

FT-IR Studies of Polymer Blends Containing an Oligo(isophthalate-co-Fumarate of Diethylene Glycol) and Different Epoxy Prepolymers

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Synopsis

Miscibility of one unsaturated polyester (UP) with different epoxy prepolymers have been examined. Thermodynamic interaction parameters have been calculated. Calorimetric and clarity measurements indicate formation of miscible blends. This is in good agreement with the theoretical predictions excepted those with the 3-dimensional solubility parameter. Fourier transform infrared (FT-IR) studies are presented. The ability of acid solvent to associate with ester group have been used to determine the shift of the carbonyl stretching frequency. Similar shift has been found in UP/DGEBA blends and is attributed to specific interactions between these two types of oligomers.

INTRODUCTION

The usefulness of unsaturated polyester resins in many applications is limited by their brittleness and susceptibility to catastrophic failure. Moreover, the shrinkage of the polyester resin during copolymerization with the reactive styrene solvent and crosslinking leads to warpage and cracking. Blends with additives are often used to improve shrinkage and toughening of unsaturated polyester networks.

Fourier transform infrared (FT-IR) spectroscopy has proven to be a useful technique to study miscible polymer blends. Several studies of polymer blends with poly(vinyl chloride), styrene-acrylonitrile copolymers, poly(bisphenol A carbonate), and poly(hydroxy ether of bisphenol A) are further examples.^{1,2}

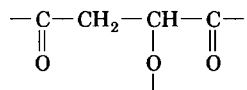
In all the publications mentioned above, it has been established that the shift to lower frequency and asymmetric broadening of the carbonyl stretching frequency observed is the consequence of specific intermolecular interaction involving the carbonyl bond. In this paper we present results on different blends based on an unsaturated copolyester (UP) used as a model. This copolymer is prepared from 1 mol isophthalic acid, 1 mol fumaric acid, and 2 mol diethylene glycol. Other components are various diglycidyl ether of bisphenol A (DGEBA) and one epoxy-terminated polypropylene oxide (PPO).

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EXPERIMENTAL

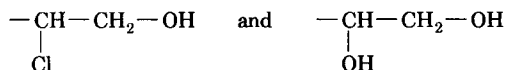
Materials

The unsaturated polyester used in this study was obtained from Norsolor. It is an amorphous low molecular weight component, ($\overline{M}_n = 455$ g/mol and $\overline{M}_w = 615$ g/mol), with a hydroxyl number $I_{OH} = 265$, and a small quantity of free diethylene glycol (DEG) (5.8%). The hydroxyl functionality can be estimated $\overline{F}_n = 1.65$. In Table I(a) we can see that we have two types of carbonyl bonds: isophthalate and fumarate. Another type is also present due to by-side addition of hydroxyl on fumarate double bonds³:



From ¹H-NMR analysis the fraction of double bonds (maleate + fumarate) transformed through this reaction is about 5.3%.

DGEBA prepolymers [Table 1(b)] are commercial products. Their characteristics are given in Table II. A previous high performance liquid chromatography (HPLC) and ¹H-NMR study have shown that a little amount of primary and secondary hydroxyl groups can also be present at the chain ends⁴:



The epoxy-terminated polypropylene oxide (PPO) is also a commercial product from Dow Chemical (DER 732) with an epoxy equivalent $ee = 305\text{--}335$. From size exclusion chromatography (SEC) analysis we obtain $\overline{M}_n = 685$ g/mol and $\overline{M}_w = 798$ g/mol [Table I(c)]. All the blends were prepared by stirring at a temperature higher than the highest T_g of the components.

