV microscope, equipped with Oxford X-rays EDS microprobe, instrument at the Chemical Engineering Department of Pisa University. Polymer processing were performed by a Brabender plastograph mixer (mod. OHG47055, 30cc) under nitrogen atmosphere. A Campana PM20/200 press was used for moulding the polymeric samples. Heat of solution measurements were performed by a Calvet type differential calorimeter Mod. BT-200 from SETARAM (France).

Materials

All reactions of air and water sensitive materials were performed under an atmosphere of argon or nitrogen, using glassware which was previously flame-dried at reduced pressure (0.05 mbar). The solvents used in the reactions (Aldrich, J.T. Baker, AnalaR, Fluka and Carlo Erba) were dried by conventional methods and freshly distilled under an inert atmosphere. Spectroscopic grade dioxane (Aldrich) was used for the absorption experiments in solution. 5,5”-bis-thiooctadecyl-2,2’: 5’,2”-terthiophene ($C_{18}S$-TT-SC_{18}) was synthesized as described in a previous work.[8] Very Low Density Polyethylene (VLDPE) supplied by EniChem (Italy) is characterized by 9 mol.-% of 1-butene as comonomer, melt flow index = 1.6 g/10min (190°C/2.16 kg, ISO 1133) and density = 0.9 g/cm^3. Ultra High Molecular Weight Polyethylene (UHMWPE), $\overline{M}_w = 3.6\cdot10^6$, density = 0.928 g/cm^3 (Stamylan UH210, DSM, The Netherlands) and Ethylene-Vinyl Acetate copolymer (EVAc, Greenflex FF35), supplied by Polimeri Europa (Italy) and characterized by 9 wt.-% of vinyl acetate and melt flow index = 1.6 g/10 min (190°C/2.16 kg, ISO 1133) were used as polymer matrices.

Film Preparation by Solution Casting

0.5 g of UHMWPE and the appropriate amount of chromophore were dissolved in 75 ml of *p*-xylene at 125°C and stirred until complete dissolution occurred; the solution was then cast on a cold glass and slowly evaporated, first at room temperature, then at 50°C. For the compatibilized sample, a 1:1 by weight respect to the dye amount of the polymeric additive was co-dissolved in xylene before adding UHMWPE.

Film Preparation by Mechanical Mixing

The blends and the polymer thin films were prepared according to a procedure previously reported.[7]

Polymer Orientation

Solid state drawings of the host-guest films was performed as reported in literature.[6]

Functionalization of VLDPE with Diethyl Maleate (VLDPE-g-DES)

The radical bulk functionalization of VLDPE was carried out according to procedures previously reported.[9] The determination of the functionalization degree (FD) was performed by proton nuclear magnetic resonance (^{1}H NMR) and infrared spectroscopy (IR). In the latter case, on the basis of Fodor et al.,[10] known amounts of PE and poly(diethyl fumarate) were mixed to give a composition close to that predictable for the functionalized polymer (from 1 to 6 –COOEt groups per 100 ethylene) in order to build a calibration curve. Poly(diethylfumarate) was previously prepared by radical polymerization of diethylfumarate according to a literature procedure.[11]

Results and Discussion

Three different strategies were accomplished in order to prepare host-guest polymeric systems with improved phase dispersion. In particular, the chemical structure of the guest dichroic molecule, the influence of the type of blending process and the use of VLDPE-g-DES as a polymeric compatibilizers were investigated.

Influence of the Structure of Terthiophene Based Dyes

The guest phase studied in our works is represented by dichroic terthiophene chromophores functionalized by long thio-alkyl lateral chain and different electron withdrawing groups.[6] In a recent work[12] it was demonstrated that the structure of the alkyl lateral chain of the dye plays a fundamental role on the molecule phase dispersion into UHMWPE films prepared by solution-casting. In particular, the favoured molecule's dispersion was achieved by functionalizing the aromatic terthiophene's core with a branched alkyl chain, 5"-thio-(3-butyl)-nonyl-2,2':5',2"-terthiophene (1), conferring the chromophore a very low tendency to crystallize. Actually, branched chromophore (1) is liquid at room temperature (m.p.= -5.6°C; ΔH_m= 21.4 J/g) whereas the linear one, 5"-thiooctadecyl-2,2':5',2"-terthiophene (2), obtained by functionalizing the terthiophene molecule with a long linear chain, presents higher melting temperature and crystallinity (m.p.= 82/91°C, ΔH_m= 122.3 J/g). As proposed in previous papers[7,13] the crystallinity of the dye plays an important role in controlling the thermodynamic of mixing. For this purpose, a group contribution procedure based on modified UNIQUAQ equation[14] was developed[15] to predict the enthalpy of mixing of all terthiophene molecules functionalized by an alkyl lateral chain. At a fixed entropy of mixing, the solution enthalpy has been considered as an index of the solute affinity for *n*-heptane, and then for linear PE, rather than a real miscibility indicator. As evidenced by the plotted curve reported in Figure 1, this quantity decreases increasing the number of carbon atoms of the alkyl chain.

