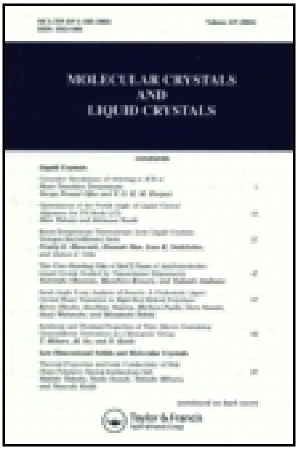

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OPTICAL AND SPECTROSCOPIC STUDIES OF PPV/PU BLENDS

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The poly(p-phenylenevinylene)/polyurethane (PPV/PU) composite films obtained from water-borne PU system with PPV precursor (PrecPPV) were investigated. UV-VIS absorption, photoluminescence (PL), thermoluminescence (TL) spectra and dynamic mechanical analysis (DMA) results of pure PPV and its composite are reported and analysed. The conversion of the PrecPPV/PU into PPV/PU composite was confirmed also by mean of dielectric spectroscopy. It was concluded from the UV-VIS absorption and PL spectra at room temperature that the conjugation length of the PPV chains in this composite and in pure PPV is similar. In the PL spectra at low temperatures positions of the peaks are the same in the pure PPV and in the composite. Upon cooling all peaks shift towards longer wavelengths and change their relative intensities. The TL spectra show that in these materials relatively shallow traps dominate, yielding TL maximum at ca. 70 K. The composite films cast from water suspension are flexible in contrast to pure PPV which forms rigid film. In DMA it is reflected by lower values of the storage modulus E' and of the amplitude of tanδ in the composites compared to pure PPV film.

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Keywords: composite; conjugated polymer; optical properties; photoluminescence; polyurethane; PPV; thermoluminescence; water-borne

1. INTRODUCTION

Poly(p-phenylenevinylene) (PPV) is the most extensively investigated conjugated polymer for its potential applications in full-polymer light emitting devices (PLED). However processing of this polymer is strongly limited due to its insolubility in common solvents [1], what is typically resolved by grafting of appropriate lateral groups on the main polymer chain.

The purpose of this work was to employ a competitive approach to produce of PPV-based polymeric materials for application in electro-optical devices, suggested in some papers [2–5]. This approach consists in mixing of the PPV precursor (PrecPPV) with an insulating polymer (matrix) which exhibits good film forming and mechanical properties, and then performing the conversion of the precursor into the PPV by proper thermal treatment.

Since the PrecPPV is soluble in water, the originality of the present work is to mix it with a PU matrix polymer using PU latex suspension in water. After mechanical mixing thin films of the composites were obtained by casting and careful dying. Optical, electronic and mechanical properties of the films were characterized by means of UV-VIS absorption, photoluminescence (PL), thermoluminescence (TL) spectroscopies and dynamic mechanical analysis (DMA).

2. EXPERIMENTAL

2.1. Synthesis

In order to obtain as high as possible conjugation length of the PPV, a two-step synthesis method was employed using PrecPPV. The starting material was a sulfonium polyelectrolyte prepared in an aqueous solution. Polymerization of the monomer was initiated by adding a strong base like NaOH. The scheme of the conversion process of the PrecPPV into the PPV is shown in Figure 1. The matrix was a water-borne polyurethane (PU) elastomer with low film formation temperature (298 K). This latex was purchased from DSM and used without further purification. Next the water solutions of PrecPPV/PU (with a content of PrecPPV in PU equal 1, 2 or 5 wt%) were prepared. The 30 g/l (for pure PrecPPV) or 250 g/l (for PrecPPV/PU mixtures) solutions in water were spin coated onto quartz substrates at 2000 rpm or drop-cast on glass substrates. Then the PrecPPV in the films were thermally converted yielding pure PPV or PPV/PU composites. That the degree of saturation of the PPV bonds can

