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Polymer-polymer interaction and modeling

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ABSTRACT

The nature of intermolecular interaction in PVC/EVA system was investigated. Bathochromic shifts in infrared region revealed that not only EVA carbonyl but the ester group participates on interaction with PVC chain. These shifts were proportional to acetate content in the copolymer and the composition of EVA in the blend. The PVC group that effectively participates on interaction was not elucidated by infrared spectrometry, but molecular modeling of low molecular weight analogues indicated that hydrogen bonding is the most probable kind of intermolecular interaction present in this system.

INTRODUCTION

Poly(ethylene-co-vinyl acetate) (EVA) is a copolymer extensively used as impact modifier of poly(vinyl chloride) (PVC) (1). Some authors reported that apparently homogeneous blends can be obtained from PVC and EVA when the vinyl acetate (VAc) content is higher than 50 wt.% (2-6). The phase behavior of PVC/EVA blends was studied using various methods, e.g., torsion pendulum (2), nuclear magnetic resonance (3), differential scanning calorimetry (4,7), viscometry (8), and theoretical approach (5,6). Morphological analysis and calorimetry of PVC/EVA system (9) have shown that microheterogeneity occurs even when the blend presents a single glass transition. Thermal analysis also characterized an interfacial region. These previous studies suggested the intermolecular interactions as responsible for the miscibility phenomena (6,7,9).

In order to get some additional information about the nature of the interactions observed in PVC/EVA systems spectrometric and molecular modeling studies were attempted.

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EXPERIMENTAL

Pertinent parameters of the polymers studied were described elsewhere (8). Pure polymers and blend films were obtained by casting 1wt.% solutions in tetrahydrofuran (THF) or methyl ethyl ketone (MEK) onto KBr disks, which were then kept in a desiccator at 298K with saturated solvent vapor for a minimum of 72 h. The obtained films were dried in vacuum at 338 ± 3K for 72 h. The complete removal of the solvent was verified by absence of infrared absorption at 1065 cm^{-1} (THF) or 1720 cm^{-1} (MEK). The absence of MEK was also verified by absence of the volatilization peak in the DSC curve.

Infrared spectra were acquired on a Nicolet 740 FT-IR spectrometer with mercury-cadmium-tellurium (MCT) detector cooled with liquid nitrogen. A minimum of 120 scans at a resolution of 0.3 cm^{-1} was signal averaged. Happ-Genzel apodization function was used to give the best resolution-band shape relationship. Areas, intensities, absorbance ratios, subtractions, derivations, deconvolution, shifts and widths were determined by computers' programs in the equipment.

Molecular interaction simulations were conducted by using a molecular mechanics program PC Model 3.0 version (Serena software) that employs the MMX force field based on Allinger's MM2 (10,11) with extensions and modifications to deal with other functional groups. A semiempirical program, MOPAC (Molecular Orbital Package), Version 6.0 (1991) was used employing the AM1 semiempirical method that uses the MNDO (Modified Neglect of Diatomic Overlap).

RESULTS AND DISCUSSION

Infrared spectrometry showed that two regions were important to assign in EVA spectrum. The first region at 1730-1740 cm^{-1} (carbonyl axial deformation) and the second at 610 cm^{-1} attributed to -COOR wagging (12). PVC and six EVA copolymers spectra are depicted in Figure 1.

EVA spectrum showed weak absorptions in the range 600-610 cm^{-1} that increases with the acetate content in the copolymer. These bands may underlie the C-Cl absorption modes from PVC, as shown in Figure 1. The carbonyl absorption is free of interferences and may be better observed. Figure 2 exhibits the spectrum of PVC, EVA50 and PVC/EVA50 blends. The frequency of the carbonyl absorption is observed to decrease slightly with increasing acetate content in the blend. The C-Cl region shows changes on intensity. This may be attributed to the changes in acetate content and the presence of interactions between the carbonyl of EVA and the H-C-Cl group of PVC.

The presence of specific interactions may be associated to size domain. EVA rich compositions with small polymeric interface can exhibit an interaction degree smaller than domains which has high interface between the two polymers, even when the blends are poor in acetate groups.