Apparatus

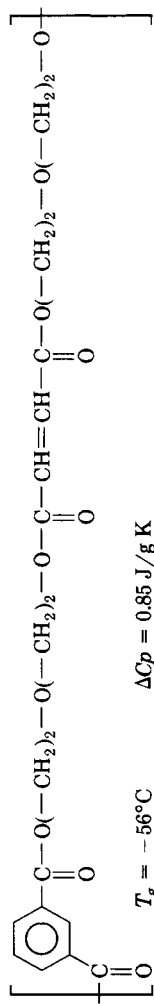
Differential scanning calorimetry (DSC) thermograms were recorded using a METTLER TA 3000 instrument, with heating rate $q = 7.5^\circ\text{C}/\text{min}$ under an argon flow. DSC was used to determine glass transition temperature T_g and specific heat capacity change ΔCp at T_g . T_g was taken as the intersection of the base line with the tangent at the inflexion point of the curve due to the change in heat capacity.

Scanning from -170°C provides excellent base lines for ΔCp determination. The difference of ΔCp between each run was not more than 5%; therefore, the average ΔCp can be estimated within 2%.

Infrared spectra were obtained from a NICOLET MX-1 spectrometer. Two hundred scans at a resolution of 2 cm^{-1} were signal average and stored on a magnetic disk system. Blends were placed between NaCl windows, and we ensure that films were sufficiently thin to be within the absorbance where the Beer-Lambert law is obeyed.² The absolute intensity of the carbonyl stretching vibration is a function of blend composition.

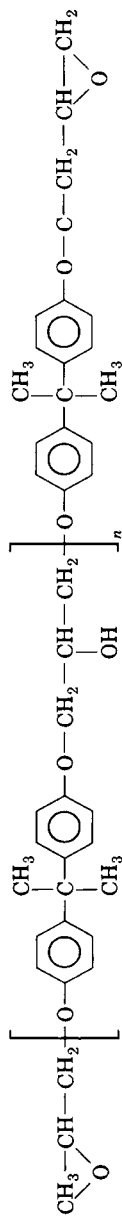
TABLE I
Formula of Different Oligomers Used in This Study

(a) Unsaturated polyester (UP)



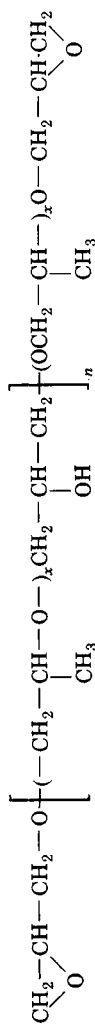
$T_g = -56^\circ\text{C}$ $\Delta C_p = 0.85 \text{ J/g K}$

(b) Diglycidyl ether of bisphenol A (DGEBA)



(see Table II)

(c) Epoxy-terminated polypropylene oxide



$T_g = -78^\circ\text{C}$ $\Delta C_p = 0.87 \text{ J/g K}$

$x = 5$ $0.7 < n < 1$

TABLE II
Characteristics of Different DGEBA Prepolymers Used

Origin	\bar{n}	\bar{M}_n (g/mol)	T_g (°C)	ΔC_p (J/g K)
DER 332 (DOW)	0.03	340	-21	0.63
Bakelite 164 (Bakelite)	0.15	380	-20	0.68
Lopox 500 (CdF Chimie)	1.6	780	28	0.71

SOLUBILITY PARAMETERS

The miscibility between the two components can be estimated through different models of solubility parameters.

The Hildebrand parameter δ^5 was intended only for nonpolar, nonassociating systems, but the concept has been extended for all systems:

$$\delta = \frac{\sum F_i}{\sum V_i} \quad (1)$$

$\sum F_i$ = sum of the group molar attraction constant⁶ and $\sum V_i$ = sum of the group molar volume.^{7,8} Hansen⁹ proposed an extension of the Hildebrand parameter method to polar and hydrogen bonding systems. It was assumed that dispersion, polar, and hydrogen bonding parameters were valid simultaneously, and related by

$$\delta_t = (\delta_d^2 + \delta_h^2 + \delta_p^2)^{1/2} \quad (2)$$

where δ_t is the 3-dimensional solubility parameter.

An evaluation of δ_d , δ_h , and δ_p can be obtained by calculation using tables of molecular physical properties:

$$\delta_d = \frac{\sum_i F_{d_i}}{\sum_i V_i} \quad (3)$$

$$\delta_p = \frac{\sum_i F_{p_i}^2}{\sum_i V_i} \quad (4)$$

$$\delta_h = \left(\frac{-\sum_i U_{h_i}}{\sum_i V_i} \right)^{1/2} \quad (5)$$

The different values of solubility parameters calculated for the polymers used in this study are summarized in Table III.