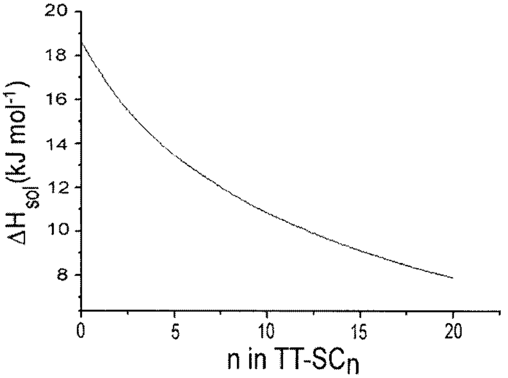

Fig. 1. Calculated ΔH_{sol} of terthiophene molecules as a function of the number of carbon atoms in the alkyl chain.

At the same time, heat of solution measurements between the alkyl terthiophene derivative and polyethylene were measured by calorimetry dissolving at 25°C the chromophore in *n*-heptane used as an *analogue* of linear PE. The $\Delta H_{sol} = 9.5$ kJ·mol^{-1} measured for the branched dye (1) whose alkyl chain is composed by 13 carbon atoms, confirmed the effectiveness of the theoretical procedure. Thus, while the introduction of alkyl linear chains on the terthiophene nuclei increases its chemical affinity for PE, the whole dissolution process is made less favoured due to the contemporary increase of molecule's crystallinity. Hence, it is confirmed by calorimetry that the branched alkyl functionalization represents the best compromise for optimized chromophore dissolution into polyethylene matrices.

Influence of the Blending Process: Use of Processable Polyethylenes as Host Matrices

Different works have been performed in these years in order to increase the dispersion of the guest phase into the polymeric matrix by changing the type of blending process.[16,17] Respect to polymer blends obtained by casting of dilute solutions, characterized by molecular segregation of the guest phase from the host matrix, the melt blending technique leads to multicomponent materials with much better phase dispersions. It has been recently[8] demonstrated that the melt processing of dichroic chromophores and polyethylenes with different molecular weight and density (HDPE and LLDPE respectively) allowed to obtain homogeneous materials leading to devices with better optical performances. According to these results, new blends based on 0.2-0.5 wt.-% of the easy prepared terthiophene derivative (C_{18}S-TT-SC_{18}) functionalized by two long linear thio-alkyl lateral chains and EVAc as polymer matrix were prepared by melt-processing in a Brabender mixer. The scanning electron microscopy images of the sections of the films prepared by compression moulding of melt-processed blends based on EVAc or polyethylenes and C_{18}S-TT-SC_{18} revealed that the polymer matrix with a significant content of polar groups (EVAc) allowed a more effective distribution of the dye within the polymer bulk (Figure 2). Actually, the distribution of the chromophore along a section of LLDPE and HDPE films is just near the contact surface polymer-air, whereas it appears very similar on the polymer film surface of both three host matrices.

In order to evaluate how the chromophore dispersion could affect its orientational behaviour and the anisotropic properties of the host-guest films, UV-Vis spectra were performed exciting the oriented polymer samples with a linearly polarized radiation respectively parallel and perpendicular to the drawing direction.

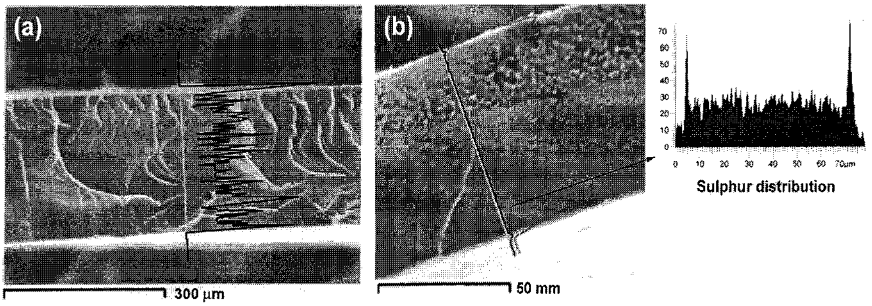

Fig. 2. Scanning electron micrographs and sulphur concentration profiles on the sections of EVAc (a) and LLDPE (b) based films ($C_{18}S$-TT-SC_{18} concentration = 0.5 wt.-%).

