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Study of Castor Oil Polyurethane - Poly(Methyl Methacrylate) Semi-Interpenetrating Polymer Network (SIPN) Reaction Parameters Using a 2^3 Factorial Experimental Design

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In this work was employed a 2^3 factorial experiment design to evaluate the castor oil polyurethane-poly(methyl methacrylate) semi-IPN synthesis. The reaction parameters used as independent variables were NCO/OH molar ratio, polyurethane polymerization time and methyl methacrylate (MMA) content. The semi-IPNs were cured over 28 h using two thermal treatments. The polymers were characterized by infrared and Raman spectroscopy, thermal analysis and swelling profiles in n-hexane. The glass transition temperature (Tg) and the swelling were more affect by the NCO/OH molar ratio variation. The semi-IPNs showed Tg from - 27 to - 6 °C and the swelling range was from 3 to 22%, according to the crosslink density. The IPN mechanical properties were dependent on the cure temperature and MMA content in it. Lower elastic modulus values were observed in IPNs cured at room temperature.

Keywords: *castor oil, semi-IPN, experimental design, poly (methyl methacrylate)*

1. Introduction

Interpenetrating polymer network (IPN) is defined as a combination of two polymer networks where at least one polymer is synthesised or crosslinked in the presence of the other. As physical blends and copolymerization the IPN is another way to combine two different polymers. There are no covalent bonds between the two polymers, so a generic A monomer reacts only with other A ones, and on the other hand B monomer reacts only with B ones. The resulting material swells but does not dissolve in a given solvent[1].

IPNs could be classified as sequential or simultaneous, depending on the way that the polymerisation is carried out. They could be also defined as a *latex IPNs*, when the polymers are synthesised by emulsion polymerisation; a *gradient IPN*, when each surface of the film is predominately of one type of polymer and there is a gradient inside the film; a *thermoplastic IPN*, when there is physical crosslink rather than chemical crosslink in the polymers, and a *semi-IPN* (SIPN) when just one of the polymers is a network[2].

In the last decades, a lot of works have been done to develop new materials for many different application using renewable resources. The castor oil has been used widely thanks to its chemical structure[1-6]. Castor oil is a naturally occurring monomer, which is a triglyceride of ricinoleic acid containing three hydroxyl groups and three double bonds. Commercial castor oil consists of triglycerides that contain 90% of ricinoleic acid and 10% of non functional acid, and it has an effective hydroxyl functionality of 2.7. The hydroxyl functionality can be used to form polyester or polyurethane network by a step-growth reaction[7].

The experiment design has been frequently used in many laboratories and it is a good methodology to have best information about the effects of the independent variables and its interactions on the dependent parameter with fewer runs. The runs must be randomized to remove the noises interference in the final results. The correlates equations of the studied parameters allow one to optimize the system according to the property evaluated or desired.

The aim of this work was to employ a 2^3 factorial experiment design in the order to evaluate the influence of the reaction parameters in the chemical structure, thermal and mechanical properties of castor oil polyurethane - PMMA semi IPN.

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2. Experimental

2.1. Materials

Castor oil (Delaware), methyl methacrylate (MMA) (Renner) and toluene diisocyanate (TDI) (Renner) were used as received. Benzoyl Peroxide (BPO) was dried in vacuum and storage under nitrogen atmosphere.

2.2. Synthesis of semi-IPN PU/PMMA

The polymerizations were carried out under nitrogen atmosphere in a 250 mL three neck flask equipped with a mechanical stirrer. The castor oil and toluene diisocyanate were added into the flask and the reaction time varied from 30 to 120 min at 50 °C. The NCO/OH molar ratio was 1.2, 1.4 and 1.6. MMA having 1 wt. (%) of benzoyl peroxide was added into the flask containing the polyurethane network and the polymerization carried on at 70 °C under stirring for 1 h. The product was poured into glass mould and the film obtained was cured by two different thermal treatment. The film was maintained at 70 °C during 24 h and after at 120 °C for more 4 h, cure thermal treatment 1 (TT1). In the other one the film was maintained at room temperature for 28 h, cure thermal treatment 2 (TT2). Yield: 78 ± 8%.

