# Effect of Solvent Type on Formation of PVC-Solvent Complex

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SUMMARY: The effect of solvent type on the structural features of PVC gels prepared from the solutions of dibutyl phthalate(DBP) and butyl benzoate(BB) were investigated. The influence of solvent type, i.e., diester solvent or monoester solvent, on the mechanical responses was characterized by dynamic viscoelastic measurements as a function of temperature, aging time, and PVC concentration. In the case of PVC/DBP aged gels, the transition phenomenon appeared close to 50°C, whereas no such transitions were observed for PVC/BB aged gels. This transition is considered to be associated with polymer-solvent complex which can be accounted for electrostatic interaction between C=O bond of solvent and H-C-Cl part of PVC. While BB solvent molecules can not form polymer-solvent complex due to no capacity to act as a bridge between PVC molecular chains. FT-IR spectroscopy and DSC investigation on either PVC/DBP gels or PVC/BB gels was reported and discussed together with the mechanical behavior. Electron micrographs of the dried gel prepared from the critical point drying technique reveal that the gel morphology consists of well developed three dimensional fibrous network structure independent of solvent type.

## Introduction

Although the gelation phenomenon of poly(vinyl chloride)(PVC) has received continuous attention over the past forty years, the mechanism of gelation and the network structure are still under discussion. Recently, systematic studies have been carried out on the mechanism of gelation and the network structure of PVC using various techniques including X-ray scattering,[1,2] light scattering,[3-5] small-angle neutron scattering(SANS),[6,7] differential

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scanning calorimetry(DSC),[8,9)] spectroscopy,[10,11)] and microscopy[8,9,12]. These studies have made considerable progress in understanding the molecular structure and the mechanism of gelation. Yang and Geil [8)] have observed fiber-like structures and it has been experimentally supported by many authors. Genet et al.[13)] have suggested two types of links on the basis of light scattering study of the pregels, i.e. one type of link is more syndiotactic sequences of PVC chain, crystallites, and the other is a polymer-solvent complex which can be formed between less stereoregular sequences and solvent molecules. Najeh et al.[14)] have investigated the structure of PVC gels in several diesters and monoesters and they suggested that the diester solvent can directly participate in the formation of the second type of crosslinks. In their fibrillar model, a polymer-solvent complex is formed by allowing the diester to bridge different chains, which can be formed by electrostatic interactions of the negatively polarized oxygen atoms of the diester solvent and positively polarized hydrogens of the PVC. Also, small angle neutron scattering and viscoelastic studies on chemically modified PVC support this model.[15-17)]

The objective of this present work is to give additional details on the structure of PVC gels by comparing gels formed with diesters, for which the above process is possible, with gels prepared from monoester. The monoester has only one carbonyl group for each molecule, which can interact with PVC chain by electrostatic interaction, but no complex can be formed in that way. To evaluate this phenomenon, several techniques including dynamic viscoelastic measurement, DSC, FT-IR spectroscopy, and microscopy have been used.

## Experimental

### Materials and sample preparation

The PVC sample was a commercial polymer prepared by suspension polymerization by LG Chem. and used as received ($M_w$=2.0×$10^5$ gmol$^{-1}$ and $M_w/M_n$=1.7). Tacticity characterization of the PVC performed by 13C NMR spectroscopy gave the following result: syndiotactic triads(rr) 0.33, heterotactic triads(rm) 0.49 and isotactic triads(mm) 0.18.[18)]

Two analytical grade solvents were used: dibutyl phthalate(DBP) and butyl benzoate(BB) were used as received. Gels containing 5~20wt % of PVC were prepared by heating the polymer-solvent mixture at 160°C by thorough stirring and then quenched to room temperature. The samples were allowed for aging for at least 7 days prior to further characterization.

## Dynamic viscoelastic measurements

Dynamic viscoelastic measurements were performed on a Rheometrics Scientific ARES 100FRTN1 rheometer using the parallel plate with 25mm in diameter, at the frequency of 0.5rad/s, 5% strain and temperature scan rate of 1°C/min. The parameters such as the storage modulus, $G'$, the loss modulus, $G''$, and the loss tangent, $\tan \delta$ were determined in the temperature range of 30 to 140°C.

