

Preparation and Properties of Catalyzed Polyimide/Dicyanate Semi-Interpenetrating Networks for Polymer Gas Membrane with Suppressed CO₂-Plasticization

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ABSTRACT: The work presents an approach to reduce the plasticization of polymeric membranes caused by condensable gases, and particularly the effect of plasticization caused on polyimides by CO₂ at high pressure. A technical polyimide, Matrimid[®], was chosen as a reference of polyimide membrane and the approach applied consisted of incorporating reactive oligomers to have cross-linkable mixed systems, which do not plasticize at high CO₂ pressure. Films of semi-interpenetrating networks (semi-IPNs) based on Matrimid[®] and phenolphthalein dicyanate as cross-linking monomer in ratios 90/10, 80/20, and 70/30, were prepared using a catalyst to lower the curing temperature from 280 to 180°C. Semi-IPNs properties such as thermal stability, mechanical properties, glass transition temperatures, or density were measured to characterize

the films and were correlated with the dicyanate monomer content. The CO₂ gas permeation behavior of the three semi-IPNs was studied using a CO₂ feed pressure ranging from 1 to 30 atm. The gas separation properties were mainly explained attending to the density of the films, which depended on the dicyanate content used. In the three catalyzed semi-IPNs, the CO₂ permeability coefficients remained almost constant all along the investigated range of CO₂ pressure while Matrimid[®] treated at 180°C did show a clear tendency to plasticization over a critical feed pressure of about 17 bar. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 713–722, 2012

Key words: polyimide; catalyst; semi-interpenetrating network; gas permeation; oligomers

INTRODUCTION

Polyimide membranes are used as functional materials for gas separation because they have better permeability–selectivity balance compared with conventional glassy polymers.¹

However, a disadvantage of polyimides to develop high-pressure separations, such as natural gas upgrading or enhanced oil recovery, is their great tendency to plasticize at high CO₂ pressures.^{2–4} In general, at low upstream pressures, the gas permeability decreases with increasing pressure, however, when the pressure is further raised, an increase of permeability is observed. The pressure corresponding to the minimum permeability is known as the plasticization pressure. Above this pressure, the seg-

mental mobility is increased because the absorbed gas molecules disrupt the polymeric chain packing. As a consequence, size sieving separation of gas molecules is more difficult and membrane selectivity is severely impaired. In addition, on the macro-scale, plasticization produces an increase of polymer softness, and a decrease of ductility and glass transition temperature.^{2,3}

As suppressing plasticization implies a reduction of the chain flexibility, cross-linking of polymeric membranes by heat treatment is a method widely used to reduce this undesired effect. Thus, it has been repeatedly observed that the thermal annealing of commercial polyimide Matrimid[®] films at 350°C during 10–30 min, successfully suppresses the CO₂ plasticization.⁵ It was hypothesized that heat treatment causes a densification of the polymer matrix due to combination of cross-linking and charge transfer complex formation.

Covalent cross-linking of the polyimide chains has been also extensively used to suppress plasticization. This method involves the presence of reactive groups in the polyimide, such as carboxylic acid groups, suitable to cross-linking through reaction with aliphatic diols.^{6–8} In this way, materials with good anti-plasticization properties can be achieved,

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and the approach has the advantage that the cross-linking degree can be easily controlled by adjusting the carboxylic acid group concentration. However, for the cross-linking to achieve great extent, a heat treatment above 200°C over a 24-h period is usually necessary to complete the curing reaction.^{6,8}

Polyimides without cross-linkable groups can also be covalently cross-linked with diamine compounds. This is an attractive approach because anti-plasticization properties can be achieved combining cross-linking times and annealing temperatures between 100 and 250°C. However, this method involves opening of the imide rings, so that the polyimide structure is not maintained any more after the treatment, and much of the inherent ability of polyimides for gas separation is lost.^{9–11}

One attractive approach to suppress plasticization could be the combination of linear polyimides with cross-linkable oligomers which can form semi-interpenetrating networks (semi-IPNs). A semi-IPN is defined as combination of two polymers in a network-form where one of them is cross-linked in the presence of the other, which is linear.¹² According with International Union of Pure and Applied Chemistry Compendium of Chemical Terminology, semi-interpenetrating polymer networks are distinguished from interpenetrating polymer networks because the polymer matrix can, in principle, be separated from the network without breaking chemical bonds, as if they behaved as polymer blends.¹³ However, the potential of semi-IPNs as polymer materials for gas separation with special merits for plasticization suppression has been scarcely explored so far.^{14–17}

For example, Bos et al. blended the linear polyimide Matrimid[®] with Thermid FA-700, an oligomer with terminal reactive acetylene groups. On heating over the curing temperature, the bis-acetylene oligomer polymerized and cross-linked inside the polyimide linear matrix, resulting in a semi-IPNs that reduced Matrimid[®] chain mobility and suppressed CO₂-induced plasticization. Nevertheless, the cross-linking of the acetylenic end groups of Thermid FA-700 occurs at very high temperature (about 300°C), which means a hazard of thermal decomposition because usually long curing times are needed for the cross-linking reaction to achieve high extent.¹⁴ Recently, Low et al. have prepared pseudo-interpenetrating networks by *in situ* polymerization of 2,6-bis(azidobenzylidene)4-methylcyclohexanone (azide) within a preformed polyimide network. These materials show suppression of the CO₂-induced plasticization due to the restriction of the polyimide chains mobility, caused by the interpenetrating network and by chemical bridges formed between the azide and the polyimide.¹⁷

One disadvantage of this strategy is the heat treatments at elevated temperatures required to produce dense films semi-IPNs, which can cause a partial degradation of the polymer structure. Thus, for practical membrane application, it is necessary to develop a cross-linking strategy at moderate temperatures that can suppress CO₂ plasticization without bringing about the degradation of the polyimide.

