



HAL
open science

Gas barrier and adhesion of interpenetrating polymer networks based on poly(diurethane bismethacrylate) and different epoxy–amine networks

V Simic, S Boileau, Laurent Bouteiller, L Gallez, P Merlin

► To cite this version:

V Simic, S Boileau, Laurent Bouteiller, L Gallez, P Merlin. Gas barrier and adhesion of interpenetrating polymer networks based on poly(diurethane bismethacrylate) and different epoxy–amine networks. *European Polymer Journal*, 2002, 38 (12), pp.2449–2458. <10.1016/S0014-3057(02)00164-7>. <hal-01696757>

HAL Id: hal-01696757

<https://hal.science/hal-01696757v1>

Submitted on 25 Jan 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

GAS BARRIER AND ADHESION OF INTERPENETRATING POLYMER NETWORKS (IPNs) BASED ON POLY(DIURETHANE BISMETHACRYLATE) AND DIFFERENT EPOXY-AMINE NETWORKS.

V. Simic¹, S. Boileau^{1*}, L. Bouteiller¹, L. Gallez², P. Merlin²

¹ *Laboratoire de Recherche sur les Polymères, UMR C7581, 2 rue Henri Dunant 94320*

Thiais - FRANCE

² *Dow Corning, Parc Industriel zone C, 7180 Seneffe, BELGIQUE*

Abstract

Interpenetrating polymer networks (IPNs) composed of poly(methacrylate) and epoxy-amine networks made in situ between two oriented polypropylene sheets were examined in terms of their oxygen barrier and adhesion to the substrate properties. A particular attention was devoted to a system presenting an obvious phase separation *. Kinetics of network formation and phase behavior were investigated by infrared and UV-visible spectroscopy, respectively. Since the poly(methacrylate) network could be instantaneously generated by photoirradiation, IPNs differing in network sequence formation were prepared. **The influence of the moment at which irradiation was induced on gas barrier properties of different films was examined.** It was shown that similar oxygen transmission rates (OTR) are obtained whatever the moment of irradiation.

Key words : Interpenetrating polymer networks (IPNs), polymethacrylate network, epoxy-amine network, gas barrier properties.

Correspondence to : S. Boileau (boileau@glvt-cnrs.fr)

Introduction

Flexible packaging films for oxygen sensitive products (such as foods and electronics) are generally made of multilayer structures. Each of these layers brings a specific property to the material **such as high oxygen barrier and good adhesion to a substrate**. The current trend is to reduce the number of these layers while keeping the same mechanical and technical characteristics [1]. The development of more “ecological” systems (absence of halogenated compounds such as poly(vinylidene chloride) and of solvents) is also a current trend. Among all the possibilities of combining different properties (polymer blends, copolymerization...), our attention was focused on the use of interpenetrating polymer networks (IPNs). IPNs are combinations of two cross-linked polymers (each made via independent reaction processes) held together by permanent entanglements and obtained under special methods of preparation [2]. The absence of cross-reactions between the two networks is an important condition to allow morphology control. So, a system which combines a free-radical polymerization of a bis(methacrylate) compound with the polyaddition of amines on epoxy resins was chosen. This type of system has not yet been extensively studied [3-6].

Generally, organic polymers which exhibit high oxygen barrier properties present crystalline domains and a compact structure [7]. So, IPNs with high crosslink densities of both networks and which have the highest possible degree of interpenetration would be the best candidates. A bis(methacrylate) bearing urethane groups able to establish strong interchain cohesion through hydrogen bonding interactions was used as the monomer and plurifunctional amines were used as hardeners for epoxy resins.

In the present paper, the results of feasibility investigations on such systems are reported. Gas barrier properties of IPNs as a function of the curing sequence are also examined.

Experimental Part

Reagents

N,N'- Bis (2-methacryloyloxyethyl) -1,9 nonylene biscarbamate (DiUdiMA-*Aldrich*) was used as the monomer. The methacrylate network formation was photo-induced instantaneously by UV irradiation with 2,2-dimethoxy-2-phenylacetophenone (1% by weight - *Aldrich*) as the photo-initiator. Triethylenetetramine (TETA-*Kodak*), 1,3-bis (3-aminopropyl) tetramethyldisiloxane (BY16871-*Dow Corning*) and N-[3-(dimethoxymethylsilyl)-2-methylpropyl]-1,2-ethylenediamine hydrolyzate (D₅ amine -*Dow Corning*) were used as hardeners. *N,N*-Diglycidyl-4-glycidyoxyaniline (DGGOA-*Aldrich*) and neopentyl glycol diglycidyl ether (NPG100-*Aldrich*) were used as epoxides.

The [NH]/[epoxy] ratio was chosen to obtain the highest glass transition temperature (T_g). The same weight proportion (50/50) of both networks was used in all experiments. The composition of the different IPNs was as follows: for diUdiMA/TETA-DGGOA: 50/10.4-39.6; diUdiMA/BY16871-NPG100: 50/18-32; diUdiMA/ D₅ amine-NPG100: 50/18.7-31.3. The crosslinking reaction of epoxides by amines was carried out at room temperature. Addition of a surfactant (Triton X100- *Aldrich*) was necessary when DGGOA was used as the epoxide to improve film wetting. All compounds were used as delivered. The formula of these precursors is listed in Table 1. For the study of crosslinking mechanisms, triethylene glycol dimethacrylate (TEGDMA-*Aldrich*) was used as potentially photo-curable monomer and a monofunctional amine : n-octyl amine (nOCTA-*Sigma*) was used as a curing agent for NPG100.

Preparation of films

Formulations were cast on polypropylene films (OPP, 30 μm thick), which had been activated by a Corona discharge treatment previously, in order to improve their wettability. A

second OPP film was laminated on the top. Samples were irradiated with a medium pressure mercury lamp (120W/cm) after different waiting times. The conveyor belt speed (0.10 m/s) and the number of exposures set to 3, were selected to achieve the highest polymer conversion. The light intensity received by samples corresponds to 12 J.cm^{-2} .

Instrumentation

IR spectra were recorded on thin samples coated onto OPP films held between two KBr discs with a Perkin Elmer FTIR 1760 spectrophotometer. ^1H NMR spectra were recorded in CDCl_3 on a Bruker AC 200 MHz spectrometer. Oxygen transmission rates (OTR) of coated samples were determined using a Mocon Ox-tran 2/20 test equipment according to the standard method ASTM D3985. The test cell was composed of two chambers separated by the film. Films were subjected to 100% oxygen on one side and to nitrogen with 3% hydrogen on the other side. Nitrogen/hydrogen gas containing oxygen which transferred through the film was conducted to the coulometric sensor, and measurements were obtained when a steady state was reached. The relative humidity (RH) of the two gases was controlled by a humidifier. All the reported results have been automatically normalized to 1 atmosphere. Peel tests were recorded on a Lloyd L500 instrument. Measurements were performed according to the ASTM standard method on 15 mm wide samples and with a peel speed of 200mm/min.