TABLE III
Calculated Solubility Parameters and Hydroxyl Concentrations for Different Oligomers
Used in This Study

Oligomers	[OH] (mol/kg)	δ^a	δ^b	δ_d	δ_p	δ_h	δ_t^c
Copolymer, UP	2.8	25.2	23.1	19.3	2.7	12.9	23.4
DGEBA, $n = 0.03$	0.1	25.7	26.2	21.5	3.5	7.4	23
DGEBA, $n = 0.15$	0.4	25.7	26.4	21.5	3.3	8	23.2
DGEBA, $n = 1.6$	1.6	25.8	27	21.5	2.3	9.9	23.8

^a Hildebrand parameter estimated from Hoy's tables in $\text{MPa}^{1/2}$.

^b Hildebrand parameter estimated from Van Krevelen's tables in $\text{MPa}^{1/2}$.

^c Hansen's 3-dimensional solubility parameter in $\text{MPa}^{1/2}$.

With the Flory-Huggins theory of polymer miscibility¹⁰ the interaction parameter χ_{AB} may be expressed in terms of Hildebrand solubility parameters δ_A and δ_B by

$$\chi_{AB} = \frac{V_r}{RT} (\delta_A - \delta_B)^2 \quad (6)$$

where V_r = reference volume based on the volume of the smallest repeating unit of the two components

In terms of the Hansen 3-dimensional solubility parameter, the interaction parameter is expressed by

$$\chi_{AB} = \frac{V_r}{RT} [(\delta_{A,d} - \delta_{B,d})^2 + (\delta_{A,p} - \delta_{B,p})^2 + (\delta_{A,h} - \delta_{B,h})^2] \quad (7)$$

There is a critical value χ_{cr} which represents the limiting value above which thermodynamic mixing cannot occur:

$$\chi_{cr} = \frac{1}{2} \left(\frac{1}{x_A} - \frac{1}{x_B} \right)^2 \quad (8)$$

where x_i = degree of polymerization of the component i . Then the miscibility is expected when $\chi < \chi_{cr}$.

The Hildebrand solubility parameters have been calculated using Hoy's table and Van Krevelen's tables from eq. (1). Hansen's 3-dimensional solubility parameters were estimated using eqs. (2), (3), and (4) with Van Krevelen's tables. χ_{cr} has been calculated with the calculated smallest constitutional repeating unit (CRU) volume, i.e., the DGEBA one, as reference volume ($230.2 \text{ cm}^3/\text{mol}$). χ has been calculated with eqs. (6) and (7) using the same reference volume. All the results are summarized in Table IV.

χ values calculated with the Hildebrand solubility parameters, which concern only dispersive forces (London-Van der Waals), predict that blends are

TABLE IV
Flory-Huggins Interaction Parameters Calculated from Hildebrand Solubility
Parameters with Hoy's Tables^a and Van Krevelen's Tables^b and
from Hansen's 3-Dimensional Solubility Parameter^c

Blend	χ_{Hoy}^a	$\chi_{\text{Van Krevelen}}^b$	χ_{Hansen}^c	χ_{cr}
UP/DGEBA, $n = 0.03$	0.02	0.89	3.4	1.24
UP/DGEBA, $n = 0.15$	0.03	1.01	2.7	1.13
UP/DGEBA, $n = 1.6$	0.03	1.41	0.9	0.73

miscible when the DGEBA molecular weight are low and immiscible for a DGEBA, $\bar{n} = 1.6$. Blends are predicted to be less miscible when the DGEBA molecular weight increase. This justifies the general idea that oligomer blends are more miscible than polymer blends.