The approach of fabricating semi-IPNs by combining a linear polymer and a cross-linkable monomer or oligomer is a recognized suitable alternative to rigidize and to increase the T_g of engineering thermoplastics, and also to improve the toughness of very stiff, difficult to process thermosets. In the 1980s and 1990s, semi-IPNs systems gained special importance as novel materials for aerospace applications. In this regard, reactive oligomers of very varied chemical nature were prepared and evaluated as components of semi-IPNs in combination with engineering thermoplastics, particularly polyimides and poly(aryl-ether)s.¹⁸ Studies on the curing kinetics of these systems highlighted that reactive oligomers containing maleimide, nadimide, or acetylene groups were especially appropriate for the preparation of high performance semi-IPNs. Other reactive groups investigated were, for instance, phenylacetylene, biphenylene, benzocyclobutene, phthalonitrile, and cyanate.¹⁸ Each individual function provides different curing temperature and curing kinetics, as well as different properties to the final cured material.¹⁸ Among them, dicyanates did not reach great significance as semi-IPN component. On the other hand, dicyanate resins have gained growing importance as special adhesives, coatings, and composites in last decades, so that a considerable basic knowledge of their properties and curing reactions and kinetics has been collected until now.¹⁸

In this work, we report novel dicyanate semi-interpenetrating polyimide networks (semi-IPNs) that were prepared at relatively low temperatures. Usually, to make semi-IPNs from dicyanates, the dicyanate/polymer mixture needs to be heated up to 250–300°C to assure complete curing of the system.^{19–22} In these conditions, the dicyanate cyclotrimerizes into an uniform three dimensional network of oxygen-linked triazine rings (cyanurate ester resin). However, dicyanate monomers can be also cured at lower temperatures in the presence of specific catalysts²³; in fact, the preparation of dicyanate-based semi-IPNs in the presence of catalyst at temperatures below 250°C has been previously reported.^{24–28}

Thus, the first objective of this work was the preparation and characterization of novel catalyzed semi-IPNs from the commercial polyimide Matrimid[®], and phenolphthalein dicyanate (Fig. 1) in ratios 90/10, 80/20, and 70/30 at moderate temperature. The semi-IPNs were cured in the presence of copper

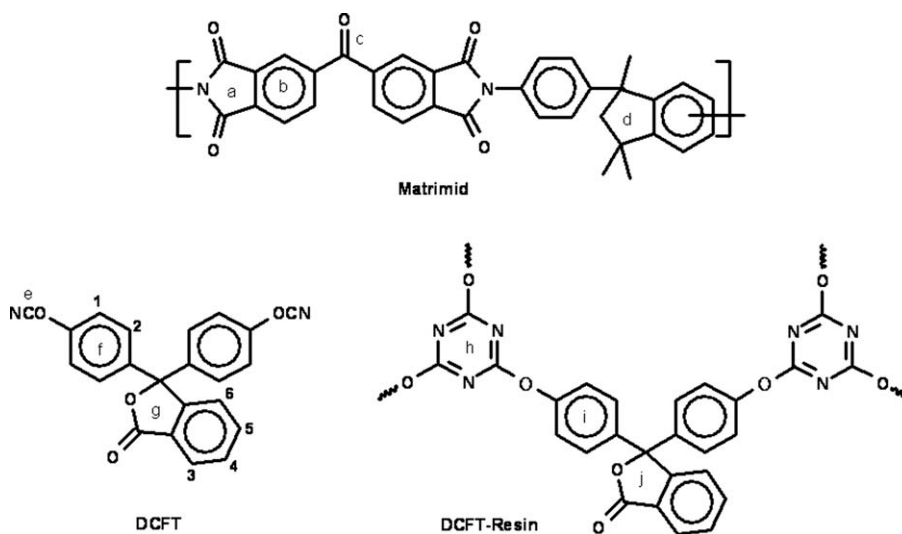


Figure 1 Chemical structure of Matrimid, phenolphthalein dicyanate (DCFT), and cyanurate ester resin (DCFT-Resin).

naphthenate and nonylphenol as catalyst, which allowed applying a moderate curing temperature of 180°C.

The practical objective of this work was to investigate the CO₂ permeation behavior of the new semi-IPN systems in the form of dense films. The results were compared with those obtained with Matrimid[®] membranes which were annealed under the same heating protocols.

EXPERIMENTAL

Materials

The polyimide Matrimid[®] 5218 (named as Matrimid in this work) was obtained from Ciba-Geigy. Phenolphthalein was supplied from Across and was used as received. Phenolphthalein dicyanate (DCFT) was synthesized following the procedure reported elsewhere.²⁹

Copper naphthenate and nonylphenol were supplied from Supelco and were used as received. Catalyst was prepared by dissolving copper naphthenate in nonylphenol according to a procedure previously reported.³⁰ Dichloromethane supplied from Supelco was used without further purification.