OTR measurements and peel tests were performed by Dow Corning.

Glass transition temperatures of the coatings were measured on a differential scanning calorimeter (DSC, Perkin Elmer Model 4). The temperature was scanned from -150 to $+150^\circ\text{C}$ at a heating rate of $20 \text{ }^\circ\text{C.min}^{-1}$. The evolution of sample turbidity as a function of reaction time was followed on a 554 Perkin Elmer UV spectrophotometer. Refractive indexes were measured at 20°C with a Prolabo universal refractometer.

Quantitative analysis of infrared spectra

The conversion, “Conv”, of the reactive groups (epoxy or C=C double bonds of the bismethacrylate monomer) in the various investigated systems was determined in the usual way : $Conv = (C_0 - C_t) / C_0$ and by assuming that the Beer-Lambert relation is valid : $Conv = (A_0 - A_t) / A_0$ where C is the concentration, A represents the absorbance, and the subscripts 0 and t denote reaction times zero and t, respectively.

The analyzed peaks were the oxirane ring deformation at 910 cm^{-1} or 859 cm^{-1} for the epoxy-amine network and the double bond deformation at 1637 cm^{-1} for the methacrylate network. The intensity of each peak was related to a reference at 1190 cm^{-1} , the intensity of which remains unchanged during all the curing process.

Results and Discussion

IPNs based on a methacrylate network (prepared according to a free-radical process) interpenetrated with an epoxy-amine network (cured at room temperature without the addition of catalyst) were studied. At first, the absence of cross-reactions between components of each network was carefully examined because non-interfering reaction routes are an essential condition for a good structure control.

Evaluation of cross-reactions between the two networks.

The Michaël addition of amines on activated C=C double bond is a well-known reaction which could reduce the crosslinking density of both networks and create covalent bonds between the two networks. As a result such reactions could affect gas barrier performances of the material (scheme 1). In order to investigate the presence of inter-crosslinking reactions,

^1H NMR spectra of two different mixtures were examined. At first TEGDMA was mixed with n-octyl amine (nOctA) in a stoichiometric ratio ($[\text{C}=\text{C}]/[\text{NH}_2] = 1$) for one night at room temperature (figure 1, (3)). The triethylene glycol dimethacrylate (TEGDMA) was used as a model molecule rather than diUdiMA (used later as the monomer for IPN preparation) for the simplicity of its ^1H NMR spectrum (figure 1, (1)). n-OctA was used rather than a plurifunctional amine to avoid the formation of a network. Its ^1H NMR spectrum is given as a reference in figure 1-(2).

It can be seen from examination of the last spectrum of figure 1 :

- the appearance of a doublet at 1.1 ppm (c') corresponding to the methyl protons of the Michaël addition product on TEGDMA.
- the decrease of the peak at 1.3 ppm corresponding to NH_2 protons (α) of n-octyl amine
- the appearance of new peaks between 2.4 and 3 ppm (see assignments on figure 1)
- the appearance of triplets (d') and (e') due to a different chemical environment for these protons after the Michaël addition.
- the decrease of the terminal vinyl protons ((a) and (b)) of TEGDMA at 6.0 and 5.5 ppm respectively.

All these observations are consistent with the occurrence of Michaël addition. Furthermore, it is possible to determine a degree of conversion for this reaction by comparing the intensities of peaks a and b in the mixture with the theoretical intensity expected for those peaks. The theoretical intensity expected for TEGDMA protons was calculated from the intensity of methyl protons of n-octyl amine knowing the $[\text{C}=\text{C}]/[\text{NH}_2]$ initial ratio. Thus, after one night at room temperature 40% of TEGDMA has reacted with the amine.

As shown above, the addition of the amine on TEGDMA ($\text{C}=\text{C}$) double bonds occurs, but in

the IPN, this reaction competes with the epoxy crosslinking process. This is why all the components necessary to build up the final “IPN” (i.e. TEGDMA, nOCTA and NPG 100 ($[C=C]/[NH_2] = 1$, ($[NH_2]/[epoxy] = 1$)) were mixed together and the resulting mixture was analyzed by 1H NMR spectroscopy after one night reaction at room temperature (figure 2). Since TEGDMA signals remain unchanged (figure 2-(2)), only the epoxy-amine reaction occurs in this case because it is faster than Michael addition (figure 2-(3)).

We have shown in this part the absence of interfering mechanisms in the bis (methacrylate)/epoxy-amine system. As the two networks can be prepared independently, a control of IPN morphology as well as an adjustment of its properties for the desired application could be expected.

The first expected property is a low oxygen permeability. So, a highly interpenetrated polymer network, with the highest crosslinking density is required in order to decrease the gas diffusion through the polymer membrane. The second desired property is a good adhesion of IPN films on a polymeric substrate (for instance, oriented polypropylene sheets) the gas barrier performances of which are insufficient for the application but has good mechanical properties. Epoxy resins were chosen to promote adhesion. As networks have to be also compact (with the lowest free volume between the chains) plurifunctional compounds of a rather small size or compounds able to establish interchain interactions such as hydrogen bonds to increase the cohesion inside the material were chosen. Thus, the following system : diUdiMA/TETA-DGGOA (see Table 1) was tested.

The IPN is formed in situ between two polypropylene sheets : epoxy-amine reaction evolves at room temperature whereas the methacrylic network formation is initiated by irradiation at given times. As the methacrylate network is instantaneously formed by photo-polymerization we can modulate the moment of its formation as a function of the degree of conversion of

epoxy-amine crosslinking reaction.

DiUdiMA/TETA-DGGOA system

First of all, kinetics for epoxy-amine crosslinking process at room temperature in the diUdiMA/TETA-DGGOA system were followed by IR spectroscopy in order to irradiate the system at pertinent times. Examples of FTIR absorption spectra, collected at different times during the curing process are presented in figure 3. The conversion was determined according to the decrease of the peak height at 910 cm^{-1} corresponding to the deformation of the oxirane ring. The peak at 1190 cm^{-1} , the intensity of which remains unchanged during all the curing process, was used as a reference. The curing rates for the poly(diUdiMA)/TETA-DGGOA system (polydiUdiMA formed immediately after the film formation) and TETA-DGGOA single network curing process were also followed (figure 4). As shown in figure 4, the epoxy-amine curing rate is slower in 50% wt. diluted system (with diUdiMA or polydiUdiMA) than in the bulk. Moreover, in dilute systems, the formation of the polymethacrylate network does not affect the reaction rate.

Visual examination of the IPN mixture reveals that after a few hours, phase separation occurs due to the molecular weight increase of the epoxy-amine network. Such a behavior is attractive for studying the influence of the IPN curing sequence (varying with the moment at which irradiation was induced) on its gas barrier properties. In fact, three significant events play a role in the development of IPN morphology and have to be considered [8] :

- the phase separation
- the gelation of the epoxy-amine network
- the gelation of the methacrylate network

The relative position of these three events along reaction time will influence the IPN

structure. Homogeneity can be achieved by choosing a system in which crosslinking occurs faster than microphase separation.