2.3. Polymer characterization

The semi-IPNs were characterized by Fourier Transformed Infrared (FT-IR) and Raman Spectroscopy, Differential Scanning Calorimeter (TA 2010 Instrument), using heating rate of 10 °C/min, and Dynamic Mechanical Analysis (TA 2980 Instrument) from zero to 18 N, sweep rate 2 N/min at 30 °C. The elastic modulus values were worked out by ASTM – D882 – 91 method. The swelling test were performed in n-hexane at 30 °C using three probes with 5 × 1.5 × 0.15 cm (L, W ,T), according to ASTM – D471 – 98 method.

2.4. Factorial experiment design

A 2^3 factorial experiment design with central point was employed to evaluate the SIPN synthesis. The statistical data treatment was accomplished through the software Statistic 4.3 in experimental design modulates. This program uses the one-way ANOVA table to analyze statistical data. ANOVA involves calculations of the some square (SS), degree of freedom (df) and media square (MS) for the main effects, interactions and residual part. Test F (media square of effects/media square of residual) and significance factor (p) are used to evaluate the significant effects. If the F value for a given effect is higher than the F value in the table, this effect is a significant one. Usually the F table used for significance level (α) is equals 0.05. When the significance factor (p) is used to evaluate the effects significance, this value must be lower than the significance level (α), so lower than 0.05[8,9].

The study was performed through 2^3 factorial experimental designs with 4 midpoint replications in a total of 12 runs. The independent variables interval used in this wok is showed in Table 1.They were selected based on a previous study of PU synthesis.

3. Results and Discution

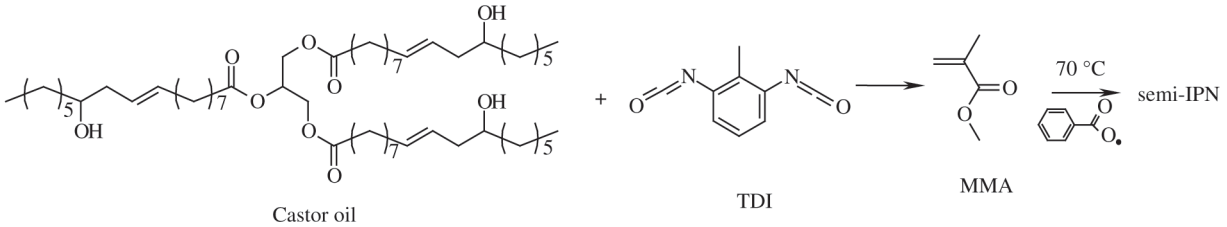
The semi-IPN synthesis consists of sequential polymerization reactions as shown in the Scheme 1. In the first reaction, a step-growth polymerization between the castor oil hydroxyl groups and isocyanate groups occurs resulting in polyurethane. The polyurethane obtained in a network form is swelled in MMA and a free-radical polymerization of it is carried out initiated by benzoyl peroxide.

The chemical structure of castor oil polyurethane network was analyzed by infrared spectroscopy. Figure 1 shows the infrared spectrums of castor oil and the PU prepolymers at zero, 30 and 120 min after the reagents mixture.

The reaction between castor oil -OH groups and diisocyanate –N=C=O groups run out after 30 min, regarding to the disappearance of the broad absorption near

Table 1. Factor levels of the independent variables semi-IPN castor oil PU/PMMA synthesis

Independent variables (units)	Low level (-1)	Midpoint (0)	High level (+1)
NCO/OH (molar ratio)	1.2	1.4	1.6
PU polymerization time (min)	30	75	120
MMA content (wt. (%))	20	40	60



Scheme 1.