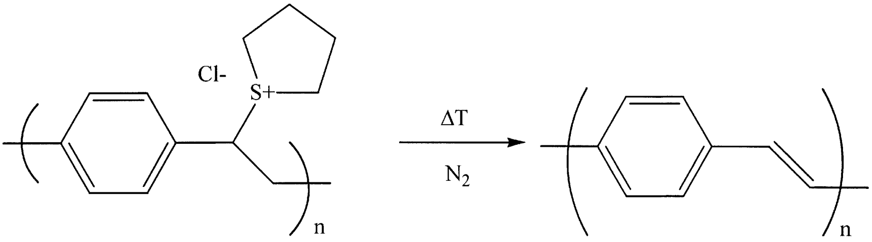

FIGURE 1 Scheme of the conversion of the PrecPPV into the PPV.

be controlled by varying the elimination temperature [6]. In our studies the elimination reaction of the PrecPPV was carried out for 2 hours at temperature 453 K under N_2 flow which leads to high degree of elimination. The samples were changing their color during the conversion from yellow to brown-orange.

2.2. Characterization

The UV-visible spectra have been obtained with a "Lambda 9300" spectrophotometer from Perkin Elmer. The PL spectra were recorded for free standing films after excitation with 420 nm light. A monochromator was used to select the excitation wavelength from the spectrum of an hydrogen lamp and the photoemission spectra were analyzed with a spectrograph associated to a "Spectrum one" CCD detector from Spex. The dielectric spectra were measured (after vacuum deposition of gold electrodes on both sides of the sample) in the frequency region 10^{-2}–10^{7} Hz at 453 K by using a Novocontrol Dielectric Spectrometer. The PL spectra at low temperatures (down to 8 K) were measured in a closed-cycle cryostat from Advanced Research Systems Inc. The samples were excited with monochromated 364 nm line of a Hg lamp and their PL spectra were successively registered by ORIEL Instaspec II diode array coupled to a 125 mm spectrograph. For the TL experiments the samples were placed between thermostated stage and sapphire plate in vacuum chamber (closed-cycle cryogenic system APD Cryogenics, type Displex); the heating rate was 7 K/min. The measurements were carried out in 15 K–300 K temperature range after photoexcitation at 15 K by using nitrogen pulsed laser ($\lambda_{exc} = 337$ nm). Characterization of thermal properties of the studied polymers was performed using TA Instruments 2920 DSC calorimeter. DMA measurements were performed for the film with dimensions $15 \times 9 \times 0.35$ mm with TA Instruments 2980 DMA analyzer at frequency 1 Hz using a tensile mode.

3. RESULTS

Evolutions of the UV-VIS absorption spectra occurring during the transformation of the PrecPPV into PPV and PrecPPV/PU into PPV/PU are shown in Figure 2. During the elimination process of the PrecPPV the number of sulfonium salt units, s, decreases and the number of phenylenevinylene units, n, increases. When the elimination process proceeds, the n/s ratio increases and the absorption spectra approach the typical spectrum of pure PPV (curve e in Fig. 2).

The two absorption peaks of PPV at 200 and 230 nm correspond to the phenyl groups absorption and the peak at 420 nm with an onset at 515 nm is related to the π-π^* transition indicating a highly conjugated system [7]. The spectra of the pure insulating matrix PU show absorption peaks at 234 and 280 nm, the onset of this absorption band being at *ca.* 305 nm. The composite exhibits the same absorption peaks at 234, 280 and 405 nm, attributed clearly to PU and PPV. The onset absorption for the composite is approximately the same as for the PPV (around 515 nm), what indicates that the effective conjugation length of PPV chains in the composite was the same as in the pure PPV.

UV-visible absorption spectroscopy was used to give a first evaluation of the conversion of the PrecPPV with and without PU, however, cannot be used as a quantitative technique for assaying polymers with high degrees of elimination [7].