To determine at which time the demixion occurs, the change of sample turbidity was followed by UV-Vis spectroscopy. The evolution of sample absorbance at 600 nm vs reaction time is reported in figure 5. The time of phase separation determined at the onset of turbidity is about 7 hours of reaction.

Gelation time of the epoxy-amine network was determined by dissolving small amounts of the reacting mixture, collected at given intervals of time, in methylene chloride. The gelation point was assumed to be reached when the samples became insoluble (at around 7.75h-8h of reaction). Gelation time of the methacrylate network is the moment of irradiation since the photopolymerization is very fast.

Then, a series of thin (9-13 μm) films based on diUdiMA/TETA-DGGOA system was prepared. The methacrylate network formation was induced by UV irradiation at different times of the epoxy-amine curing process. These tests were carried out with a view to determine the influence of the moment of irradiation on film properties.

Three different situations were considered:

- films irradiated beyond 7h of epoxy-amine reaction. IPNs presenting a very poor level of interpenetration are expected as the phase separation occurred.
- films irradiated after a short waiting time ($t < \sim 2\text{h}$). As epoxy and amine are still fluid enough, it can be assumed that, after photopolymerization of the methacrylate, diffusion towards microdomains is still possible and thus could lead to demixion.
- films irradiated after an intermediate waiting time ($\sim 2\text{h} < t < 7\text{h}$). In this case, one can suppose that diffusion is limited by the increase of viscosity due to epoxy-amine curing

process, and thus a better network interpenetration is expected.

Films based on diUdiMA (photocured at different times)/TETA-DGGOA system were prepared and morphology studies were performed by using DSC and optical microscopy. Unfortunately, it was impossible to detect glass transitions of IPNs and all films were transparent whatever the moment of their irradiation.

At the same time, oxygen permeability of laminates was evaluated. OTR results obtained for these laminates are reported in table 2. Measurements were performed at 50 and 80 % of relative humidity (RH). As OTR values depend strongly on coating thickness (e), a correction has been done in order to normalize the results. OPP contribution on laminates permeability has also been subtracted according to:

$$\frac{1}{\text{OTR(Laminate)}} = \frac{2}{\text{OTR(OPP)}} + \frac{e}{\text{OTR(corr)}}$$

or

$$\text{OTR(corr)} = \frac{\text{OTR(Laminate)} * \text{OTR(OPP)}}{\text{OTR(OPP)} - 2\text{OTR(Laminate)}} * e$$

where OTR(OPP sheet of 30 μ m thickness) is equal to 1620 cc/m².day at 50% RH and 1545 cc/m².day at 80% RH ; e denotes sample thickness.

Consequently, OTR(corr) corresponds to the permeability of a 1 μ m thick IPN layer.

In order to evaluate the contribution of each network, single network laminates were also prepared and their oxygen permeability was measured. The evolution of corrected OTR values for films irradiated after different waiting times in the case of diUdiMA/TETA-DGGOA system is reported in figure 6. Firstly, one can notice that at 50% RH, IPN behavior in terms of gas barrier performance is intermediate between those of each single network

(polydiUdiMA network being the most permeable). Moreover, one can notice that similar OTR values are obtained whatever the moment of irradiation.*** When the RH value is increased to 80%, higher OTR values are obtained but a similar trend as before is observed. The best OTR results are obtained for the TETA-DGGOA single network. The high crosslinking density inside the cured layer can be responsible for the observed O₂ barrier effect.

In the case of IPNs, a good adhesion between the different layers has been observed. Films were always torn during peel tests. This means that the adhesive strength is higher than 6N/15mm.

Two other amines were tested: 1,3-bis (3-aminopropyl) tetramethyldisiloxane (BY16871) and N-[3-(dimethoxymethylsilyl)-2-methylpropyl-1,2-ethanylethylenediamine] hydrolyzate (D₅ amine). The triepoxy compound (DGGOA) was replaced by a difunctional one (NPG100) for miscibility reasons in the case of D₅ amine and partial wetting in the case of BY16871. It will be possible with these new formulations to compare the influence of crosslinking density on IPN gas barrier properties.

DiUdiMA/BY16871-NPG100 system

This system is different from the previous one since turbidity does not increase during the epoxy-amine addition. Phase separation occurrence is not excluded before irradiation but the corresponding domain size is smaller than visible light wavelengths (400-700 nm). Indeed, refractive indexes of the two networks were measured and were found to be equal to 1.485 and 1.455 at 20°C for the diUdiMA and the NPG100-BY16871 mixture, respectively. In comparison, the system which exhibited an obvious phase separation (TETA-DGGOA)

presented a comparable refractive index difference: 1.485 for diUdiMA and 1.524 for the TETA-DGGOA mixture.

Different films were prepared and irradiated at different times after film formation. Results of OTR measurements on these laminates are collected in table 3. In the same manner as before, corrected OTR values as a function of photo-curing time are reported in figure 7. It is clear from these results that BY16871 has a very “negative” effect on oxygen permeability performances, since OTR values are extremely high. One can also notice that similar OTR values are obtained whatever the irradiation time. Moreover, no significant difference between measurements at 50% and 80% RH is observed. Peel tests on these laminates were performed. A good adhesion between sheets was observed since the substrate was always torn during the measurements.

DiUdiMA/ D₅ amine-NPG100 system

DiUdiMA/ D₅ amine-NPG100 system is an initially clear formulation which remains transparent until the end of epoxy-amine reaction. Same experiments as before were performed on this system. O₂ permeability results for this system are reported in table 4. As shown in figure 8, the same OTR values were obtained whatever the instant of irradiation. Moreover, films are little affected by RH increase from 50 to 80%. One can also notice that film gas barrier performances are better than those obtained with the other aminofunctional siloxane (BY16871). The substrates were always torn during peel tests.

The gas permeability through a membrane depends both on **diffusivity** (i.e. the mobility of polymer chains, the size of the free volume or the size of gas molecules) and **solubility** of the gas in the polymer. T_g values of networks (table 5) reflect the differences of crosslinking density which exist between all these materials. If we compare networks containing

aminofunctional siloxane (BY16871 and D₅ amine) the difference observed for gas barrier properties could be assigned to a difference of network compactness.

Conclusion

Based on the above investigation it can be concluded that cross-reactions in the IPNs prepared from a free-radically photocured bis(methacrylate) compound and epoxy resins (cured with plurifunctional amines) are absent. Thin films containing a diUdiMA/TETA-DGGOA interpenetrating polymer network as the central layer present rather good gas barrier properties. The introduction of BY 16-871 in IPNs dramatically drops laminate gas barrier performances. When D₅ amine is used as the hardener an intermediate gas barrier behavior is observed. In none of the studied systems an influence of the curing sequence (modulated by the moment of irradiation) on IPN gas barrier properties has been shown. This result clearly indicates whether the moment of irradiation does not affect IPN structures or it has no effect on IPN properties. Finally, good adhesion properties between the different layers are observed in all examined systems.