Table 1. Dichroic parameters of oriented films prepared by melt-processing.

Blend	Polymer	$C_{18}S$-TT-SC_{18} (wt.-%)	λ	R
LL-0.5	LLDPE	0.5	8	3.9
LL-0.5	LLDPE	0.5	12	11.4
LL-0.2	LLDPE	0.2	10	6.5
LL-0.2	LLDPE	0.2	12	10.6
HD-0.5	HDPE	0.5	8	5.3
HD-0.5	HDPE	0.5	12	10.8
HD-0.2	HDPE	0.2	9	5.7
HD-0.2	HDPE	0.2	12	10.0
EVAc-0.5	EVAc	0.5	3	3.2
EVAc-0.5	EVAc	0.5	8	4.4
EVAc-0.2	EVAc	0.2	3	3.5
EVAc-0.2	EVAc	0.2	8	7.3

The anisotropic behaviour of the films reported in Table 1 as a function of the drawing ratio (λ, defined as the ratio between the length of the sample after and before the stretching of the film respectively) revealed interesting dichroic ratio (R) values for films based on EVAc denoting a good tendency of the chromophore to align along the oriented fibres of the copolymer. Comparing the dichroic behaviour of all the oriented blends prepared by melt processing, EVAc-0.2 showed the highest dichroic ratio (R= 7.3) at λ maximum (λ= 8).

Influence of the Polymeric Compatibilizer on the Chromophore Dispersion into UHMWPE

The degree of functionalization (FD), defined as the number of functional groups grafted on the polyolefin backbones per 100 repeating units (FD in mol-%), evaluated by IR using a calibration curve and ^{1}H NMR spectroscopy calculating the integrals of the diagnostic signals, and the molecular weight of VLDPE-g-DES are reported in Table 2.

Table 2. VLDPE-g-DES features.

Polymer	FD (mol-%)[1]	FD (mol-%)[2]	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
VLDPE-g-DES	1.7	1.8	76400	363900	4.8

[1] evaluated by IR; [2] evaluated by ^{1}H NMR

The effect of VLDPE-g-DES on the phase dispersion of $C_{18}S$-TT-SC_{18} into UHMWPE films prepared by casting of xylene solutions (Table 3) was evaluated by SEM, DSC and by optical analyses.

Table 3. UHMWPE blends prepared in this work.

Blend	Polymer	$C_{18}S$-TT-SC_{18} (wt.-%)	VLDPE-g-DES (mg, [wt.-%])
UH3-3	UHMWPE	3	-
UH3-VL	UHMWPE	3	15, [3]

SEM images of UHMWPE films revealed an increased phase dispersion of the chromophore in host-guest systems containing the polymeric compatibilizer (Figure 3).

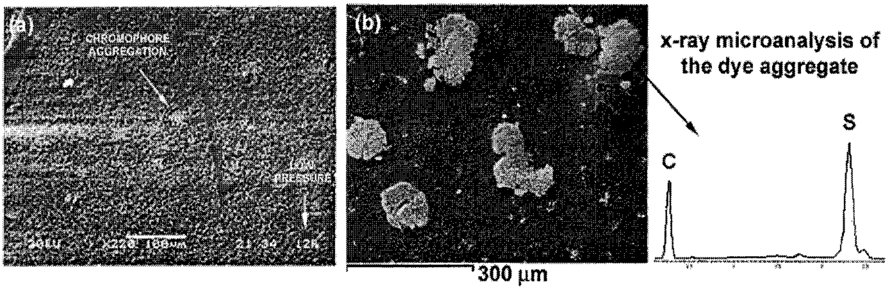

Fig. 3. SEM of UH3-VL (a) and UH3-3 (b) films.

In compatibilized UH3-VL film, the dispersed chromophore particles, smaller than those evidenced in UH3-3, were detectable just increasing the resolution of the instrument using the low pressure technique at 12 Pa. The increased homogeneity of UH3-VL film was also confirmed by differential scanning calorimetry (Figure 4). The melting peak of the chromophore dispersed in UH3-VL recorded by the first heating trace at about 100°C appeared much less pronounced than that showed by the endotherm of UH3-3. In fact the ΔH_f value evaluated for $C_{18}S$-TT-SC_{18} in UH3-VL was 0.15 J/g respect to 1.17 J/g determined for the UH3-3 film.