## Infrared spectroscopy

Thin films of PVC/solvent mixture were prepared by casting from dilute THF solution. After drying in air for about 3 days, the films were heated at 70°C until THF was completely removed. The removal was monitored by the disappearance of the IR band at $1065\text{cm}^{-1}$, characteristic of THF. All IR spectra were recorded on a Bio-rad FTS 375C spectrometer and the signals of thirty-two scans were averaged at a resolution of $2\text{cm}^{-1}$.

## Thermal analysis and morphology observation

Thermal analysis was carried out with a TA instrument 2910 differential scanning calorimeter.

A "volatile sample" pan was used and heating rate was 20°C/min. The morphology of the dried gels prepared by critical point drying technique was investigated by using scanning electron microscope (Hitachi S-4200).

## Results and discussion

Dynamic viscoelastic measurements of PVC/DBP and PVC/BB gels have been studied as a function of temperature, aging time, and concentration. In order to study the effect of solvent type on the dynamic viscoelastic properties, two types of solvents, DBP and BB were selected. DBP has two carbonyl groups, whereas BB has the same alcohol size with DBP but contains only one carbonyl group for each molecule.

The storage modulus, G′, and tan δ as a function of temperature for PVC/DBP gels(conc. 20wt%) are shown in Figure 1. Although not shown in the figure, the results obtained for the rest of the concentrations show the same behavior. In the case of aged gels of DBP, one can clearly observe the existence of the transition, which takes place at a temperature vicinity of 50°C and independent of concentration. A great resemblance is observed between our result

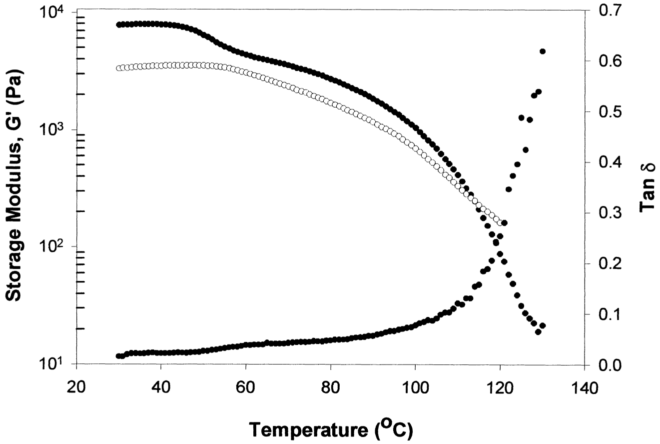

Figure 1. Storage modulus, G′ and tan δ profile as a function of temperature for aged( ● ) and fresh gel(O) of PVC/DBP 20wt%.

and Santamaría et al.'s result (i.e. PVC/DOP gels) [19, 20]. The existence of a transition at this intermediate temperature (close to 50°C) is considered as typical spectra of aged PVC gels in diesters. However, in the case of fresh gel, fused at 150°C and then kept for 20min at room temperature, such a transition does not exist. This transition and the difference of plateau modulus at low temperature (<40°C) between the aged and fresh gels are considered to be associated with the existence of the polymer-solvent complex, can be formed due to the bridging ability of diester molecules with two different PVC chains, by heat.

In Figure 2 we present the storage modulus, G′ and tan δ of PVC/BB gel as a function of temperature. As can be seen, the aged and fresh gels of PVC/BB possess nearly the same modulus in the range of temperature considered in this work and there is no transition between 40°C to 60°C. This implies that the polymer-solvent complex does not exist in the PVC/BB gel system. However, we observed the presence of a maximum in tan δ at intermediate temperature. At this point, we have to bear in mind that BB can promote electrostatic interaction between BB and PVC, but has no capacity to act as a bridge between PVC chains because it has only one carbonyl group for each molecule. Therefore, we infer that the presence of maximum in tan δ might be due to the dissociation of weak hydrogen

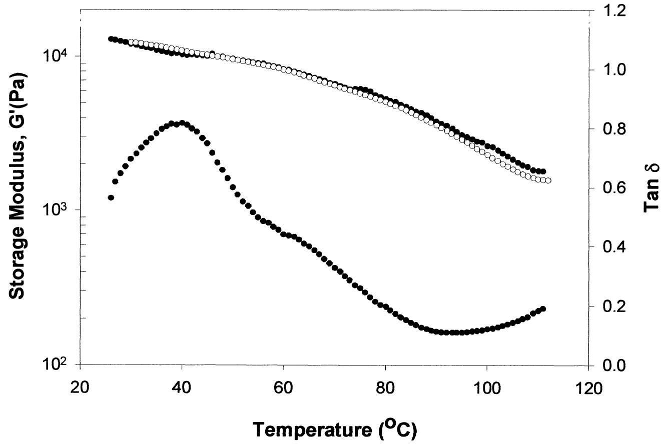

Figure 2. Storage modulus, G′ and tan δ profile as a function of temperature for aged( ● ) and fresh gel(O) of PVC/BB 20wt%.

bonding between the negatively polarized atoms of the BB and the positively polarized hydrogen atoms of the PVC.