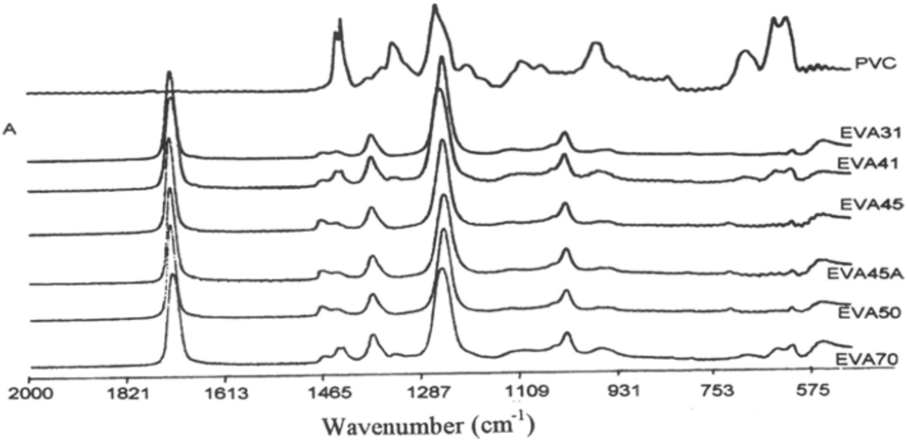

Figure 1 - FT-IR spectra of PVC and EVA films cast from THF solution.

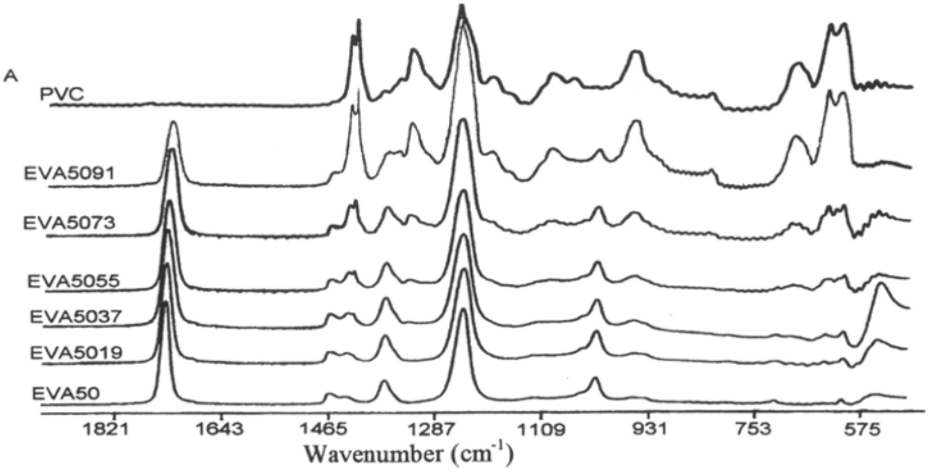

Figure 2 - FT-IR spectra of PVC/EVA50 blends as films cast from THF solution.

The spectra of the carbonyl region is depicted in Figure 3. Absorption shifts to lower frequencies are observed. The shifts become higher when the PVC content increased in the composition. The same occurs when the acetate content in EVA copolymer increases. This suggests the existence of intermolecular interactions.