Figure 3 shows an evolution of the PL spectra occurring during the transformation of the PPV precursor into PPV both in its pristine form and in PU matrix. The PL spectra of PrecPPV and PrecPPV/PU, obtained after excitation with 420 nm wavelength, show emission band about 533 nm. After heating at 453 K during 2 hours, the PPV emits yellow-green light with three emission maxima. The peak 1 at 512 nm results from the purely electronic transition, denoted S1→S0 (0-0), while the peak 2 at 553 nm and the peak 3 at 588 nm are attributed to the phonon-assisted S1→S0 (0-1) and S1→S0 (0-2) transitions, respectively [8]. A contribution of pure PU to the PL spectra is negligible, therefore the spectra reflect the influence of the matrix on the conformation of the PPV chains. The positions of the PL maxima of the PPV/PU composites are similar to the PPV ones, however the ratio of their intensities is changed. In the pristine PPV film, the ratio of the peak 2 to the peak 1 (so called 2/1 intensity ratio) is 7.46. When the PPV is dispersed in the PU matrix, the 2/1 ratio is strongly altered. A possible interpretation is that a dilution of the PPV in the PU matrix separates the PPV chains and coupling of the aromatic rings of PPV decreases leading to a decrease of the phonon-assisted transitions (peak 2 at 553 nm and peak 3 at 588 nm) and an increase of the electronic transition (peak 1 at 512 nm).