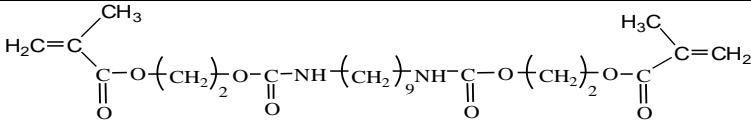
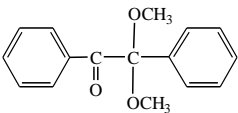
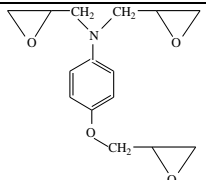
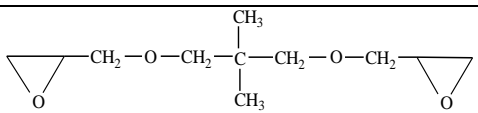
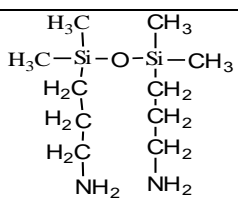
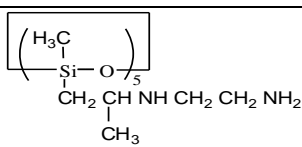
ACKNOWLEDGEMENTS

The authors wish to thank R. Bischoff for initiating this research project.

References

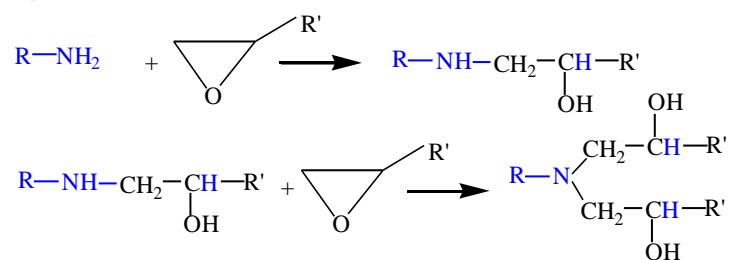
1. A. L. Brody, G. Strupinsky, *Polym., Laminations Coat. Conf.*, **1**, 293-303 (1999)
2. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum Press, New York, 1981
3. A. Dubuisson, D. Ades and M. Fontanille, *Polym. Bull*, **3**, 391-398 (1980)
4. S. Tan, D. Zhang, E. Zhou, *Acta Polym.*, **47**, 507-510 (1996)
5. A. Leistner, E. Fabrycy, J. Wagner, J. Leistner and A. Bledzki, *Int. Polym. Sci. Tech.*, **25**, 96-100 (1998)
6. F. J. Hua, C. P. Hu, *Eur. Polym. J.*, **36(1)**, 27-33 (2000)
7. D. J. Brennan, J. E. White, A. P. Haag, S. I. Kram, M. N. Mang, S. Pikulin, C. N. Brown , *Macromolecules*, **29**, 3707-3716, (1996)
8. L. H. Sperling, V. Mishra, *Polym. Adv. Tech.*, **7**, 197-208 (1996)

Table 1. The reagents for IPN preparation

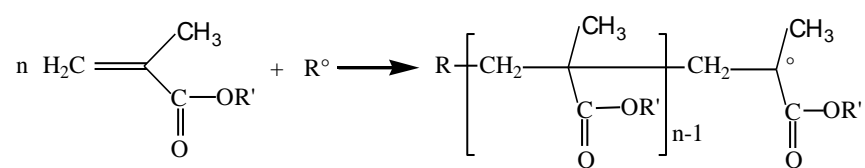
Abbreviation	Formula	Source
DiUdiMA	 <p><i>N,N'</i>-Bis(2-methacryloyloxyethyl)-1,9-nonylene bis-carbamate</p>	Aldrich
DMPA	 <p>2,2-Dimethoxy-2-phenylacetophenone</p>	Aldrich
DGGOA	 <p><i>N,N</i>-Diglycidyl-4-glycidyl-oxyaniline</p>	Aldrich
NPG100	 <p>Neopentyl glycol diglycidyl ether</p>	Aldrich
TETA	$\text{H}_2\text{N}-(\text{CH}_2-\text{CH}_2-\text{NH})_3-\text{H}$ <p>Triethylenetetramine</p>	Kodak
BY16-871	 <p>1,3-Bis(3-aminopropyl)tetramethyldisiloxane</p>	Dow Corning
D ₅ amine	 <p><i>N</i>-[3-(Dimethoxymethylsilyl)-2-methylpropyl]-1,2-ethylenediamine hydrolyzate</p>	Dow Corning

Scheme 1.