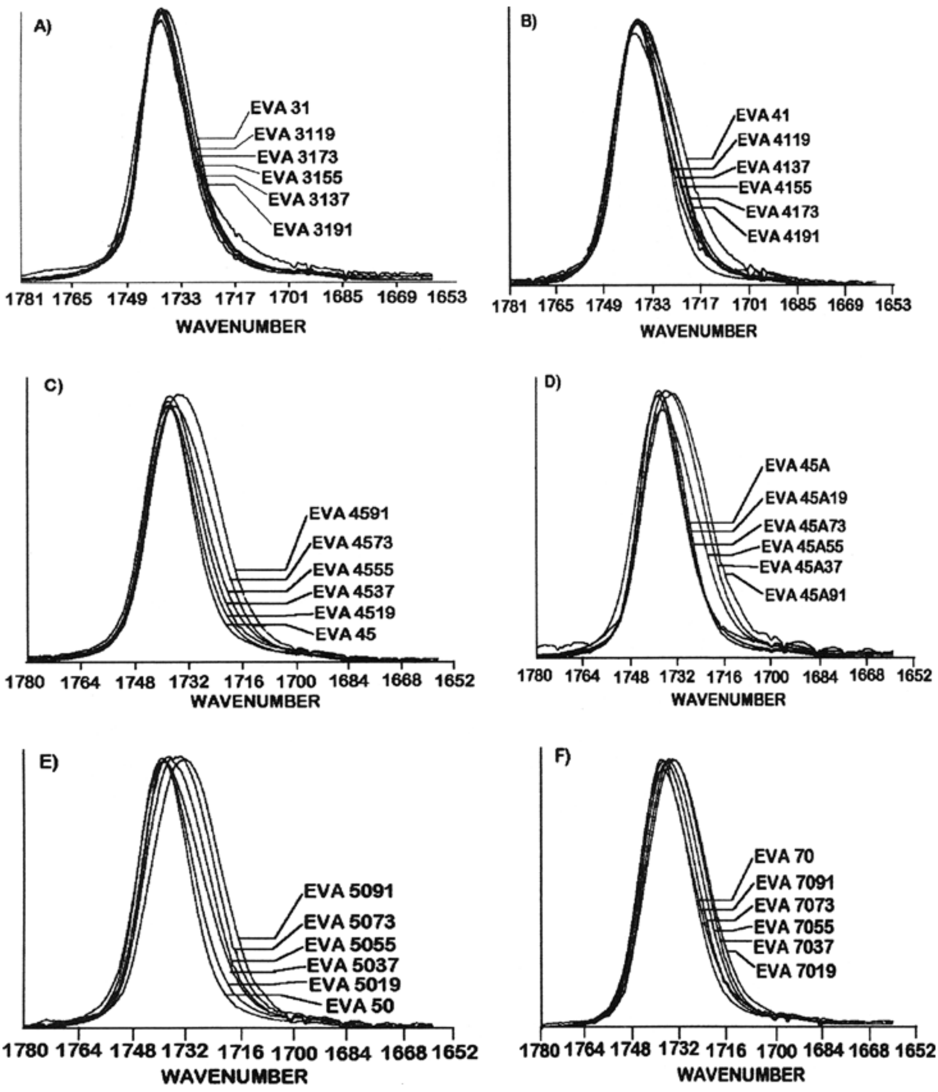

Figure 3 - Carbonyl region expansion of FT-IR spectra of PVC/EVA blends as films cast from THF solution.

The frequency shift behavior is shown in Figure 4. Low acetate content copolymer (EVA31) shifts the carbonyl absorption to a higher wavenumber and it characterizes a dilution effect between the components of the blend. The shifts are very small and there is a slight influence of composition.

The influence of the blend composition becomes more evident with the increase of the acetate content in the copolymer. The dilution effect may be also considered in PVC/EVA41 system for low PVC concentrations. When the PVC content rises, the C=O frequencies shift to lower values indicating specific interactions between the components of the blend; the effect is more evident for blends with EVA45, EVA45A, EVA50 and EVA70.

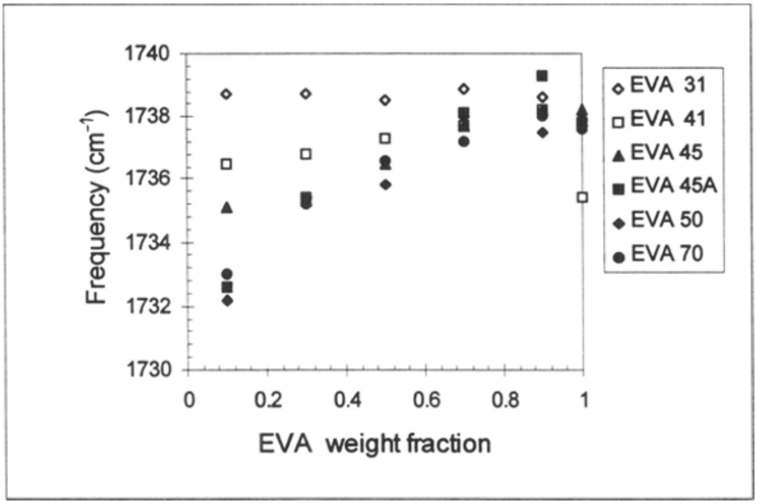

Figure 4 - Maximum absorption carbonyl peak as a function of EVA concentration for PVC/EVA blends.

Changes in the band-width ($\Delta\nu_{1/2}$) were also observed. However, the influence of the blend composition on the half band-width is not clear. The band broadening was observed for all PVC/EVA blends including these with dilution effect. This supports the hypothesis of typical occurrence of interactive and random effects. Blends from low acetate content in EVA (EVA 31) show a little dependence of half band-width with EVA composition, but the peak position is practically constant. This suggests little specific interaction influence and the dilution effect predominates. PVC/EVA41 system presents carbonyl shifts to lower frequencies and oscillation on half band-width values. PVC/EVA45 and PVC/EVA 45A systems show higher frequency shifts. However, fluctuations on half band-width suggest random effects. PVC/EVA50 and PVC/EVA70 systems have shown that the interaction effect predominates in EVA rich compositions, whereas little shifts are recognized when the EVA content in the blend is low. Similar trends were also observed for PVC/EVA70 with dilution influences for PVC rich compositions. It agrees with previous information obtained from calorimetry data (9) about PVC rich phase (phase I) and EVA rich phase (phase II) in PVC/EVA blends There is a tendency of EVA rich phase to dissolve more PVC than the PVC rich phase dissolves EVA.