On the contrary, the χ values calculated with the Hansen 3-dimensional solubility parameter indicate that blends are not miscible. But they tend to become more miscible when the DGEBA molecular weight increases, i.e., χ decreases when \bar{n} increases. In this case, the hydrogen bonding contribution in the DGEBA 3-dimensional solubility parameter (which is principally due to the presence of secondary hydroxyl groups) increases. It favors miscibility. Unfortunately, the 3-dimensional solubility parameter did not take into account the donor or acceptor character of the different groups so that experimental evidence of specific interaction is required.

RESULTS

Calorimetric Analysis

Calorimetric measurements were conducted on UP/DGEBA $\bar{n} = 0.03$, $\bar{n} = 0.15$, and $\bar{n} = 1.6$ and UP/PPO blends. The results obtained are presented on Figures 1-4. A single glass-transition temperature T_g is recorded for each blend and each composition at a temperature intermediate between those of UP and DGEBA (Figs. 1, 2, and 3) or PPO (Fig. 4). These results indicate the formation of miscible blends since two T_g 's are expected each composition for phase separated mixtures.

Several theoretical and empirical equations have been used to describe the T_g -composition dependence of polymer/polymer blends. We have considered three equations:

$$T_g = W_1 T_{g_1} + W_2 T_{g_2}, \quad \text{"Di Marzio"}^{11} \text{ or rule of mixture} \quad (9)$$

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}}, \quad \text{"Fox"}^{12} \text{ or inverse rule of mixture} \quad (10)$$

$$\ln T_g = \frac{W_1 \Delta C p_1 \ln T_{g_1} + W_2 \Delta C p_2 \ln T_{g_2}}{W_1 \Delta C p_1 + W_2 \Delta C p_2}, \quad \text{"Couchman"}^{13} \quad (11)$$

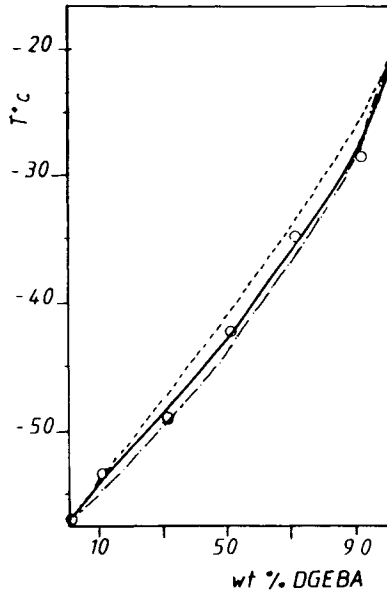


Fig. 1. Glass transition temperature vs. composition for UP-DGEBA, $\bar{n} = 0.03$ blends: (○) experimental values ($q = 7.5$ K/min); (---) Fox model; (—) Couchman model; (-·-) Di Marzio model.

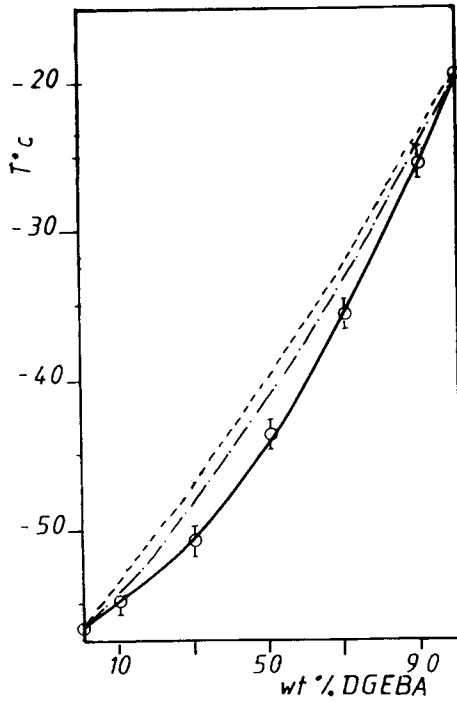


Fig. 2. Glass transition temperature vs. composition for UP-DGEBA, $\bar{n} = 0.15$ blends: (○) experimental values ($q = 7.5$ K/min); (---) Fox model; (—) Couchman model; (-·-) Di Marzio model.