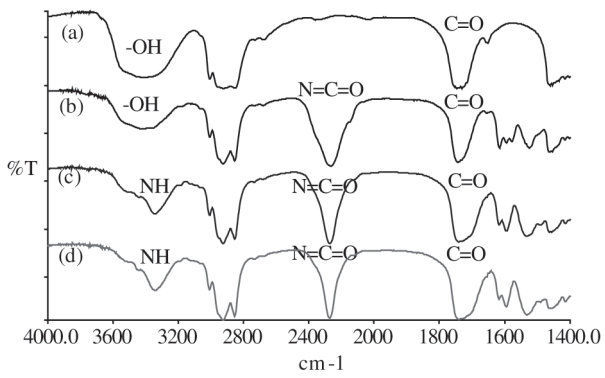


Figure 1. FTIR spectra of a) castor oil; b) castor oil polyurethane at zero; c) 30; d) 120 min of reaction.

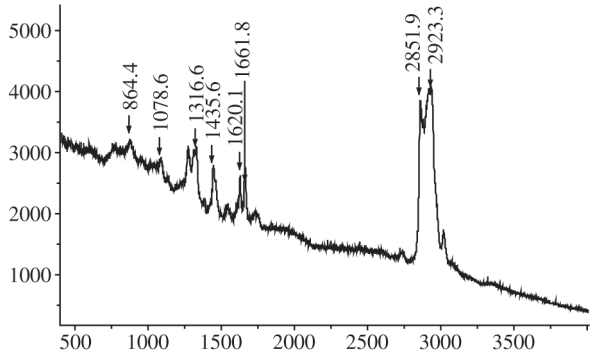


Figure 2. Raman spectrum of polyurethane after cure (NCO/OH = 1.6).

3418 cm^{-1}, due to - OH axial stretching vibration, and the appearance of a narrow absorption in 3344 cm^{-1}, related to the - NH axial stretching vibration. The C-N axial stretching vibration in 1537 and 1220 cm^{-1} also is a typical PU absorption band. On the other hand the carbonyl absorption at 1737 cm^{-1} changes the profile from the castor oil monomer to the polyurethane been wider in that one obtained after 120 min. All polyurethane spectra showed axial stretch C=C absorption due to toluene diisocyanate aromatic ring (1620-1575 cm^{-1} e 1470-1440 cm^{-1}).

Raman spectroscopy was used to analyse the polyurethane after its cure as showed in the Fig. 2. The mainly observation from the spectrum was the absence of –N=C=O absorption at 2270 cm^{-1}. As expected, the amount of free isocyanate after the cure is very small, not detectable by the method. Although the typical N–H urethane absorption appears very weak in Raman spectroscopy the C–N axial stretch (1550 cm^{-1}) one confirm the urethane structure. It is possible also to identify C=C and C–H axial stretch absorptions of aromatic ring at the same wavelengths of infrared spectrum.

The influence of the IPNs synthesis variables, for both cure treatment, in the glass transition temperature (Tg), swelling and elastic modulus evaluated through the factorial experiment design can be seen in Table 2. The significance of the independent variables was evaluated through the data statistical treatment. The significance factor (p) values for all dependent variables were expressed as function of independent ones. The dependent variable has a significant influence when the significance factor (p) is lower

Table 2. Tg, swelling and elastic modulus of semi-IPNs cured according to thermal treatment