The participation of C=O group in the intermolecular interaction was identified but the nature of PVC group is not clear. Axial methine deformation in PVC is relatively weak and occurs in the same frequency range as the stretching modes of methylene from PVC and EVA. Dipole-dipole interaction involving the C=O and C-Cl groups has been suggested (13,14) and could be characterized by frequency shifts of C-Cl axial deformation (690-612cm^{-1}). However, these stretching modes are highly coupled and conformational sensitive. It is also observed the CH_3-CO_2 copolymer absorption overlap.

Over the years the specific interactions were studied and represented not only by hydrogen bonding but also by dipole-dipole interaction (6,13-17). The carbonyl frequency shift has been observed for systems like polyvinylidene chloride ($PVCl_2$)/poly(ε-caprolactone) (PCL); since $PVCl_2$ does not have any α-hydrogen available, the specific interaction must then involve either the β-hydrogen (very unlike) of $PVCl_2$ or the chlorine (15).

The miscibility of PVC/EVA blends may be explained by three interactive mechanisms that acts together. Two of them can be described as dispersive contributions and the required energy to separate self-associated carbonyls (endothermic nature). The interactions between the C=O and CHCl are the exothermic component and the balance of forces is subtle. The result presented here agrees with this hypothesis because the frequency shifts to lower values were obtained only for samples with higher acetate content in EVA. This indicates the acid-base nature of the interaction between PVC and EVA, but dipole-dipole interactions remain possible.

In order to get deep information about specific interaction in PVC/EVA system molecular modeling (MM) was applied using two analogues to represent the interactive mers of the components. Simulations used ethylene chloride and ethylene acetate as analogues of vinyl chloride mer in PVC and vinyl acetate mer in EVA respectively. In these simulations the effect of tacticity and polydispersion was not considered.

To evaluate the minimum energy that corresponds to one conformation a series of approximated structures was employed initially with molecular mechanics using classical physics concepts where potential energy is the sum of valence geometry energy, torsion, non bonded potentials (steric and electrostatic) and hydrogen bonding contributions. The obtained force fields contain parameters like bond length and dihedral angles. However, in methods based in conventional heuristic search as molecular dynamics (MD) and Monte Carlo (MC) techniques, sampling is applied in a minor part of spatial configuration. For MD is difficult to overcome large energy barriers to search higher degree of freedom. MC can overcome greater but narrow barriers (18,19). These methods can be improved with searches at elevated temperatures that favors selection of higher conformational entropies. It is solved by the use of annealing techniques where conformational search begins at high temperatures and the system is cooled slowly. The pair with previous minimized components of the mixture made in a semiempirical program (MOPAC AM1), was placed in contact and then the pair was minimized by the simulated annealing technique in the PC Model environment (20,21). Annealing simulation is a stochastic method and there is no warranty that global minimum energy can be reached and then some iterations apart from different configurations must be made. The global minimum energy conformation was obtained by a semiempirical method that uses experimental data with some basic principles of quantum mechanics. The atomic orbitals from each atom of the system were combined in order to search the lower energy conformation. Results from AM1 were better than similar ones even considering hydrogen bonding and repulsive intermolecular interactions.

The nature of interactions between the components of PVC/EVA systems was evaluated by computing the intermolecular distances. The atom from PVC analogue that showed the best approximation to EVA analogue may be considered the one that effectively participates in the interaction. Table 1 shows the bond distances calculated which was selected as the more important to intermolecular interactions.

Table 1 - Intermolecular bond distances calculated for analogues of PVC and EVA mers

Bond pair	**Distance (Å)**
C=O......αH	2.32
C=O......β1 H	3.70
C=O......β2H	4.10
C=O......H	5.00
C=O......Cl-C	4.21

The smaller intermolecular distance was assigned for C=O..αH and then it may be inferred that the more probable kind of molecular interaction is made by hydrogen bonding between the carbonyl from ethyl acetate and the α-hydrogen of ethylene chloride. It may be supposed that the same occurs in PVC/EVA system. It must be emphasized that the influence of intermolecular repulsion was not analyzed here. Studies with semiempirical and also "ab initio" methods showed that the hydrogen bonding is the main interaction in methyl chloride and formic acid (22). These calculations show that the carbon atom can be a good hydrogen donor in the intermolecular bond since activated by one electron acceptor. One chlorine atom acting as an electron acceptor is strong enough to make the carbon atom as a proton donor. The miscibility in this blend is a result of not only one specific interaction but a product of interaction balance (23).

CONCLUSIONS

The presented study does not permit a definitive conclusion about the nature of the interactions observed in the PVC/EVA system. However, it gives some support to evaluation and constitutes one contribution that may be extended to analogues compounds with higher complexity in a way that actual limitations and restrictive suppositions could be overcome by approach with theoretical calculated model and experimental evidences.

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