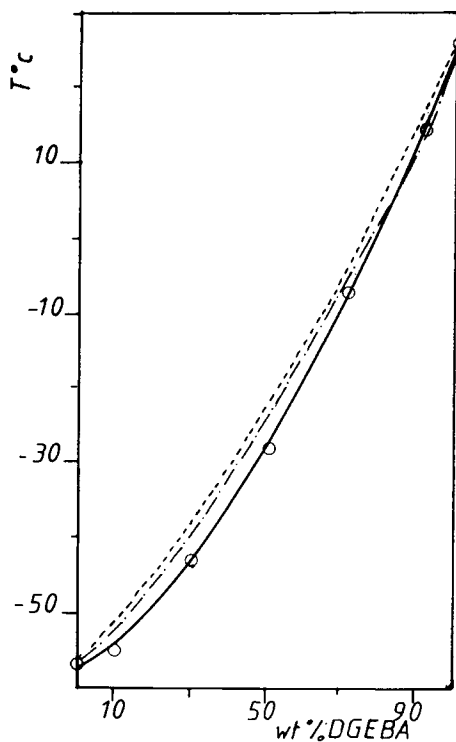


Fig. 3. Glass transition temperature vs. composition for UP-DGEBA, $\bar{n} = 1.6$ blends: (○) experimental values ($q = 7.5$ K/min); (---) Fox model; (—) Couchman model; or Di Marzio model.

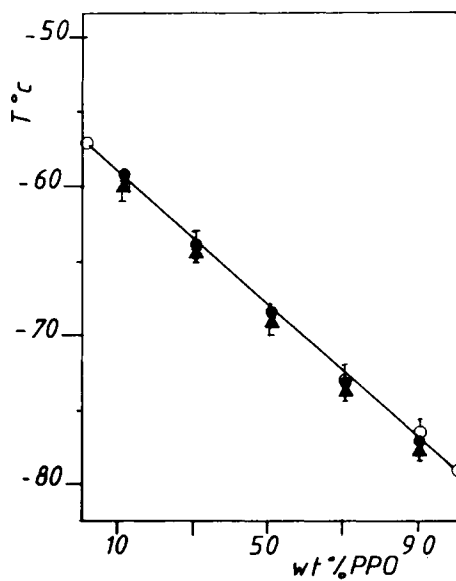


Fig. 4. Glass transition temperature vs. composition for UP-PPO blends: (○) experimental values ($q = 7.5$ K/min); (▲) Fox model; (●) Couchman model; or Di Marzio model.

where T_{g_i} = glass transition temperature of the component i , $\Delta C p_i$ = heat capacity change at T_{g_i} , and W_i = mass fraction of the component i .

We note that for blends based on DGEBA prepolymers the experimental curves exhibit a certain concavity (Figs. 1, 2, and 3). The concavity can depend on interactions existing between the chains or on a large difference of expansion coefficients at the glassy state. The predictions of Di Marzio but also Fox and Couchman equations lie beyond the experimental data.

For blends based on PPO epoxy terminated prepolymer the predictions present a good fit with the experimental data. In this case $\Delta C p_1 \cong \Delta C p_2$ (Table I) and eqs. (9) and (11) are quite similar.

FT-IR Analysis of Prepolymers

The infrared spectrum of the oligo(isophthalate-co-fumarate of diethylene glycol) (Fig. 5) shows in the range of 1850–1550 cm^{-1} a large band corresponding to the carbonyl stretching mode.¹⁴ This band is broad; this phenomenon is assigned to different factors:

- (i) There are at least three carbonyl bands: isophthalate and fumarate have the same frequency 1725 cm^{-1} , but the C=O providing from the by-side reaction absorbs like an acetate at 1740 cm^{-1} .
- (ii) Relatively strong intramolecular hydrogen bonding may exist between the carbonyl bonds and the hydroxyl terminal groups.