Semi-IPNs preparation

0.9, 0.8 or 0.7 of Matrimid were dissolved in 10 mL of CH₂Cl₂ and phenolphthalein dicyanate was added to the solution in the desired ratios (90/10, 80/20, and 70/30 wt % Matrimid/Phenolphthalein dicyanate monomer, respectively). Copper naphthenate dissolved in nonylphenol, as indicated in Table I, was added to the above solutions and stirred for 10 min, and afterwards the solution was filtered and poured on a levelled glass plate covered with a hood, leaving a small gap to allow the solvent to slowly evaporate. The films were removed from the glass and were dried under vacuum oven at 80°C during 12 h to remove any remaining solvent. Finally, the films were placed into a glass container and were purged with N₂ and degassed under vacuum three times. The degassed glass container was introduced in a vacuum oven and the temperature was raised up to 180°C for 1 h to accomplish cross-linking. Taking into account the DCFT content, semi-IPNs were designed as semi-IPN 10, semi-IPN 20, and semi-IPN 30, respectively. Films thickness at the end of the process was 80–120 μm.

For comparative purposes, we preserved pieces of uncured films that were named as Mat/DCFT-10, Mat/DCFT-20, and Mat/DCFT-30, respectively.

TABLE I
Composition and Designation of Matrimid Films and Catalyzed Semi-IPN

Membrane designation	Matrimid (CH ₂ Cl ₂)	DCFT	Catalyst	Curing temperature
Untreated Mat	1 g (10 mL)	–	–	–
Mat-180	1 g (10 mL)	–	–	180°C
Semi-IPN 10	0.9 g (10 mL)	0.1 g	18 mg	180°C
Semi-IPN 20	0.8 g (10 mL)	0.2 g	36 mg	180°C
Semi-IPN 30	0.7 g (10 mL)	0.3 g	54 mg	180°C

Matrimid films preparation

Two dense films were prepared from two solutions (1 g of Matrimid in 10 mL of CH_2Cl_2) and following the procedure above described. The films were dried in a vacuum oven at 80°C during 12 h to remove any remaining solvent. One of these films was designed as untreated Matrimid. The second one was thermally treated in a degassed glass receptacle at 180°C for 60 min and was named as Matrimid-180. Films thickness was 85–90 μm .

Measurements

^1H NMR spectra were recorded on a Bruker 300 spectrometer operating at 300 MHz (Oestliche Rheinbrueckenstr. 49, Karlsruhe, Germany).

Microanalyses were made with a Carlo Erba EA1108 elemental analyzer (Rodano, Italy) and the mass spectra were recorded on a MSD5973 of Agilent Technologies (5301 Stevens Creek Blvd, Santa Clara, CA).

Fourier transform infrared (FTIR) spectra of polymer films were recorded on a Perkin-Elmer RX-1 instrument (940 Winter Street, MA).

Thermogravimetric analysis (TGA) data were obtained on a TA TGA Q-500 analyzer (159, Lukens Drive New Castle, DE) under nitrogen atmosphere, using around 5 mg of sample under a flow of nitrogen of 60 mL/min and at a heating rate of $10^\circ\text{C}/\text{min}$ from 50 to 850°C .

Differential scanning calorimetry (DSC) data were obtained on a TA DSC Q-2000 (159, Lukens Drive New Castle, DE) instrument from around 5 mg samples at a $20^\circ\text{C}/\text{min}$ scanning rate under a flow of nitrogen of 50 mL/min. The glass transition temperatures were taken as the midpoint of the transition during the second run. Densities were measured in an analytical Sartorius balance by weighing the samples in air and then in a liquid of known density (isooctane). The density of the sample was calculated from the expression:

$$\rho_{\text{sample}} = \rho_{\text{liquid}}[(w_{\text{air}} - w_{\text{liquid}})/w_{\text{air}}].$$

At least six density measures were recorded for each film. Ultraviolet–visible (UV–vis) absorption spectra were measured from films at room temperature using a UV–vis Perkin-Elmer Lambda 16 spectrophotometer (940 Winter Street, MA).

Tensile strength, elongation at break, and Young's module of the membranes were measured with a MTS Synergie 200 apparatus (14000 Technology Drive, Eden Prairie, MI), fitted with a 100N load cell at room temperature. The samples of 5-mm width were clamped at both ends with an initial gauge

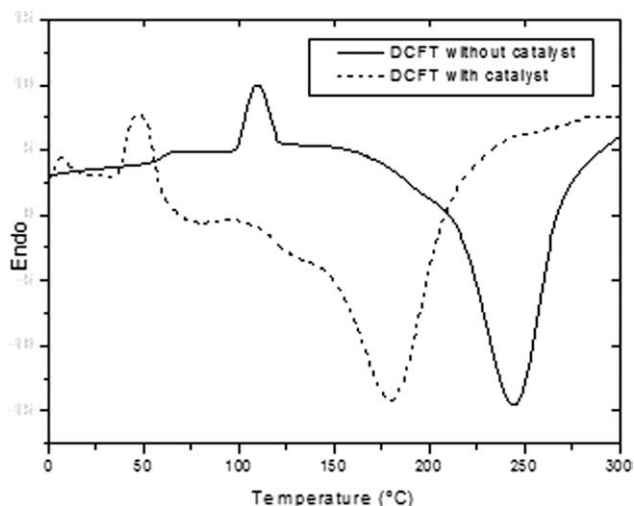


Figure 2 DSC curves of phenolphthalein dicyanate with and without catalyst.

length of 12 mm at 5 mm/min. At least eight samples were tested for each membrane.