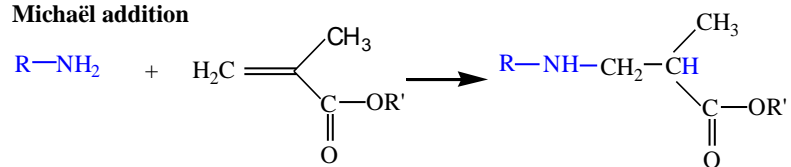
(a) Epoxy-amine reaction



(b) Free-radical polymerization of the methacrylate



(c) Michaël addition



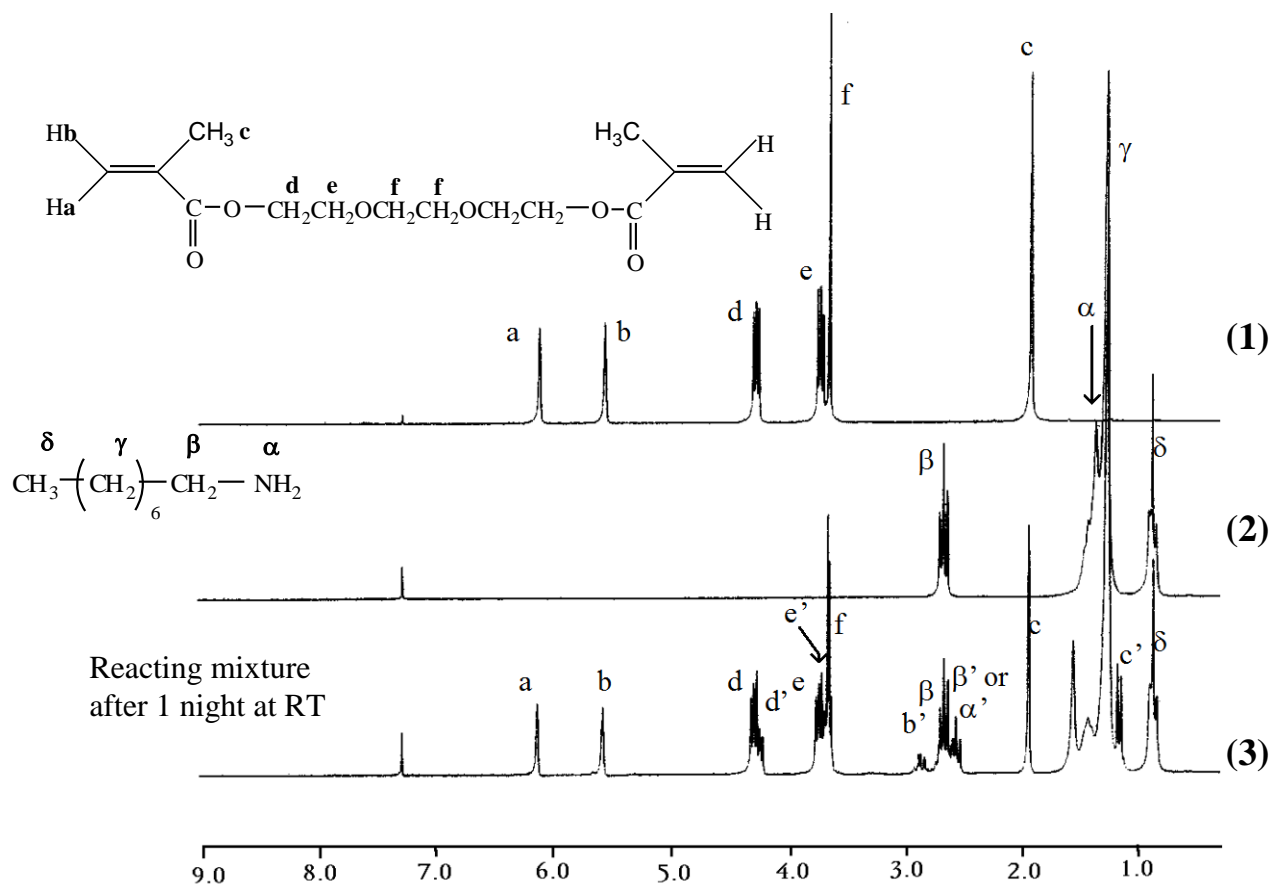


Figure 1. ^1H NMR spectra of (1) TEGDMA (2), n-octyl amine, (3) TEGDMA+n-octyl amine after 1 night at room temperature.

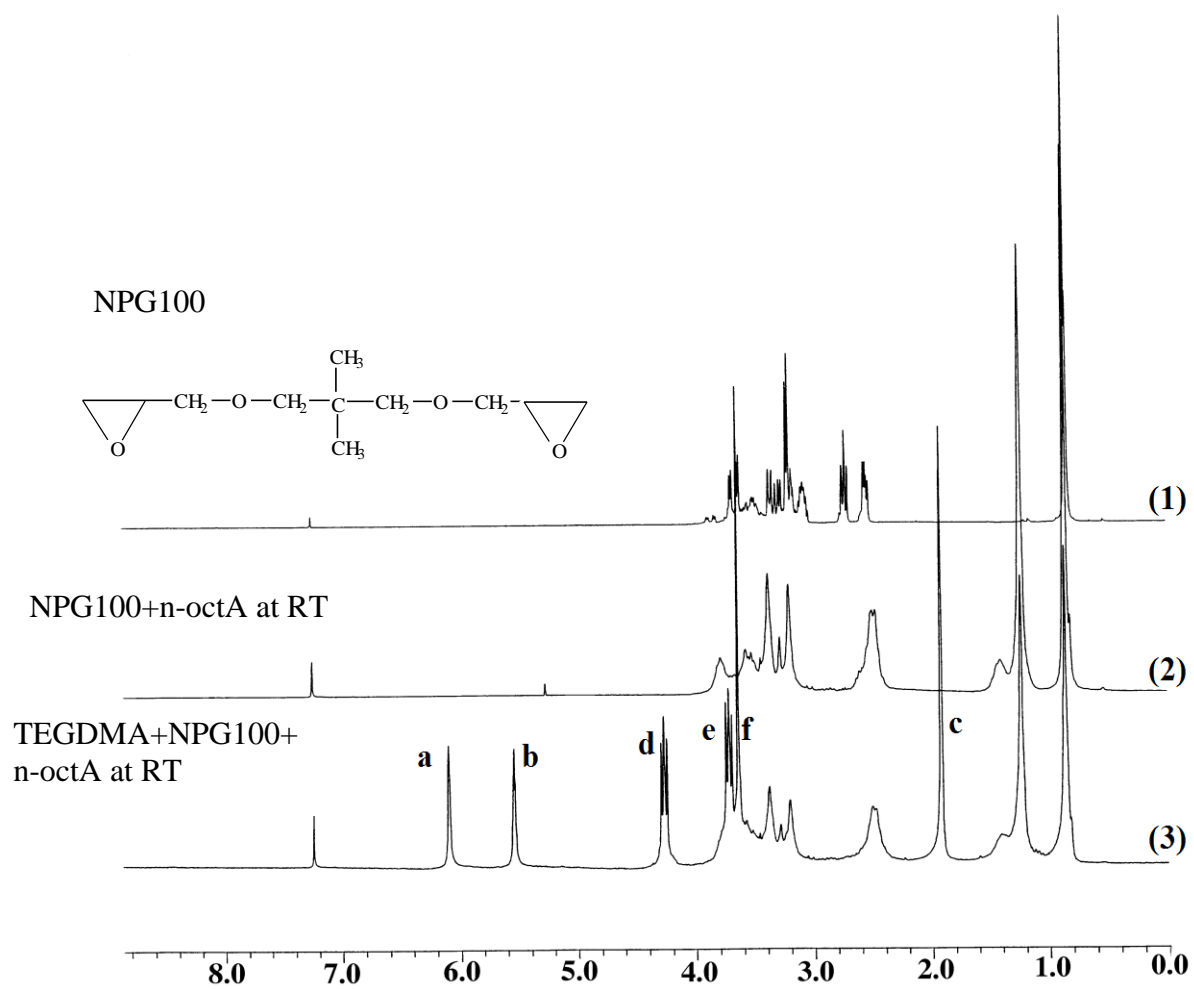


Figure 2. ¹H NMR spectra of (1) NPG100, (2) NPG100 +n-octyl amine after 1 night at room temperature, (3) TEGDMA+NPG100+n-octyl amine after 1 night at room temperature.