The infrared spectrum of the diglycidyl ether of bisphenol A DGEBA (not presented here) is characterized by relatively narrow bands attributed to localized normal vibrations associated mainly with the rigid phenyl and

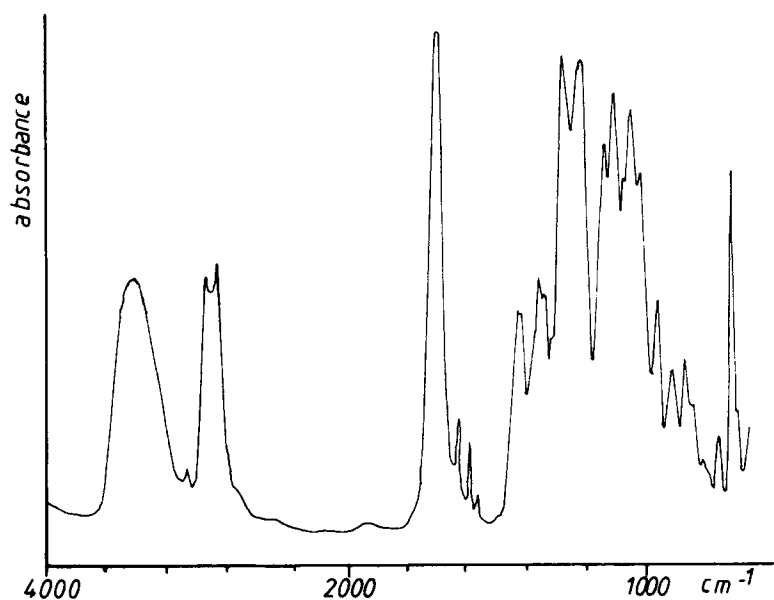


Fig. 5. FT-IR spectra recorded at 25°C for oligo(isophthalate-co-fumarate of diethylene glycol).

methyl groups and relatively broad bands which are attributed predominantly to the remaining chemical groups which are highly coupled, conformationally sensitive modes. One particular interest of this study is that there is a "window" in the $1850\text{--}1650\text{ cm}^{-1}$ region of the spectrum which is essentially free of underlying absorbance. This is very important to readily observe changes in the UP carbonyl stretching mode in the blends.

The infrared spectrum of the poly(propylene oxide) epoxy-terminated oligomer (not presented here) presents a small absorbance in the range of $1650\text{--}1850\text{ cm}^{-1}$ attributed to the existence of some carbonyl groups in the polymerization initiator of PPO which are always present in the chain. Like in DGEBA prepolymers the absorbance of the hydroxyl stretching mode in the range of $3700\text{--}3100\text{ cm}^{-1}$ is observed.

Specific Interactions in Dilute Solutions

The carbonyl stretching frequency observed in solution depends strongly on the nature of the solvent. This is due to the sensitivity of $\text{C}=\text{O}$ to conformational and interaction changes.¹⁵

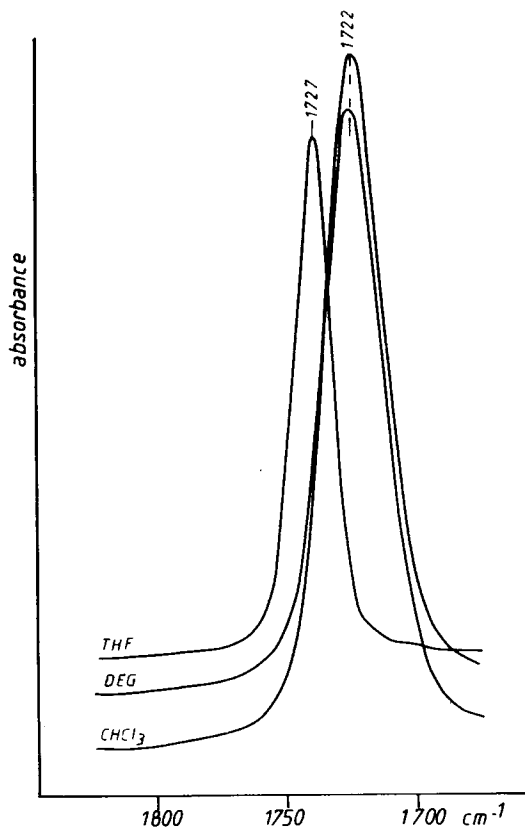


Fig. 6. FT-IR spectra recorded at 25°C in the carbonyl stretching region $1675\text{--}1775\text{ cm}^{-1}$ for the UP oligomer solutions (1% by weight) in different solvent.