Permeability measurements

The gas permeation properties were determined for pure CO_2 feeds using a constant volume/variable pressure apparatus at 30°C . The downstream pressure was kept below 10^{-2} mbar, while the upstream pressure was varied from 1 to 30 bar.

Permeability coefficients (P) were determined from the slope of downstream pressure versus time, plotted once steady state had been achieved, according to the equation:

$$P = K(B \times L)/P_0$$

where K is an apparatus constant that joined some parameters such as temperature, cell permeation area, and volume of the system; B is the slope of downstream pressure versus time; L is the film thickness; and P_0 is the upstream pressure.

To ensure reproducibility of results, each membrane was measured twice.

RESULTS AND DISCUSSION

Semi-IPNs preparation and characterization

To establish the curing conditions, the polymerization of phenolphthalein dicyanate (DCFT) was investigated by DSC. Catalyzed and non-catalyzed samples were measured (Fig. 2). Uncatalyzed DCFT displayed a melting endotherm at 110°C and a broad curing exotherm peak with a maximum at 244°C . Surprisingly, the data are far from those reported by Zhang et al., who had previously observed a melting point of 135.6°C and a maximum of curing exotherm

TABLE II
Characterization Data of DCFT

Molecular formula		Elemental analysis			m/z (IE)	
$C_{22}H_{12}N_2O_4$; $M_w = 368.35$ g/mol		Calculated	C%	H%	N%	368
		Found	71.74	3.28	7.61	282
			71.55	3.58	7.42	250
1H NMR (acetone- d_6)						
H ₁	H ₂	H ₃	H ₄	H ₅ and H ₆		
7.60 ppm, dd, 4H	7.71 ppm, dd, 4H	7.95 ppm, m, 1H	7.91 ppm, m, 1H	7.76 ppm, m, 2H		

of 302°C for this dicyanate.²⁹ However, 1H NMR and mass spectra data (Table II) indicated the absence of by-products associated to the monomer synthesis such as diethylcyanamide or carbamates.³¹ The elemental analysis indicated also enough monomer purity (Table II) and the mass spectra showed the presence of the desired compound (m/z 368) and two components at m/z 282 and 250 referable to cyanates and benzofuranone fragmentations, respectively.

The width of the processing window (temperature interval between the melting temperature and onset temperature of the curing exotherm) can be taken also as a rough measure of monomer purity.³¹ In this regard, the DSC of phenolphthalein dicyanate exhibited a processing window of around 100°C, similar to that reported by Zhang et al.²⁹ Finally, the polymerization enthalpy obtained by integrating the curing exotherm was 383 J/g, which was also very close to that obtained by Zhang et al. of 377 J/g.²⁹

In the presence of catalyst, DCFT evolved to the corresponding cyanurate ester resin at lower temperature as it could be observed by calorimetry. The DSC curve displayed a curing exotherm peak with a maximum around 180°C and a narrower processing window than that of the uncatalyzed reaction, so that all the curing experiments to prepare the semi-IPNs were performed at 180°C.

To prepare the semi-IPNs, Matrimid was first dissolved in dichloromethane, and DCFT was added to the Matrimid solution in ratios Matrimid/DCFT 90/10, 80/20, and 70/30 and the catalyst was added in the last step. Although many classes of compounds can be used as catalyst, particularly protic acids and Lewis acids and bases,³² combinations of active hydrogen compounds with transition metal complexes are at present widely used to prepare cyanate ester resins at temperatures around 200°C.^{33–36} The reaction proceeds in two main steps: first the phenol forms an imidocarbonate with one cyanate group, which reacts then with two more cyanate groups to generate a triazine ring. The transition metal serves as a coordinating template to promote the ring formation. In this work, a mixture formed by nonylphenol and copper naphthenate was used as catalyst. It was prepared according to a procedure previously reported.³⁰

In absence of catalyst, the semi-IPNs of this work needed a curing temperature of 280°C for 1 h to be completely formed. Under these conditions, the CO₂-induced plasticization of Matrimid was suppressed. So, preparation of semi-IPN at 280°C to reduce plasticization has no sense since the thermal treatment of Matrimid at that temperature was enough to suppress this effect.

The use of catalyst permitted the preparation of semi-IPNs of this work by curing the corresponding Matrimid/DCFT/catalyst films at a much lower temperature, just at 180°C for 60 min. As it was checked by FTIR and DSC, after this treatment, dicyanate seemed to be entirely converted into the corresponding cyanurate ester resin, as it happened with the Mat/DCFT-20 sample.