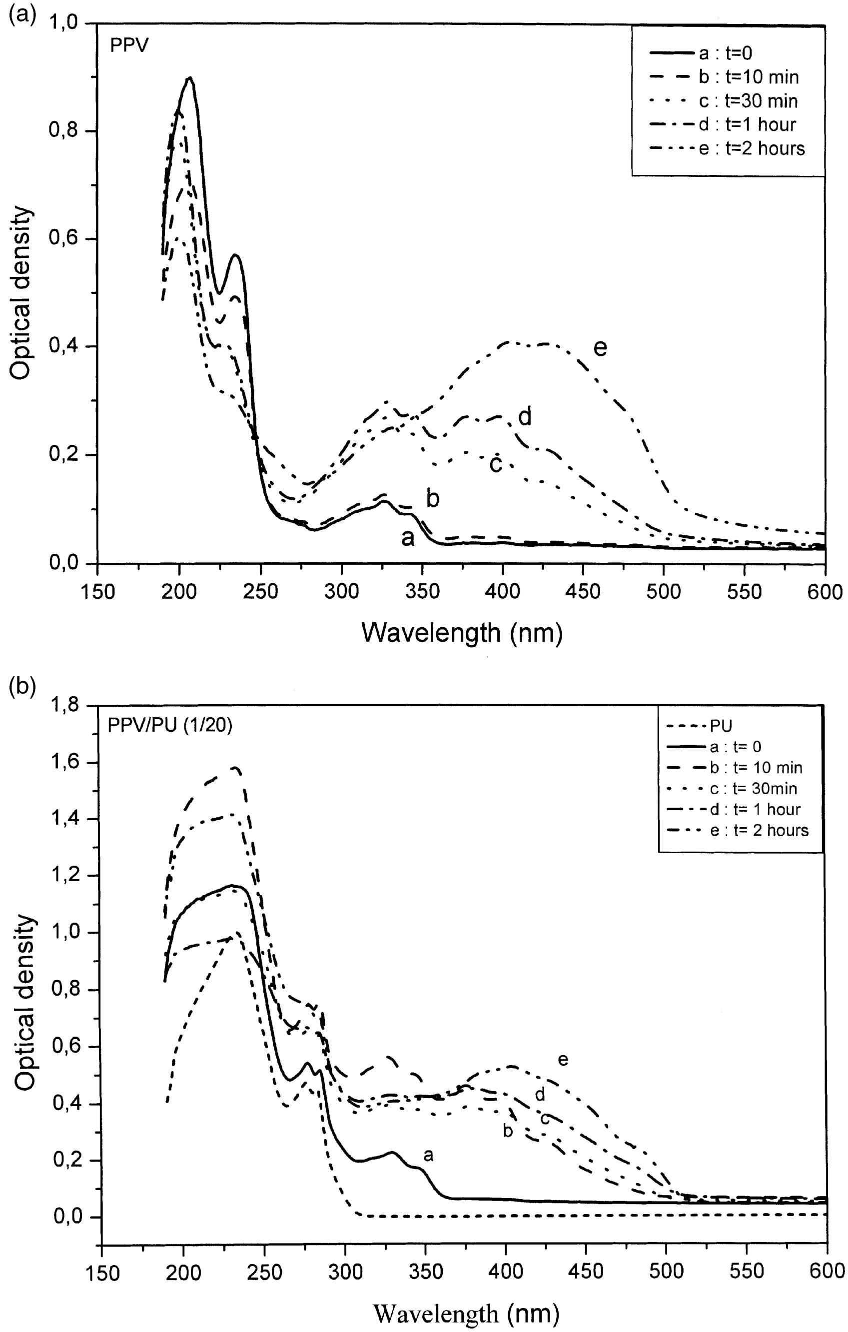

FIGURE 2 Changes in the optical absorption spectrum of PrecPPV and PrecPPV/PU (1:20 wt) thin films during its conversion. Spectra: a, as-cast; b, 10 min; c, 30 min; d, 1 h; e, 2 h at 453 K.

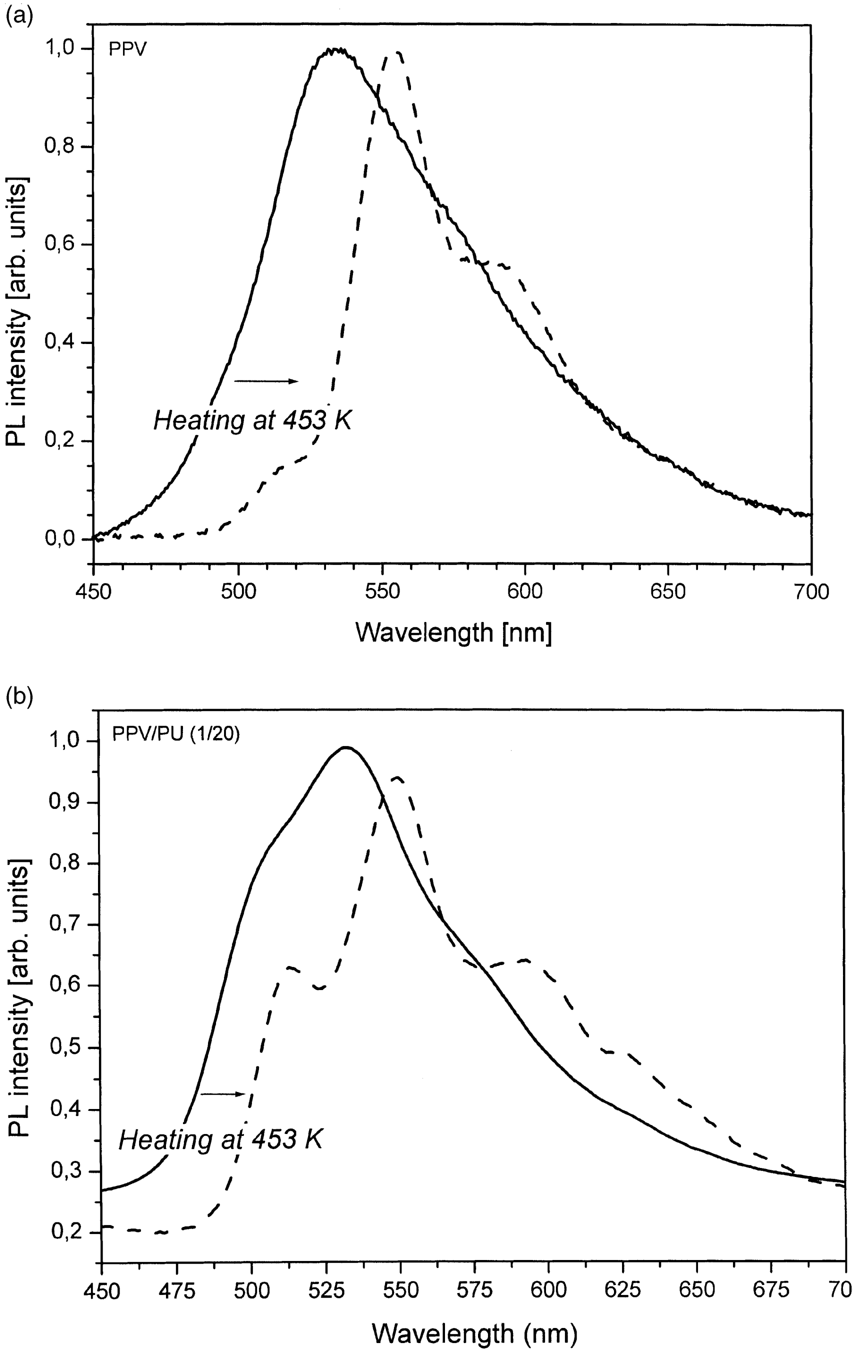

FIGURE 3 Changes in PL spectrum of PrecPPV and PrecPPV/PU (1:20 wt) films during its conversion. Heating 2 h at 453 K.