Run (IPN)	Independent Variable			Dependent Variable					
	NCO/OH (molar ratio)	PU reaction time (min)	MMA (%)	Tg (°C) [a] TT1[c]	TT2[d]	Swelling (%) TT1[c]	TT2[d]	E (MPa)[b] TT1[c]	TT2[d]
1	1.2	30	20	- 25.0	- 23.8	22.6	23.1	1.48	0.94
2	1.2	30	60	- 21.7	- 24.6	17.4	17.0	6.49	1.41
3	1.2	120	20	- 20.6	- 26.8	22.2	21.3	1.62	1.32
4	1.2	120	60	- 17.7	- 20.4	13.3	18.1	8.37	3.52
5	1.6	30	20	- 9.2	- 8.5	19.8	19.1	3.68	3.16
6	1.6	30	60	- 7.7	- 9.0	15.5	17.4	7.12	5.74
7	1.6	120	20	- 6.8	- 6.5	20.2	15.6	3.62	3.12
8	1.6	120	60	- 6.9	- 8.3	15.1	15.5	7.19	3.63
9	1.4	75	40	- 9.7	- 13.5	14.5	18.3	2.51	2.24
10	1.4	75	40	- 9.8	- 13.4	16.4	18.9	2.83	2.79
11	1.4	75	40	- 12.7	- 18.5	18.3	18.8	3.89	2.06
12	1.4	75	40	- 10.6	- 9.2	18.8	18.5	3.06	2.85

a) Tg obtained by DSC;
b) Modulus elastic obtained by DMA according ASTM–D882–91;
c) Thermal treatment TT1, oven 24 h at 70 °C and 4 h at 120 °C;
d) Thermal treatment TT2, room temperature 28 h.

than 0.05. The dependent variable equation represents the surface response as function of only those factors that have had significant influence on it.

3.1. IPN Glass transition temperature (Tg)

SIPNs cured at high temperature (TT1) are dependent of NCO/OH molar ratio and PU reaction time. The increase of NCO/OH molar ratio provoke a dramatically rise in Tg value. The increase of diisocyanate amount result in polyurethane network with higher crosslink density and consequently higher Tg value[7]. The PU reaction time effect on Tg values is similar to the NCO/OH molar ratio one and longer reaction time gives higher crosslink increasing the IPNs Tg values.

The Eq. 1 describes the surface variation for the Tg as function of the NCO/OH molar ratio (x), PU reaction time (y) and MMA content (z) in the polymerization medium, where x, y and z varied from - 1 to 1 for each dependent variable according to the values in Table 1.

$$Tg\ (°C) = -\ 13.196 + 6.8087x + 1.444y + 0.964z - 0.634xy - 0.609xz - 0.244yz \quad (1)$$

Where, x is the NCO/OH molar ratio; y is the reaction time and z is the MMA content

Equation 1 can be simplified taking down only the dependent variables that had significant factor on Tg value, as showed in Eq. 2. The same analysis and procedure were done for all the other equations. It is important to point out that the influence of NCO/OH molar ratio (x) on Tg was about five times higher than reaction time (y).

$$Tg\ (°C) = -\ 13.996 + 6.809x + 1.444\ y \pm 2\ °C \quad (2)$$

The IPNs that were submitted at room temperature cure treatment (TT2) showed Tg dependence of only NCO/OH molar ratio. Equation 3 describes Tg variation as function of NCO/OH molar ratio (x).

$$Tg\ (°C) = -\ 15.207 + 7.911x \pm 2°C \quad (3)$$

3.2. IPN swelling

The only significant factor in SIPN swelling, cured by thermal treatment TT1, was MMA content. This behaviour is mathematically described by the Eq. 4, simplified as the previous ones. The swelling percentage went down with the MMA content increase since that the volume between the PU cross-links have been occupied by the MMA linear macromolecules hindering the solvent entrance.

$$Swelling\ (\%) = 17.842 - 2.94z \quad (4)$$

The swelling behaviour of IPNs cured at room temperature was different from the IPN cured at high temperature. In this case the swelling depends on all independent variables, as can be seen in the Eq. 5. Analyzing the equation it is possible to observe that as the higher the NCO/OH and the longer the reaction time the lower is the IPN swelling. This behaviour is related to the polymer crosslink density considering that the higher crosslink density less free space between the polymer molecules and the solvent entrance was more difficult, consequently the swelling decrease. The MMA content has a similar effect on swelling as described for the thermal treatment TT1.

$$Swelling\ (\%) = 18.47 - 1.50x - 0.78y - 1.37z - 0.58xy + 0.93xz + 0.56yz \quad (5)$$