Figure 3 shows the FTIR spectra of the semi-IPN 20 (down) compared with the film Mat /DCFT-20 before curing (up). The letters in parentheses indicate the location of each group in the Matrimid, DCFT, and cyanurate resin shown in Figure 1. The spectrum before curing showed the characteristic peaks of the main components, Matrimid, and DCFT. Most of the absorption bands corresponded to Matrimid. The peaks at 711 and 722 cm⁻¹ were assigned to the C–N groups; the absorptions at 1207, 1367, and 1425 cm⁻¹ corresponded to the CH, CH₃, and CH₂ bonds of the five-member rings; the peak at 1675 cm⁻¹ was assigned to the carbonyl group of the ketone group and finally, the absorptions at 1716 and 1779 cm⁻¹ corresponded to the CO groups of the imide rings. All Matrimid signals were coincident with reported assignments for this polyimide.³⁷

The spectrum displayed also the split bands characteristic of aromatic cyanate stretching at 2271 and 2237 cm⁻¹ as it was previously reported,²⁹ whereas the other bands attributed to the DCFT monomer were overlapped by the Matrimid absorptions.

The IR spectrum of semi-IPN 20, did not show the absorption of the dicyanate groups, which confirmed the quantitative formation of the cyanurate ester resin. The presence of two new bands at 1580 and 1370 cm⁻¹, characteristic of the triazine ring in the cyanurate structure, was also a proof of the resin formation.^{33–36} Unfortunately, the spectrum exhibited only one of the bands, at 1580 cm⁻¹, because

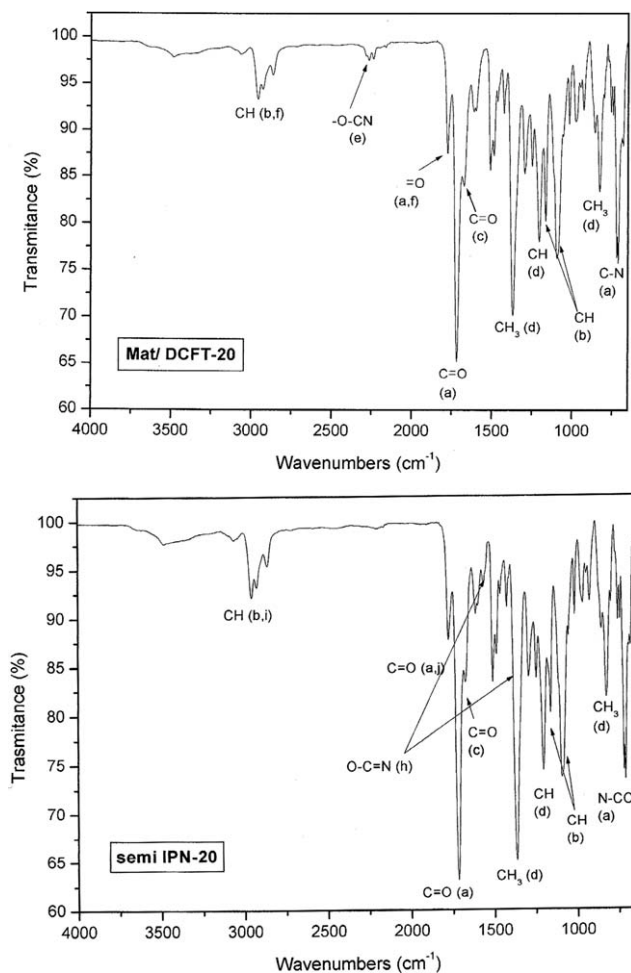


Figure 3 FTIR spectra of Mat/DCFT-20 (up) and semi-IPN 20 (down).

the other one was overlapped by the very strong Matrimid absorptions.

Semi-IPNs properties

Glass transition temperatures and density

Matrimid film treated at 180°C showed a glass transition temperature (T_g) higher than that of untreated Matrimid by about 15°C (Table III). This indicated that the thermal treatment did have an influence on the chain stiffness, although minor densification or

cross-linking had occurred. This fact could be attributed to the treatment temperature, which was below the Matrimid T_g but it was high enough to remove occluded solvent and water. In fact, most of the thermally treated Matrimid films reported in the literature were heated at higher temperatures, above the T_g , yielding films with higher T_g values.⁵ Whether this rising of T_g and insolubilization were due to “densification” and increase of molecular packing, or if it was due to an effective cross-linking and tightening of interchain attraction forces through CTCs, has never been clearly elucidated. Most probably, a combination of all these possible processes takes places simultaneously, each one playing a more significant role depending on the polyimide chemical composition and on the annealing time and temperature. In any case, the experimental evidence proved that Matrimid-180 showed slightly higher density than that of the untreated one. Moreover, the densities of both films were lower than those reported for Matrimid films treated at higher temperatures. This was also in agreement with data reported by Bos et al. who found a density of 1.28 g/cm³ for Matrimid treated at 350°C for 30 min,² and it confirmed the lower molecular packing of Mat-180 film. To check densification and/or the existence of cross-linking, both films were dipped into the original casting solvent, assuming that a cross-linked film would not dissolve anymore.^{5,14} After 30 min, both films were completely dissolved, confirming that their cross-linking degree was actually negligible. In addition, the colour of Matrimid films changed from yellow to light brown when Matrimid was cross-linked by thermal treatment at high temperature⁵; however, Mat-180 still exhibited a pale yellow colour after the thermal treatment, just as the untreated film did.