The conversion of the PrecPPV/PU into the PPV/PU composite was monitored also by dielectric spectroscopy. Figure 4 shows an evolution of tan(δ) vs. frequency plots with the conversion time at 453 K under nitrogen flow. The most pronounced changes occur in less than 30 seconds. The spectra remain practically unchanged after 1 hour time of heating.

In the PL spectra obtained at low temperatures the positions of the three peaks are essentially the same in the pure PPV and in the PPV/PU composite, and are consistent with literature [9]. Upon cooling all peaks shift towards longer wavelengths and change their relative intensities. As it is shown in the Figures 5(a) and 5(b), the 0-0 peaks increases the most when temperature decreases, particularly in the PPV/PU sample. Its bathochromic shift at 8 K is about 16 nm in the PPV and 7 K in the PPV/PU samples. This shift is smaller than the one observed for two other peaks, which are shifted for about 30 nm at 8 K. Peak 0-1 in both samples behaves differently: in pure PPV this peak shifts to longer wavelength continuously.

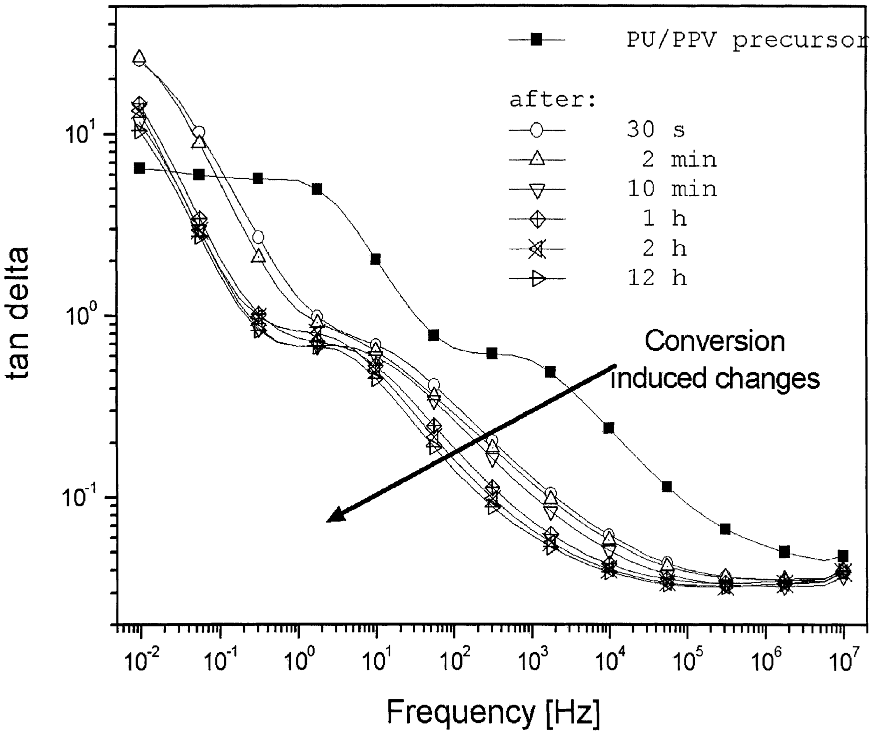

FIGURE 4 Evolution of the dielectric tan(δ) plots of the PrecPPV/PU composite during the conversion into the PPV/PU at 453 K under nitrogen flow.