In order to verify the above explanation, the molecular interaction of PVC with DBP and BB has been investigated by FT-IR spectroscopy. During the last two decades several research groups widely investigated the mixtures of PVC/polyesters and PVC/solvents systems, having the carbonyl function groups, to identify the nature and origin of the molecular interaction.10,21,22) According to them, there is no exact evidence whether the atoms of PVC that are able to interact with C=O are methine hydrogens,22) methylene hydrogens, or chlorine atoms.10) The former may be considered to be a type of hydrogen bonding while the latter has been described as a dipole-dipole interaction. However, it is now generally favored that the principal mode of interaction between PVC and polyesters or solvents is a hydrogen bonding of the type –C=O ···H-C-Cl which involves the methine hydrogen of PVC.21, 22)

It is generally accepted that the shift of the carbonyl stretching vibration to lower frequency in the infrared spectra of PVC with solvents or polyesters mixtures as a evidence of molecular

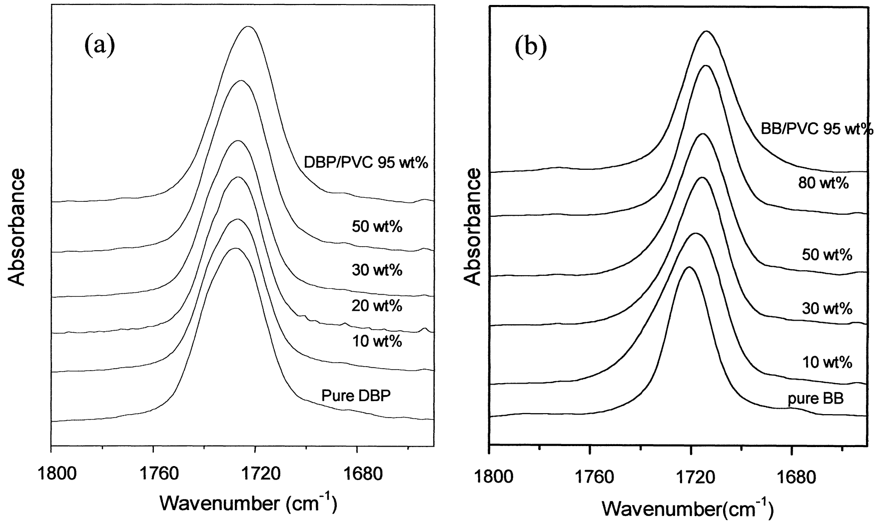

Figure 3. FT-IR spectra in the carbonyl stretching region of pure solvents and gels for various concentrations: (a) PVC/DBP gels; (b) PVC/BB gels.

interactions. The change of the carbonyl band for the PVC/DBP and PVC/BB thin films of different composition, is shown in Figure 3, respectively. As can be seen in the figure the shift of the carbonyl band toward lower frequencies is observed as the PVC content increases. This result strongly indicates the existence of molecular interaction as a type of hydrogen bonding between the carbonyl group and the hydrogen attached either to the same carbon atom as the chloride, in the both gel systems.

Thermal analysis has been carried out to verify the interaction. Either PVC/DBP gels or PVC/BB gels, the thermal behavior is almost the same (Figure 4). Two endotherms were found in both gel systems. Mutin and Guenet [9,13)] have investigated the thermal properties of PVC gels in various solvents, reporting the existence of two endotherms, i.e., a low temperature melting endotherm and a high temperature one which corresponds to the polymer-solvent complex and the gel crystal melting, respectively. Also, they clearly showed by measuring the compression modulus that the low temperature endotherm is due to the existence of a polymer-solvent complex which forms during aging. Based on their results, the