All the semi-IPN films showed a single T_g (see Fig. 4 and Table III), which indicated that all of them were one phase materials, as it had been reported for other dicyanate semi-IPNs.¹⁷ For most of the semi-IPNs reported, the T_g s were between the values of the separated components. However, in our case, the T_g 's were between 292 and 304°C, slightly lower than that for Matrimid ($T_g = 313^\circ\text{C}$) and lower than that of the phenolphthalein

TABLE III
Thermal Properties and Densities of Matrimid Films and Catalyzed Semi-IPNs

Film	T_g (°C)	Density (g/cm ³)	T_d onset (°C) 1 st step	Weight loss (%)	T_d onset (°C) 2 nd step	Chard yield (850°C)
Untreated Mat	313	1.231	495			
Mat-180	328	1.241	495			
Semi-IPN 10	294	1.253	350	8.93	493	52
Semi-IPN 20	292	1.262	352	14.27	493	50
Semi-IPN 30	304	1.274	347	19.15	491	49

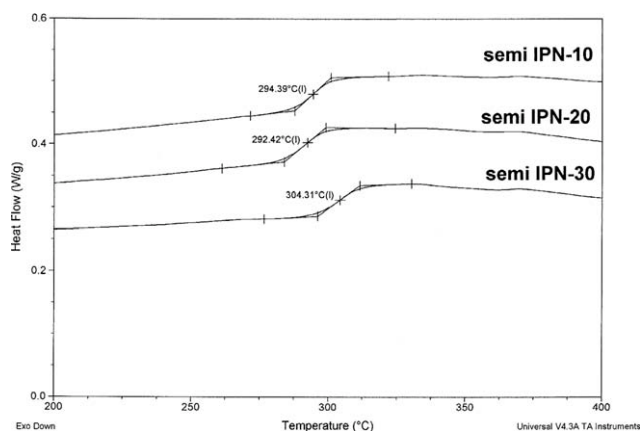


Figure 4 DSC curves of catalyzed semi-IPNs.

cyanurate ester resin ($T_g = 362^\circ\text{C}$,²⁹). An explanation to this unexpected result could be that the bulky phthalide moiety of the resin contributed to a more open polymer matrix, which reflected in a drop of T_g . On the other hand, no obvious relationship was observed between the dicyanate monomer content and T_g s, as all of the semi-IPNs exhibited similar values.

This decrease of T_g was surprising as the densities of the semi-IPNs (Table III) were higher than those of Matrimid films. So, it is to presume that the presence of the cyanurate ester resin within the Matrimid matrix clearly caused a densification of the films, as it was reported also for other semi-IPNs,¹⁴ in such a way that the higher the dicyanate content the higher the T_g . Even a linear relationship between the DCFT content and the semi-IPNs density could be found, as is depicted in Figure 5.

Thermal stability and mechanical properties

Table III and Figure 6 show the thermal degradation behavior of Matrimid films and the three semi-IPNs.

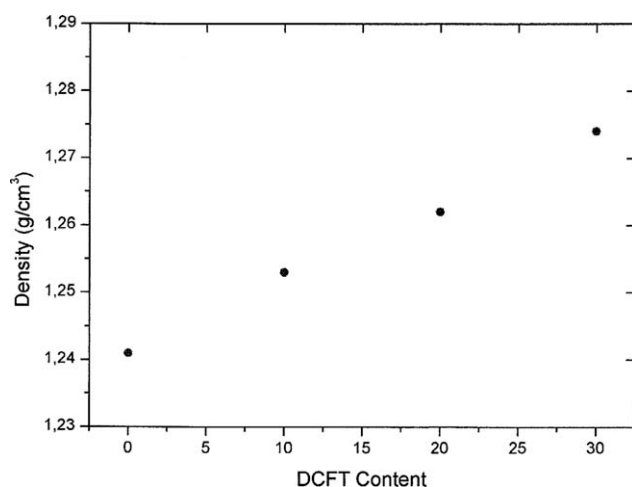


Figure 5 Density versus phenolphthalein dicyanate monomer (DCFT) content.

Untreated Matrimid and Mat-180 showed a thermal decomposition in one step beginning at 495°C , while semi-IPNs exhibited a two-step degradation pattern. The first weight loss temperature was around 350°C and it was attributed to the cyanurate resin component because the pure thermoset resin has a decomposition temperature of 414°C .²⁶ Moreover, the weight loss associated to the first step increased with the dicyanate content as it was observed also with other semi-IPNs.^{17,38}

The second step, assigned to the Matrimid decomposition, occurred at around 493°C . These results indicated that thermal stability of semi-IPNs was governed by the concentration of the less stable component.

Data on mechanical resistance of Matrimid and semi-IPNs films are given in Table IV. Untreated Matrimid showed the same mechanical properties of Matrimid film reported by Zhao et al.³⁹ However, Jiang et al. have recently reported Matrimid film with slightly higher tensile strength and Young's module and lower elongation at break.⁴⁰ Matrimid