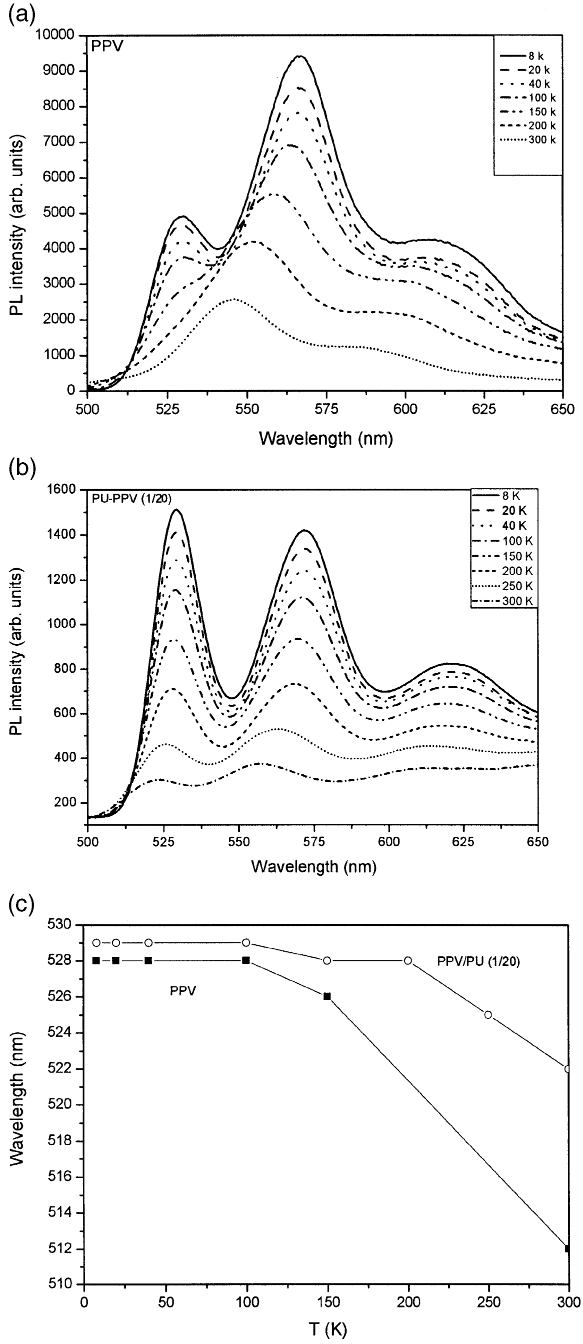

FIGURE 5 Temperature dependence of th PL of PPV and PPV/PU (1:20 wt). Temperature dependence of the 0-0 PL transition wavelength for PPV and PPV/PU PU (1:20 wt).

In the composite, it attained a certain position at about 200 K and then hardly moved. All these observation indicate that there was a significant difference in the conformation of the polymer chains in pure PPV and in the composite. Although this explanation, already suggested in the bibliography [10], seems reasonable, it needs further investigations. This also shows, that the blending can be used for the tuning of properties of optical polymers, as an alternative to chemical modifications [11].

The TL spectra for the PPV/PU (1:100 and 1:50 wt) samples excited at 15 K are presented in Figure 6. Both spectra are dominated by broad maximum with peaks around 70 K, corresponding to relatively shallow traps. Similarity of these two TL spectra indicates that the depth and distribution of charge carriers traps is weakly dependent on the blend composition. The intensity of the thermoluminescence was not high enough to perform the partial heating experiments in order to determine the depth of the traps, however one can note, that for the sample with higher PPV content the high temperature shoulder of the TL maximum is enhanced, showing increasing population of deeper traps. Deconvolution of this TL spectrum yields the second TL maximum at ca 150 K, as shown in the inset in Figure 6.

The DSC analysis performed in the temperature range 123 K–873 K (well above the decomposition temperature) for the fully eliminated pure PPV indicates very weak inflection at around 323 K which can be considered