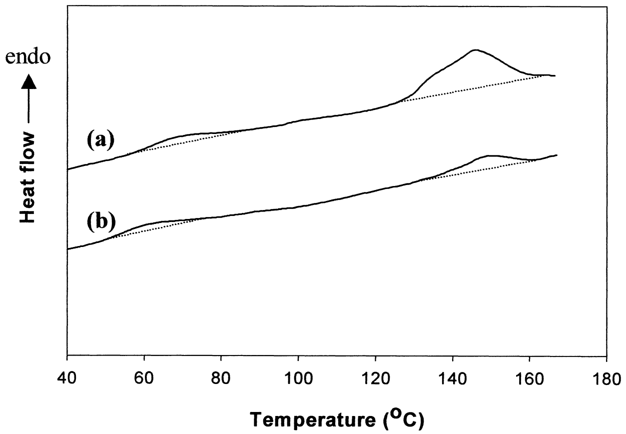

Figure 4. DSC thermograms for two different aged gels (conc. 20wt%) at 20°C/min:
(a) PVC/DBP gel; (b) PVC/BB gel.

endotherm at lower temperature of PVC/DBP gel represents melting of polymer-solvent complex, while endotherm observed in PVC/BB gel might be due to the dissociation of weak hydrogen bonding. The coincidence of the temperature range of the low endotherm with transition temperature obtained by viscoelastic measurements confirms our explanation.

The morphology of the gel was investigated for the dried gel prepared by the critical point drying technique using electron microscopy. Critical point drying was conducted using transitional fluid($CO_2$) which goes from liquid to gas through the critical point. The dried gels were prepared as follows; the gel sample was placed into extraction cell and the liquid $CO_2$, as a transitional liquid, was pumped into extraction cell. After all the solvents in the gel sample are removed and replaced by the liquid $CO_2$, extraction cell was heated and pressurized to above the critical temperature(304.2K) and the critical pressure(72.8 bar) of $CO_2$ in order to pass through the 'critical point'(that temperature and pressure where the densities of the liquid and vapor phases are the same and they coexist thus, there is no surface tension). Then, the system was depressurized and the cell was removed from the system. Critical point drying allows the gel sample and fluid to be taken directly to gas phase without experiencing any surface tension, thus we could obtain dried gel without distortion or some alteration to the gel structure.

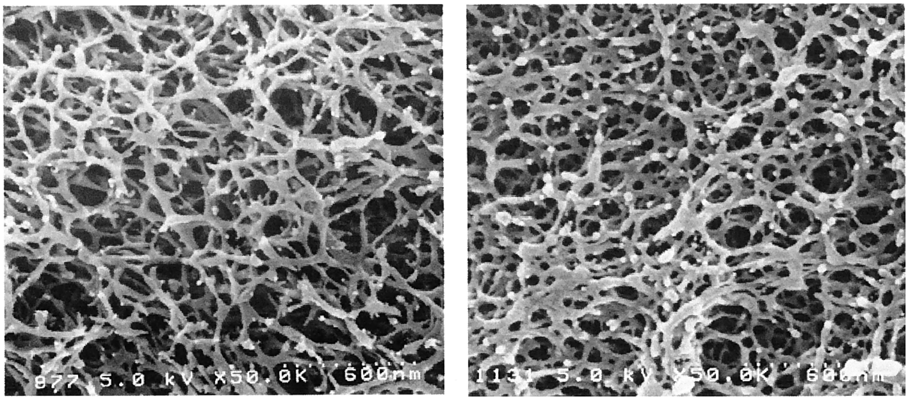

Figure 5. Electron micrographs of dried gels prepared by critical point drying technique: (*left*) PVC/DBP 20wt% gel; (*right*) PVC/BB 20wt% gel.

Electron micrographs show that the gel morphology consists of well developed three dimensional fibrous network structure in both gel system (Figure 5(a) and (b)). This result reveals a network with a mesh size of about 200~300nm which consists of fibers of diameter ranging 30~50nm, roughly. There was no considerable difference in gel morphology with solvent type and aging time; the same type of fibrous network being seen in fresh and aged gels.

## Conclusions

The solvent type has an important influence on the structure and dynamic viscoelastic properties of PVC gels. The aged PVC gels containing diester solvents show transition close to 50°C, whereas no such transitions were observed for aged PVC gels containing monoester solvents in that temperature range. This transition is associated with the formation of polymer-solvent complex in which diester solvents can act as a bridge between PVC molecular chains.

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