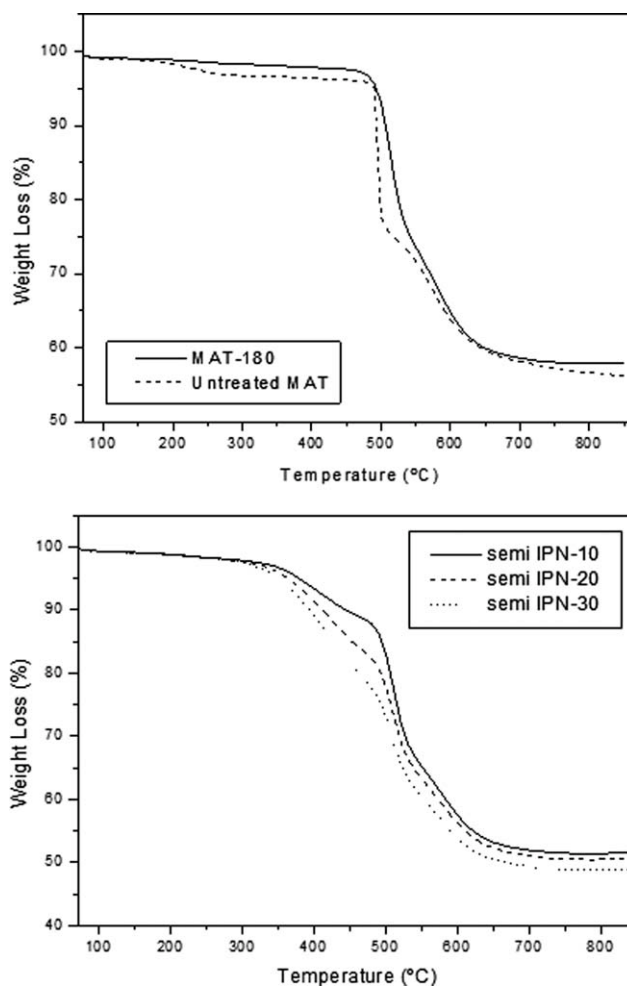


Figure 6 TGA of Matrimid films (up) and catalyzed semi-IPN (down).

TABLE IV
Mechanical Properties Matrimid Films and
Catalyzed Semi-IPNs

Film	Young's module (Gpa)	Tensile strength (Mpa)	Elongation at break (%)
Untreated Mat	1.50	70.2	15.96
Mat-180	1.24	59.0	7.65
Semi-IPN 10	1.57	84.2	7.82
Semi-IPN 20	1.71	84.7	6.82
Semi-IPN 30	1.72	75.8	5.71

film treated at 180°C was less strong and tough than that untreated. On the contrary, all semi-IPNs showed higher tensile strength and Young's module than Matrimid films, which confirmed that semi-IPNs are more rigid and more resistant than the linear polyimide matrix.³⁸ For example, Young's modulus of semi-IPN 10 increased around 5% respect untreated Matrimid, whereas for semi-IPN 20 and semi-IPN 30 increases of 14 and 19% respectively were observed. As to the tensile strength, there was a significant increase from untreated Matrimid to semi-IPN 10 and semi-IPN 20 (around 20%) with a lower increase for semi-IPN 30. The biggest change was observed for the elongation at break that diminished by about a 50% when Matrimid was heated to 180°C. The expelling of water absorbed and residual solvent, combined with molecular densification, should account for this effect. Interestingly, the semi-IPNs showed a linear relationship between the DCFT content and the elongation at break, which diminished when the DCFT content increased (Fig. 7). This result was concordant with a higher difficulty for Matrimid film to stretch on cyanurate ester resin formation.

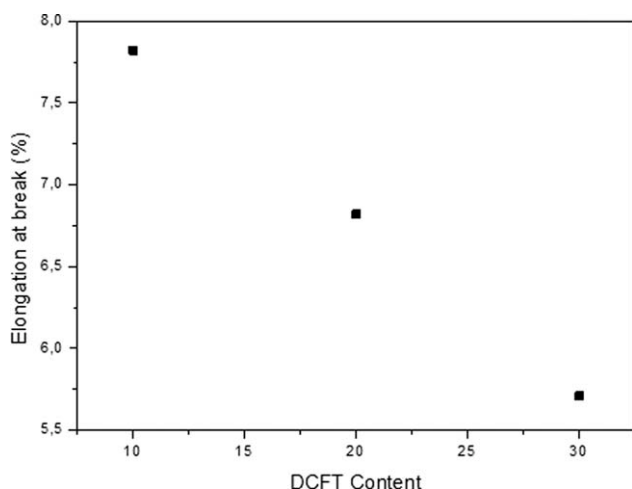


Figure 7 Elongation at break versus phenolphthalein dicyanate (DCTF) content.

CO₂ plasticization behavior

Plasticization can be described by the permeability behavior as a function of pressure. As the permeation lag time for dense membranes was relatively high, between 2 and 6 h, for each permeation experiment, CO₂ feed pressure was increased from 1 to 30 atm over a period of 10–15 days. Figure 8 shows the CO₂ permeability coefficient as a function of CO₂ feed pressure for the two Matrimid films. The untreated Matrimid showed a minimum in the permeation isotherm at 13 atm, which is coincident with the values reported for untreated Matrimid films.^{3,9,14} The Matrimid film heated at 180°C still showed the increase in permeability but the plasticization pressure was higher (around 17 bar) than that of the untreated Matrimid. So, the thermal treatment at 180°C somehow cut down the plasticization effect by shifting the plasticization pressure at higher value. Nonetheless, it was not sufficient to suppress plasticization efficiently.