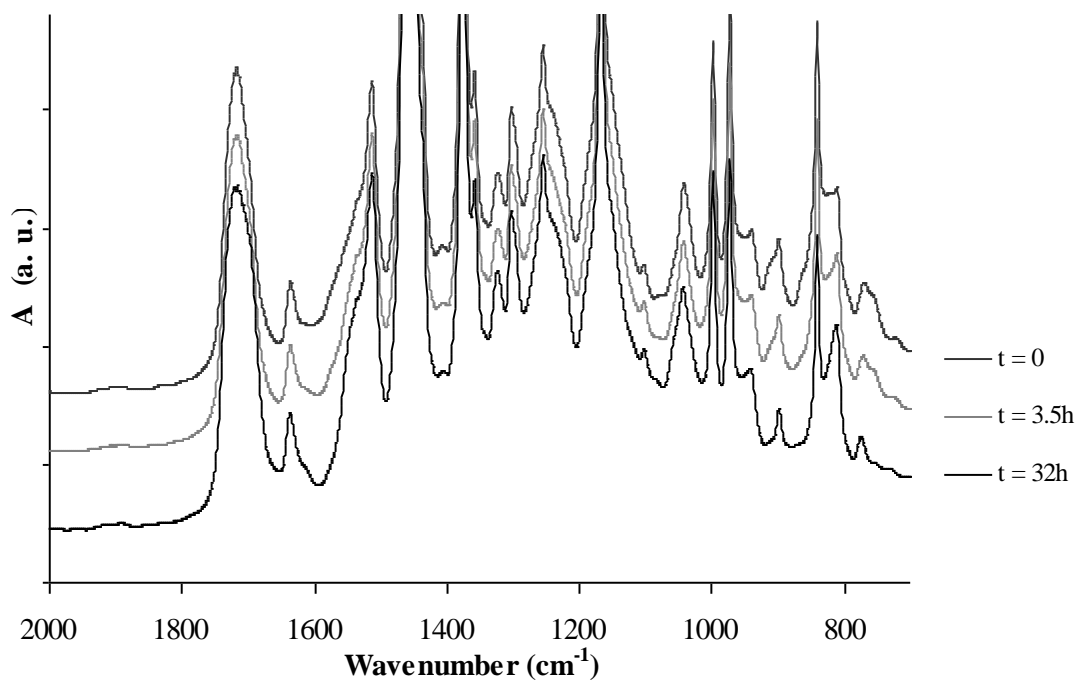


Figure 3. FTIR absorbance spectra in the 2000-600 cm^{-1} wavenumber range, collected at different times for the curing process on the diUdiMA/TETA-DGGOA system.

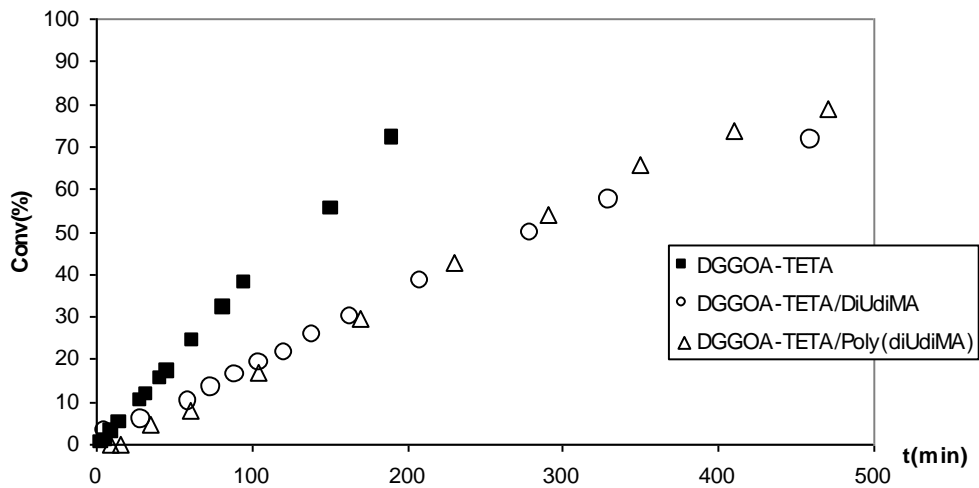


Figure 4. Conversion (Conv) versus time plots for the epoxy-amine crosslinking process at room temperature of DGGOA-NPG100 (■), DGGOA-NPG100/diUdiMA (○), and DGGOA-NPG100/poly(diUdiMA) (△) systems.

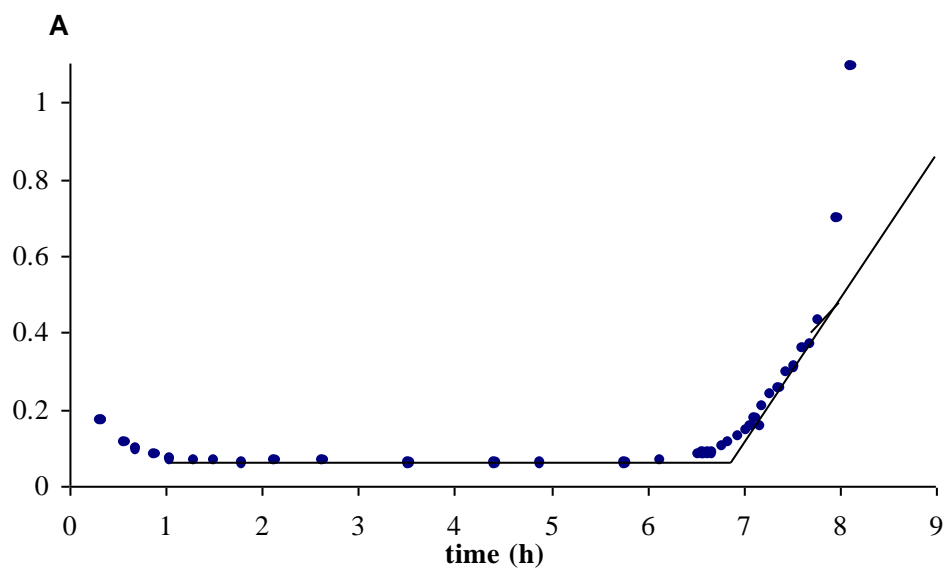


Figure 5. Evolution of diUdiMA/TETA-DGGOA absorbance at 600nm vs reaction time. Sample thickness : 2mm, temperature : 24°C

Table 2. Oxygen permeability measurements on DiUdiMA/TETA-DGGOA system and corresponding single networks, performed at 50 and 80% RH. The methacrylate polymerization was induced by irradiation at different times after films formation (called “waiting time”).

Sample reference	Waiting time (h)	Sample thickness (μm)	OTR 50% RH $\text{cc}/\text{m}^2/\text{day}$	OTR 80% RH $\text{cc}/\text{m}^2/\text{day}$	OTR corr 50% RH $\text{cc}/\text{m}^2/\text{day}$	OTR corr 80% RH $\text{cc}/\text{m}^2/\text{day}$
151 to	0	12.8	80	83	1136	1190
151 to+1h	1	13.6	34	33	483	469
151 to+3h30	3.5	17.5	59	82	1114	1606
151 to+5h	5	13.1	79	119	1147	1843
151 to+6h30	6.5	15.4	43	57	699	948
151 to+8h08	8	15	36	47	565	751
151 to+8h30	8.5	11.6	74	116	945	1584
150 to+15h30	15.5	16.5	39	43	676	751
150 to+18h30	18.5	14.5	46	55	707	859
150 to+22h	22	13.3	43	50	604	711
150 to+25h	25	11.5	43	53	522	654
150 To+39h15	39.25	10.8	45	49	515	565
150 To+42h10	42.17	10	59	74	636	819
150 To+47	47	11.7	53	64	664	817

1.5% by weight of triton X100 was added in the formulation to improve wetting and films were laminated at 50°C.