The carbonyl oxygen of esters are basic (electron donor) sites. They can form acid–base bonds with the electron accepting sites of acidic molecules such as chloroform or alcohol. Inversely a basic solvent like tetrahydrofurane can interact only by dispersion forces with carbonyl groups.¹⁶

The carbonyl stretching frequencies of the bulk UP have been evaluated using three probes, tetrahydrofurane (THF), diethylene glycol (DEG), and chloroform (CHCl_3) to evaluate the different carbonyl stretching frequencies present in the bulk up.

The FT-IR analysis at room temperature gives (Fig. 6):

- (i) For 1% by weight of oligomer UP in THF, a narrow band centered on 1727 cm^{-1} attributed to “free” carbonyl bonds.
- (ii) For 1% by weight for oligomer UP in DEG, a narrow band centered on 1722 cm^{-1} . The carbonyl group of esters seems to form acid–base bonds with the acid hydrogen groups of C—OH in the DEG. The carbonyl shift, 1727 cm^{-1} in THF to 1722 cm^{-1} in DEG, is attributed to hydrogen bonding.
- (iii) The same behavior of dilute solutions in CHCl_3 than in DEG. This is an acidic molecule which can also form hydrogen bonds with the carbonyl groups of the UP.

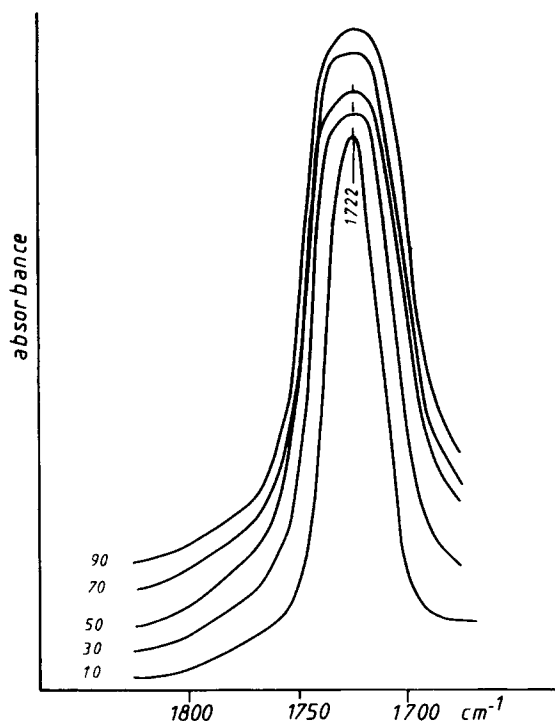


Fig. 7. FT-IR spectrum recorded at 25°C in the range $1675\text{--}1775 \text{ cm}^{-1}$ for UP-DGEBA, $\bar{n} = 0.03$ blends at different percent by weight of UP.

So in conclusion, using basic and acid solvents, referring to the basic C=O groups, we obtain two carbonyl stretching frequencies:

- 1727 cm^{-1} corresponding to the “free” carbonyl groups
- 1722 cm^{-1} corresponding to the hydrogen bonded carbonyl groups

Specific Interactions in Polymeric Blends

In blends containing DGEBA, $\bar{n} = 0.03$ and $\bar{n} = 0.15$ for 1% by weight of oligomer UP, the carbonyl stretching frequency appears as a narrow band centered on 1722 cm^{-1} (Figs. 6 and 7). It is difficult to prepare films with more than 50% wt of DGEBA, $\bar{n} = 1.6$ because at room temperature blends become vitreous (Fig. 8). But the same behavior than for the other DGEBA with the apparition of a band centered on 1722 cm^{-1} is observed. As in dilute solutions in DEG or CHCl_3 , this carbonyl stretching frequency is attributed to associated carbonyl bonds. There are hydrogen bonds between the secondary alcohol of the DGEBA (and also some primary alcohol of some chain ends) and the C=O of the UP.