The CO₂ permeation behavior for the three catalyzed semi-IPNs compared with the corresponding Matrimid treated film has been depicted in Figure 9. It should be noticed that all semi-IPNs clearly exhibited a suppression of the plasticization effect. The plasticization suppression was attributed to the densification of the semi-IPNs as all semi-IPNs showed higher density than Matrimid films, and this should be attributed to a compacting effect caused by the presence of the cyanurate ester resin into the Matrimid matrix. As a consequence, the chain mobility was hindered and the CO₂ plasticization suppressed. The densification caused also a lowering of the permeability coefficients of semi-IPNs compared with the Matrimid films. The same had been reported by Bos et al. who attributed also the lower permeability

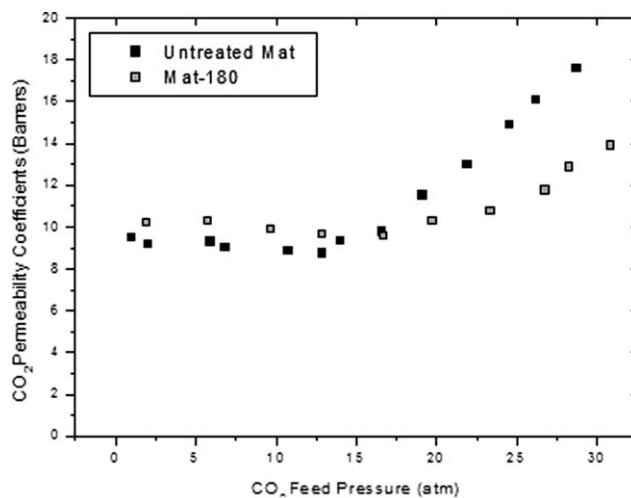


Figure 8 CO₂ Permeability-feed pressure curves of Matrimid films.

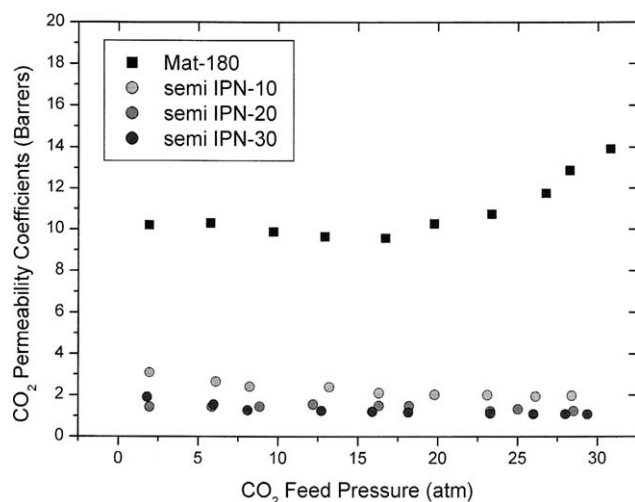


Figure 9 CO₂ Permeability-feed pressure curves of catalyzed semi-IPNs compared with Mat-180.

of thermally treated Matrimid films to a densification of the material.¹⁴ Moreover, the permeability coefficients slightly decreased from 2.5 for semi-IPN 10 to 1 barrers for semi-IPN 30, although these differences were not large enough to be significant, because they fall within the probable error in the permeability value of 10%, the decreases were consistent with the trend of semi-IPN density. Thus, the semi-IPN 30, which had the highest density, showed the lowest permeability coefficient of the series.

As the amount of catalyst used to prepare the semi-IPNs was rather high (18%) we evaluated also its effect on the CO₂ permeability coefficient. The P(CO₂) of Matrimid containing 18% of catalyst was reduced 1.25 times compared with pure Matrimid, which can be considered as acceptable, and confirm that reduction of the permeability coefficients of semi-IPNs was due to the network formation that the high content of catalyst.

As it has been also confirmed in this work, all studies reported on plasticization suppression display as main disadvantage that the permeability coefficients are reduced considerably.^{2-11,14,17} Thus, the elimination of plasticization effect without damage of the permeability continues being a pending challenge, and there is still enough room to optimize the approach to eventually solve this drawback in the application of gas polyimide membranes.

CONCLUSIONS

From this study, it can be concluded that the combination of a lineal technical polyimide as Matrimid with a dicyanate, such as phenolphthalein dicyanate (DCFT), leads to systems that can be readily converted into semi-interpenetrating polymer networks (semi-IPNs). Semi-IPNs based on Matrimid and cyanurate ester resin, prepared at moderate temperature (180°C), are a real alternative to successfully suppress CO₂-induced plasticization. This strategy can be extended to any soluble polyimide since the formation of catalyzed semi-IPNs does not change the polyimide chemical structure.

Thermal and mechanical properties of the novel semi-IPNs were also governed by the cyanurate ester resin content. Thus, the glass transition temperatures were lower than that of Matrimid because the bulky phthalide structure of the resin contributes to a more open polymer matrix, and the thermal stability also diminished with the resin content. The presence of cyanurate ester resin into the semi-IPN also affected the mechanical properties of the films, which showed higher tensile strength, higher Young's module, and lower elongation at break than Matrimid.

The CO₂ plasticization suppression was attributed to the reduction of the chain mobility caused by the densification of the semi-IPNs. The densification obeys to the presence of a cyanurate ester resin into the Matrimid matrix because density increases with the dicyanate monomer content (DCFT). To this effect contributes also the formation of charge intermolecular transfer complexes (CTC) between neighboring polyimide chains. On the other hand, as a consequence of the densification, catalyzed semi-IPNs exhibited lower permeability coefficients than neat Matrimid® films.

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