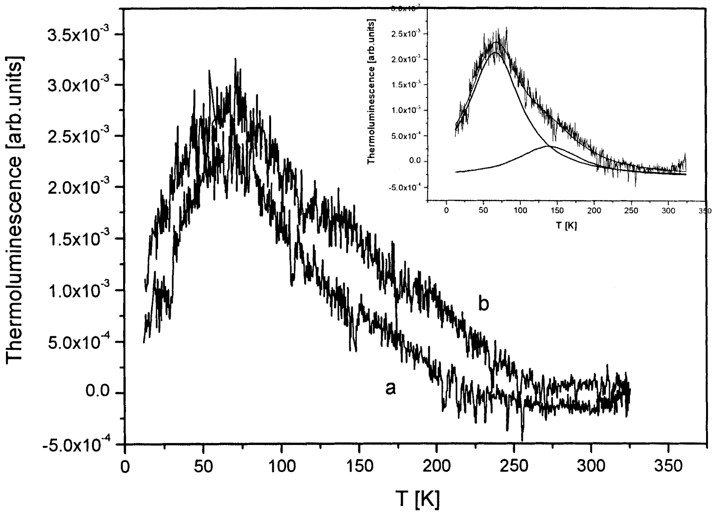

FIGURE 6 TL spectra for PPV/PU (a) 1:100 and (b) 1:50 wt obtained at heating rate 7 K/min after excitation with 337 nm light at 15 K.

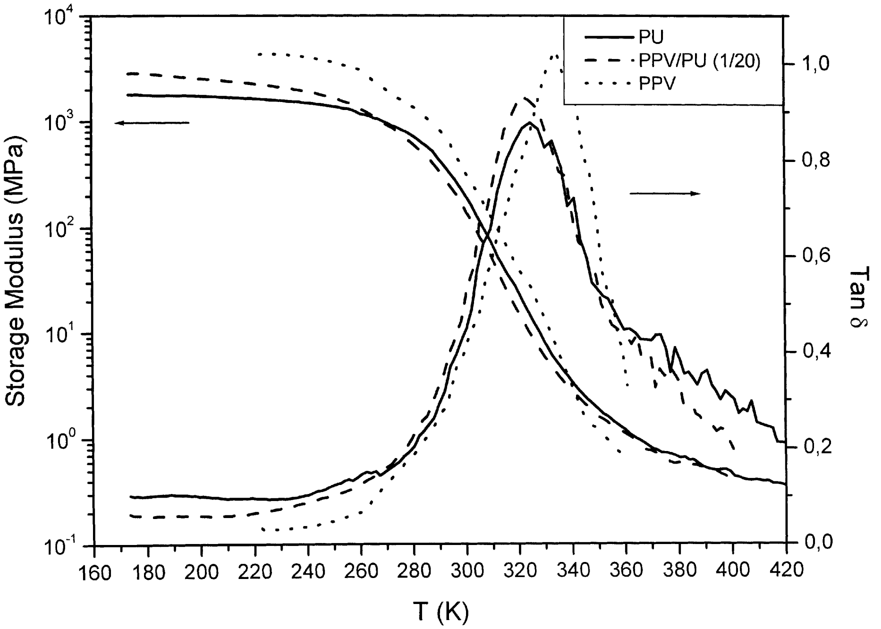

FIGURE 7 Dynamic Mechanical Analysis spectra of PU, PPV/PU (1:20 wt) and PPV at 1 Hz.

as T_g of PPV, taking into account the DMA results discussed below. In the composites we have noticed two inflection points on the DSC curves around 233 K and 324 K, corresponding to two T_g of the PU soft and rigid segments, respectively (the T_g of the PPV component can't be detected due to low content of PPV in the composite).

Figure 7 shows the DMA results obtained for pure PPV, pure PU and for the PPV/PU (1:20) composite. The storage modulus E' and tan δ are represented in function of temperature. In the glassy state, the storage modulus of the composite is lower than this of pure PPV film. This is in agreement with the observation that pure PPV films are rigid and brittle whilst waterborne composite films are more flexible. The position of the tan δ maxima at 1 Hz can be related to the glass transitions of PPV (at 334 K, for pure PPV), of PU soft and hard segments (at 262 K and 324 K, for pure PU) and for hard segments of PU (at 321 K, for the composite).

4. CONCLUSION

New PPV based materials were elaborated. The fabrication of the waterborne composites is environmentally friendly method avoiding a use of usually harmful, volatile solvents. In contrast to brittle pristine PPV films, the composite form self-standing films, easy to be peeled off from the glass substrate used for spin coating. The PPV based composites preserve several electronic and optical properties of PPV.

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