Sample reference	Sample thickness (μm)	OTR 50% RH $\text{cc}/\text{m}^2/\text{day}$	OTR 80% RH $\text{cc}/\text{m}^2/\text{day}$	OTR corr 50% RH $\text{cc}/\text{m}^2/\text{day}$	OTR corr 80% RH $\text{cc}/\text{m}^2/\text{day}$	Adhesion (N/15 mm)
TETA-DGGOA *	8.5	13.9	15	120	130	Substrate tears
Poly (diUdiMA)	9.4	144	155	1646	1823	1.15

* formulation was cast on OPP films after 1 hour of reaction in the pot in order to obtain the same coating thicknesses as those obtained for IPNs. 1% of triton X100 was added to improve wetting and the film was laminated at 50°C.

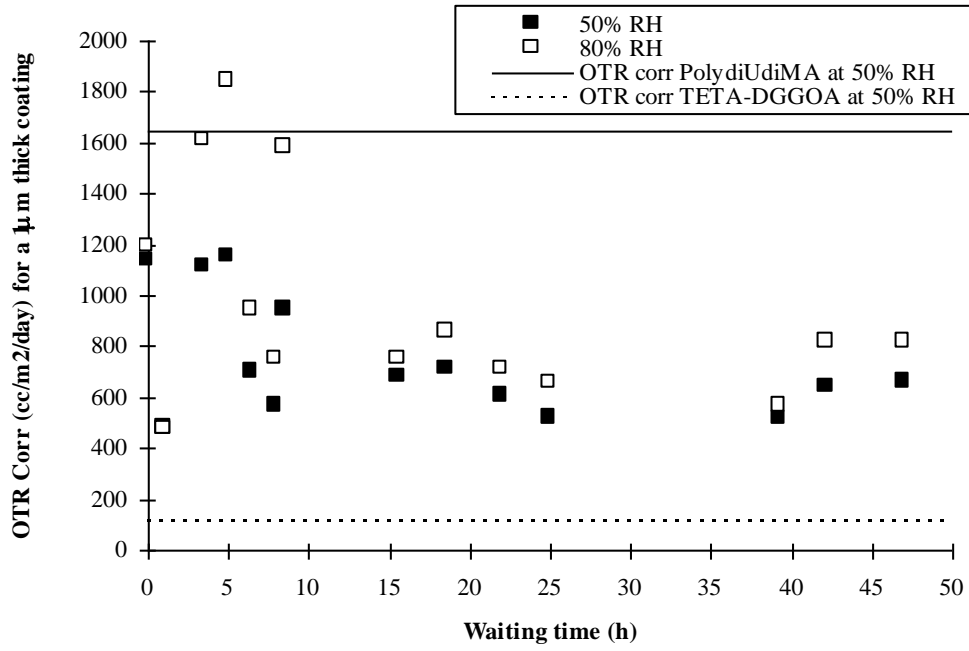


Figure 6. Oxygen permeability measurements on diUdiMA/TETA-DGGOA films versus time between mixing of all components and irradiation of the mixture.

OTR values at 50% RH of poly(diUdiMA) single network (straight line) and TETA-DGGOA single network (dotted line) are also given.

Table 3. Oxygen permeability measurements on diUdiMA/BY16871- NPG100 system irradiated at different time after films formation and corresponding single networks.

Sample reference	Waiting time (h)	Sample Thickness e (μm)	OTR 50% RH $\text{cc}/\text{m}^2/\text{day}$	OTR 80% RH $\text{cc}/\text{m}^2/\text{day}$	OTR corr 50% RH $\text{cc}/\text{m}^2/\text{day}$	OTR corr 80% RH $\text{cc}/\text{m}^2/\text{day}$
90 (t_0)	0	12	435	445	11283	12618
90 ($t_0 + 2\text{h}$)	2	11.3	437	461	11389	12944
90 ($t_0 + 4\text{h}$)	4	11.5	445	461	12092	13173
90 ($t_0 + 8\text{h}$)	8	9	508	518	13386	14188
100A ($t_0 + 21\text{h}$)	21	11	438	446	11146	11628
90 ($t_0 + 24\text{h}$)	24	10	492	497	13581	13969
90 ($t_0 + 29\text{h}$)	29	/	465	477	/	/
100A ($t_0 + 51\text{h}$)	51	13	381	400	9786	10799
90 ($t_0 + 55\text{h}$)	55	/	461	491	/	/
100A ($t_0 + 67\text{h}$)	67	12.6	391	424	9989	11861

Sample reference	Sample Thickness e (μm)	OTR 50% RH $\text{cc}/\text{m}^2/\text{day}$	OTR 80% RH $\text{cc}/\text{m}^2/\text{day}$	OTR corr 50% RH $\text{cc}/\text{m}^2/\text{day}$	OTR corr 80% RH $\text{cc}/\text{m}^2/\text{day}$	Adhesion (N/15 mm)
86 Poly(diUdiMA) network	9.4	144	155	1646	1823	1.15
107 NPG100-BY16871 network	9.5	596	559	21468	19280	Substrate tears

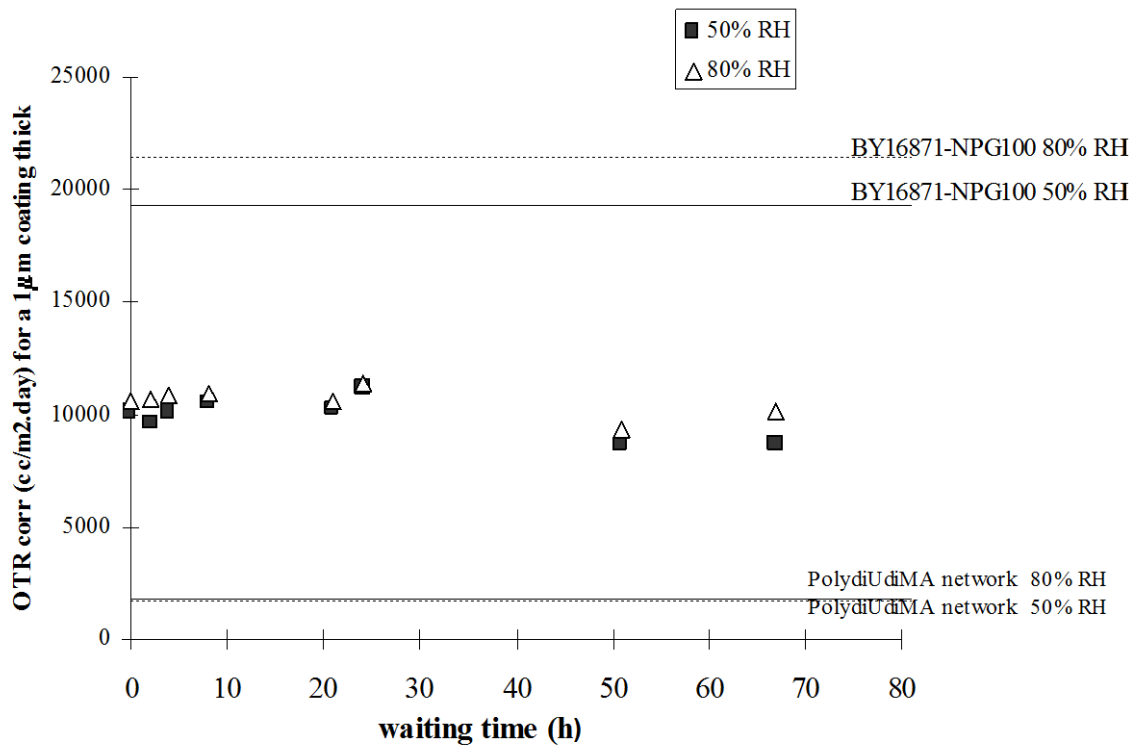


Figure 7. Oxygen permeability measurements on diUdiMA/BY16871-NPG100 films in relation to the moment of irradiation. OTR values of both single networks measured at 50% RH (straight lines) and at 80% RH (dotted lines) are also represented.