3.3. Mechanical properties

The mechanical properties were evaluated by stress-stain curves obtained through dynamic mechanical analysis. The IPNs films cured at room temperature (TT2) showed lower elastic modulus when compared with the same material cured at higher temperature (TT1). This behaviour is more pronounced for the SIPN compositions with a higher MMA content. Experimental results showed that the elastic modulus depended on the NCO/OH molar ratio and MMA content. There was a significant influence of MMA content on the IPN elastic modulus in both cure treatment. The influence of NCO/OH molar ratio on the IPN elastic modulus was observed only for films cured at room temperature, as showed in Eqs. 6 and 7, respectively.

$$Elastic\ Modulus_{(TT1)}\ [MPa] = 4.13 + 1.87z \quad (6)$$

$$Elastic\ Modulus_{(TT2)}\ [MPa] = 2.73 + 1.06x + 0.72z \quad (7)$$

SIPNs with 60 wt. (%) of MMA had higher elastic modulus as can be seen in Fig. 3. The PMMA addition in a polyurethane matrix improves the mechanical properties of this

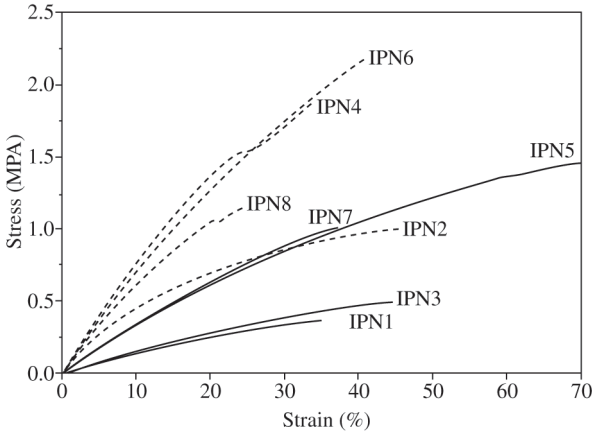


Figure 3. Stress-stain curves of semi-IPN cured as thermal treatment TT2.

Table 3. Significance factors (p) for the dependent variables Tg and swelling and Modulus for both cure thermal treatment (TT1 an TT2).

Independent variables	Significance factors (p)					
	Tg		Swelling (%)		Modulus	
	TT1	TT2	TT1	TT2	TT1	TT2
NCO/OH (x)	0.000097	0.003600	0.384134	0.000263	0.198152	0.016555
Time (y)	0.029430	0.713767	0.420053	0.003267	0.606904	0.881002
MMA (%) (z)	0.091123	0.767483	0.009427	0.000372	0.009409	0.053937
x×y	0.218968	0.895186	0.420553	0.009371	0.348671	0.095089
x×z	0.234359	0.486650	0.401995	0.001656	0.135873	0.853408
y×z	0.605231	0.602751	0.420553	0.010749	0.149855	0.881003

once the PMMA has Tg around 100 °C and so it is a rigid material. Polyurethane is more flexible and less resistant than acrylic polymer. The same trend was pointed out in many works with IPN made of polyurethane and acrylic polymers[7,10-12]. Figure 3 shows the influence of crosslink content in SIPNs with 20 wt. (%) of MMA (IPN1, 3, 5 and 7). In this case, samples with higher NCO/OH molar ratio were more crosslinked (IPN 5 and 7) and showed higher resistance and elastic modulus than that ones with lower NCO/OH molar ratio (IPN 1 and 3).

4. Conclusions

2^3 factorial experimental designs simplify the significance analysis of independent variables. Statistic method was very accurate on the SIPN proprieties evaluation. The results showed a strong influence of NCO/OH molar ratio on the Tg values, swelling and elastic modulus, mainly for the SIPN cured at room temperature. Swelling profile and mechanical properties are dependent of MMA content. This behaviour was observed in SIPN cured in both thermal treatments.

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