For a high concentration of PPO in the blend, the carbonyl stretching frequency appears as a band centered on 1725 cm^{-1} (Fig. 9). But it is difficult

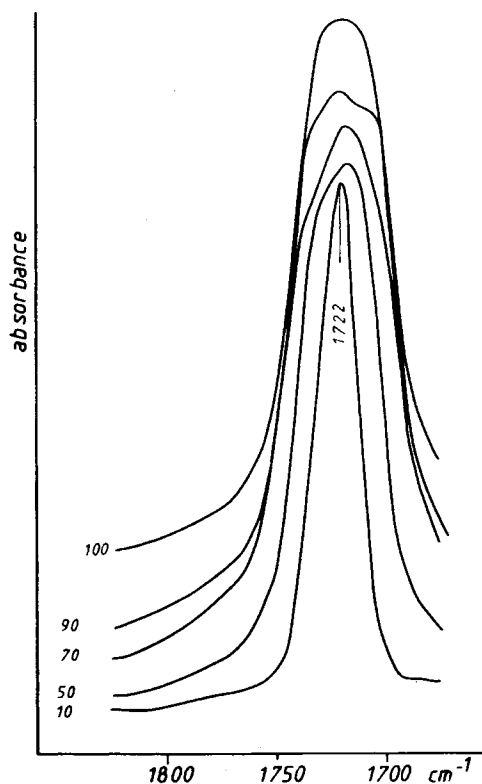


Fig. 8. FT-IR spectrum recorded at 25°C in the range 1675–1775 cm^{-1} for UP-DGEBA, $\bar{n} = 0.15$ blends at different percent by weight of UP.

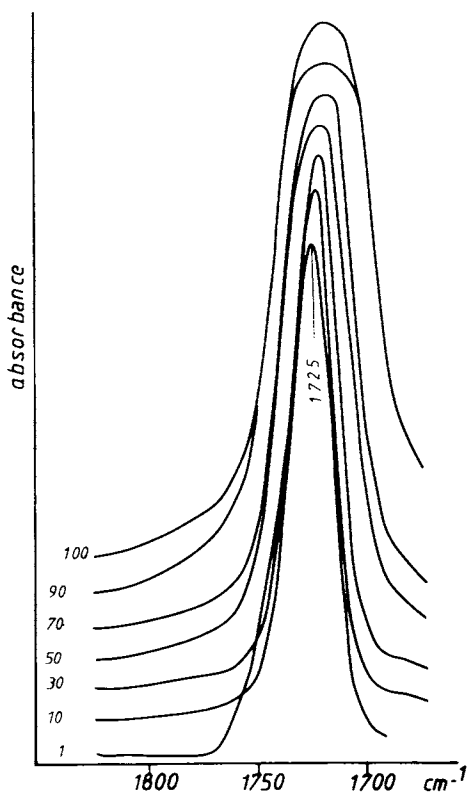


Fig. 9. FT-IR spectrum recorded at 25°C in the range 1675–1775 cm^{-1} for UP-PPO blends at different percent by weight of UP.

to conclude in this case because there is little absorption in the carbonyl stretching region of the pure PPO and this absorption masks an eventual shift of the carbonyl band.

CONCLUSION

The purpose of this paper was to look for the miscibility between an unsaturated polyester prepolymer and different epoxy-terminated prepolymers.

All the oligomer blends considered are miscible. From a theoretical point of view, blends containing low molecular weight DGEBA are miscible due to the height value of the combinatorial part of the free energy of mixing. When the DGEBA molecular weight increases, the combinatorial part of the free energy of mixing decreases; but this effect is compensated by the ability of the carbonyl group of UP to form hydrogen bonds through hydroxyl groups.

For blends containing polypropylene oxide, miscibility is due to the low molecular weight of this component; hydrogen bonding has not been exhibited.

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