Table 4. DiUdiMA/D₅ amine-NPG100 system. O₂ transmission rates measured for samples irradiated after different waiting times.

Sample reference	Waiting time (h)	Sample thickness (µm)	OTR 50% RH cc/m ² /day	OTR 80% RH cc/m ² /day	OTR corr 50% RH cc/m ² /day	OTR corr 80% RH cc/m ² /day
154 to	0	9.8	194	199	2500	2628
154 to+2h	2	10.1	154	156	1921	1975
154 to+3h30	3.5	12.7	135	150	2058	2365
154 to+4h30	4.5	11.1	151	171	2060	2439
154 to+5h30	5.5	9.5	157	175	1850	2150
154 to+6h30	6.5	11.1	145	161	1961	2258
154 to+7h30	7.5	11.9	140	165	2014	2497
154 to+24h	24	10.4	148	177	1884	2389
154 to+26h	26	8.15	179	205	1873	2275
154 to+30h	30	10	144	164	1752	2083
154 to+48h	48	12.7	131	152	1983	2404

Sample reference	Sample Thickness e (µm)	OTR 50% RH cc/m ² /day	OTR 80% RH cc/m ² /day	OTR corr 50% RH cc/m ² /day	OTR corr 80% RH cc/m ² /day	Adhesion (N/15 mm)
86 Poly(diUdiMA) network	9.4	144	155	1646	1823	1.15
180 NPG100-D ₅ amine network	8.9	455	516	9871	12735	Substrate tears

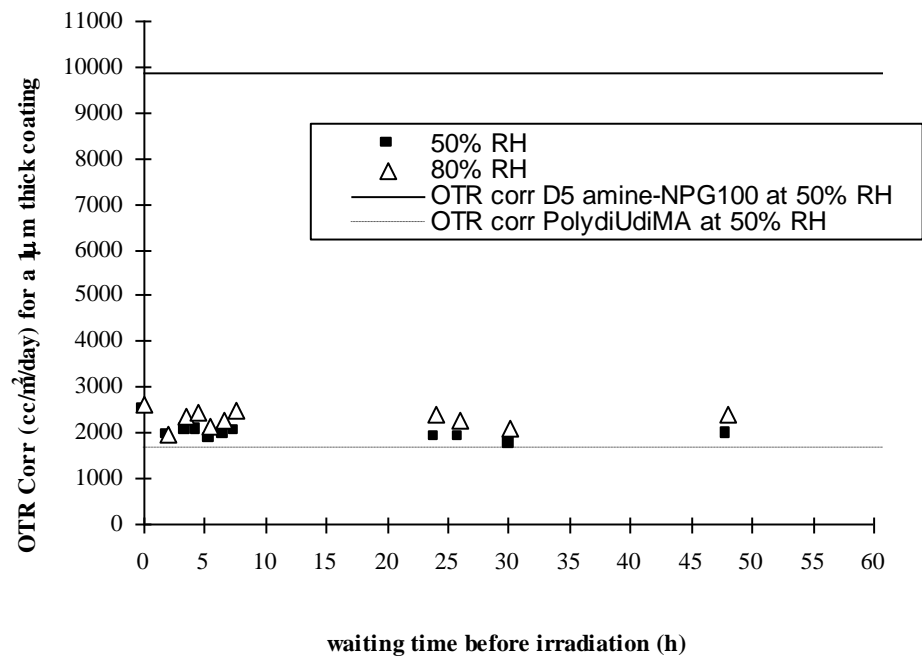


Figure 8. DiUdiMA/D₅ amine-NPG100 system. Gas barrier performances vs time at which irradiation was induced.

Table 5. Glass transition temperatures (T_g) of the different networks

Network	T_g (°C)
Poly(diUdiMA) network	not detected
TETA-DGGOA network	not detected
BY16871-NPG100 network	-10
D ₅ amine-NPG100 network	+33

Table 1. The reagents for IPN preparation

Figure 1. ^1H NMR spectra of (1) TEGDMA, (2) n-octyl amine, (3) TEGDMA+n-octyl amine after 1 night at room temperature.

Figure 2. ^1H NMR spectra of (1) NPG100, (2) NPG100 +n-octyl amine after 1 night at room temperature, (3) TEGDMA+NPG100+n-octyl amine after 1 night at room temperature.

Figure 3. FTIR absorbance spectra in the 2000-600 cm^{-1} wavenumber range, collected at different times for the curing process on the diUdiMA/TETA-DGGOA system.

Figure 4. Conversion (Conv) versus time plots for the epoxy-amine crosslinking process at room temperature of DGGOA-NPG100 (■), DGGOA-NPG100/diUdiMA (○), and DGGOA-NPG100/poly(diUdiMA) (△) systems.

Figure 5. Evolution of diUdiMA/TETA-DGGOA absorbance at 600nm vs reaction time. Sample thickness : 2mm, temperature : 24°C

Table 2. Oxygen permeability measurements on DiUdiMA/TETA-DGGOA system and corresponding single networks, performed at 50 and 80% RH. The methacrylate polymerization was induced by irradiation at different times after films formation (called “waiting time”).

Figure 6. Oxygen permeability measurements on diUdiMA/TETA-DGGOA films versus time between mixing of all components and irradiation of the mixture.

OTR values at 50% RH of poly(diUdiMA) single network (straight line) and TETA-DGGOA single network (dotted line) are also given.

Table 3. Oxygen permeability measurements on diUdiMA/BY16871- NPG100

system irradiated at different time after films formation and corresponding single networks.

Figure 7. Oxygen permeability measurements on diUdiMA/BY16871-NPG100 films in relation to the moment of irradiation. OTR values of both single networks measured at 50% RH (straight lines) and at 80% RH (dotted lines) are also represented.

Table 4. DiUdiMA/NPG100-D₅ amine system. O₂ transmission rates measured for samples irradiated after different waiting times.

Figure 8. DiUdiMA/NPG100-D₅ amine system. Gas barrier performances vs time at which irradiation was induced.

Table 5. Glass transition temperatures (T_g) of the different networks