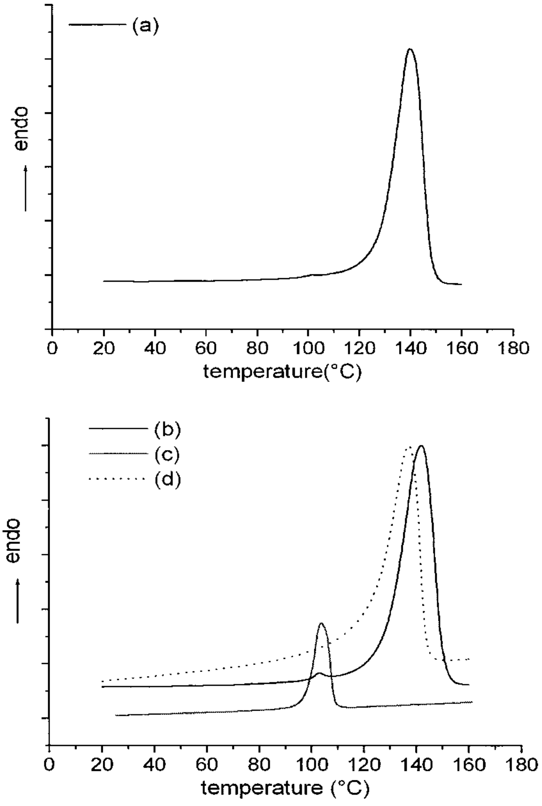

Fig. 4. First heating DSC traces of UH3-VL (a), UH3-3 (b), the neat dye (c) and second heating trace of UH3-3 (d).

UV-Vis spectroscopy in polarized light was performed on oriented UH3-VL and UH3-3 films in order to quantify the influence of the increased chromophore dispersion into UHMWPE on the optical performances of the prepared devices. The dichroic ratio R, related to the chromophore orientation along the stretched macromolecular fibres, is reported in Table 4.

Table 4. Dichroic ratios of oriented UH3-VL and UH3-3 films as a function of λ.

Sample	λ	R
UH3-VL	20	10±0.6
UH3-VL	30	15±0.6
UH3-VL	40	12.2±1.1
UH3-3	20	7.5±1.2
UH3-3	30	10±0.7
UH3-3	40	5±1.3

The optical properties showed by oriented films of UH3-3 and UH3-VL evidenced how the increased chromophore dispersion, due to the presence of polymeric compatibilizer, positively affects the performances of the host-guest devices. Hence, VLDPE-g-DES resulted as a proper compatibilizer between the guest phase of the terthiophene derivative and UHMWPE as evidenced by microscopy images and calorimetry measurements.

Conclusions

The three different strategies performed in obtaining good phase dispersion of terthiophene based guest dyes and the polyethylene host matrix allowed the preparation of multicomponent materials characterized by high degree of homogeneity. Heat of solution measurements of terthiophene derivatives in *n*-heptane, as *analogue* of linear PE, confirmed that functionalization with branched alkyl chains represent the best chromophore modification to increase the dye dispersion in polyethylene matrices. Microscopy and optical analyses evidenced that EVAc as polymer matrix allowed the preparation by melt-processing of binary blends based on $C_{18}S$-TT-SC_{18} as guest with very high dispersion degree. In addition, EVAc showed increased homogeneity respect to blends based on processable polyethylenes (LLDPE and HDPE), already characterized by good homogeneity and optical properties. Moreover, the use of VLDPE-g-DES as polyolefinic compatibilizer represented another important new useful strategy for the preparation of host-guest PE blends by solution-casting characterized by good homogeneity and phase behaviour of the guest chromophoric component. Finally, optical measurements in linearly polarized light performed on oriented blend films is confirmed as an effective investigation to analyse the dispersion degree of these binary host-guest systems. On the other side, the obtained results can provide indications for the preparation of high performance materials for applications as linear absorbing polarizers.

List of Abbreviations

PE: polyethylene; UHMWPE: ultra high molecular weight PE; LLDPE: linear low density PE; HDPE: high density PE; EVAc: ethylene vinyl acetate copolymer; VLDPE: very low density PE; VLDPE-g-DES: VLDPE functionalized with diethylmaleate; 5,5"-bis-thiooctadecyl-2,2': 5',2"-terthiophene: $C_{18}S$-TT-SC_{18}.

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