Polyurethane–poly(methyl methacrylate) interpenetrating polymer networks: 2. Influence of compositional parameters on the synthesis; physical properties

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According to a previously established general preparation scheme, polyurethane–poly(methyl methacrylate) interpenetrating polymer networks with various compositions and crosslinker contents were prepared. The influence of kinetics of the individual networks on the resulting composites was also examined. Only about 5% soluble species were extractible, thus showing a satisfactory completion of the different reaction systems. Physical properties such as transparency, refractive index, density and swelling behaviour were determined.

Keywords Polyurethane; poly(methyl methacrylate); interpenetrating polymer networks; compositional parameters; synthesis; physical properties

INTRODUCTION

Interpenetrating polymer networks (IPN's) represent a new approach to the problem of mutual incompatibility of polymers. Contrary to polymer blends, no further phase separation occurs once both components have been crosslinked. Sperling[1] and Frisch[2] and their coworkers, have done pioneering research in the field of IPN's. They have also established that in many cases the interpenetration of the two phases yields materials with new or enhanced properties.

During the two-step synthesis, only grafting reactions between the networks may occur, but in the one-step mode, where all the initial reagents are mixed together, some unwanted interactions between the latter can complicate or even alter the formation of one or both networks. Therefore, a thorough knowledge of the different reaction possibilities from the initial mixture to the end of the crosslinking process, appears as an inevitable requirement before structure/property relationships can be established.

In a previous paper[3], the synthesis of polyurethane/poly(methyl methacrylate) (PUR/PAc) IPN's was examined. The PUR elastomer network is formed by an aromatic triisocyanate and a polyether glycol (POPG) and catalysed by stannous octoate (OcSn). The PAc network results from the AIBN-initiated radical copolymerization between methyl methacrylate and a trimethacrylate. The PUR network is formed first at room temperature, and then the PAc by raising the temperature. Several side effects were observed in the early stages of network formation[3]. Thus, the premature polymerization of the methacrylic monomers yields non transparent IPN's, as PMMA and POPG are incompatible. This may be avoided by incorporating the glycol in the PUR network before the onset of the radical copolymerization. In addition light must be excluded. The PUR catalyst, OcSn, interacts in two ways with the acrylic system: in the absence of AIBN, it is able to start the polymerization, which is very slow; secondly, when combined with AIBN, as in the present system, it produces an overall acceleration of the radical copolymerization. Though not completely explained, this effect does not have an adverse influence on the synthesis of PUR/PAc IPN's, and therefore, both AIBN and OcSn will be utilized in further work. The formation of the individual networks has also been examined in various experimental conditions. The above mentioned interaction between OcSn and AIBN does not alter or delate the formation of the PUR network, as compared with other reaction mediums such as ethyl acetate. Furthermore the occurence of intersystem graftings has been examined, as the presence of radicals may result in some chain transfer to the PUR component. It was found that if some grafting does exist, it is negligible and therefore does not have to be taken into account in the discussion of structure/property relationships.

This preliminary study has allowed a general preparation scheme for PUR/PAc IPN's to be worked out, which is detailed below (Experimental). One point has not yet been examined which is the purpose of this paper: the influence on synthesis of compositional parameters like the PUR content, crosslink density, initiator concentration and the catalyst, respectively. Some physical properties like transparency, refractive index, density and swelling behaviour are also reported.

EXPERIMENTAL

Reagents and synthesis

All reagents used were described in detail previously (see ref. 3 *Table 1*), as well as the determination of the compositional parameters[3].

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Table 1 Time to gel for IPN's with various PUR content

% PUR	Time to gel (min)	% AIBN	Remarks
5	∞	0.025	no network formed
15	100	0.25	slight syneresis
25	45	1.00	transparent gel
34	22	1.00	transparent gel
40	18	1.00	transparent gel
50	12	1.00	transparent gel

Catalyst concentration for all samples: C_0 = 1.45% at room temperature

When necessary, functional and other analyses were carried out to check the indications given by the manufacturers. Water traces were eliminated, whereas the methacrylic monomers were not freed from the inhibitor molecules. A standard synthesis proceeds as follows: the calculated amounts of the various reagents are mixed and stirred thoroughly in a dry nitrogen atmosphere for a few minutes. The blend is poured into a glass mould. The PUR network is formed first at room temperature, in 15 to 20 min and without noticeable exothermy. 30 min after complete mixing of the reagents (taken as the origin of reaction times), the mould is transferred into a heating oven at 56°C where the radical copolymerization of the PAc phase is initiated. A forced air circulation in the oven allows an effective temperature regulation within ±2°C.

A thermocouple introduced into the mould indicates the heat evolution which is plotted against time. After 1 h at 56°C, the temperature is raised to 75°C for further 2 h. Then, the IPN is annealed: 75°C overnight and 3 h at 120°C.

Solvent extraction

1 mm thick pieces of IPN were solvent extracted in a Soxhlet apparatus with ethyl acetate. The refluxing was stopped when no more soluble parts were released. The amount of extract was determined and analysed by i.r. spectroscopy using a Perkin-Elmer model 225 apparatus.

Physical characterization

The refractive index was measured on a O.P.L. refractometer (D ray of sodium). The density was determined according to ASTM D 1505-63 T. The density gradient was obtained with various aqueous calcium nitrate ($Ca(NO_3)_2$, 4 H_2O) solutions which do not swell the samples. The equilibrium swelling degree was determined by the method described by Weiss[4]: weighed samples are immersed in the solvent until equilibrium swelling has been reached. The weight, or the volume equilibrium swelling degree, Q_w or Q_v, is respectively given by:

$$Q_w = \frac{m_s + m_c}{m_c}$$

$$Q_v = 1 + (Q_w - 1)\frac{V_s}{V_c}$$

where: m_s: weight of solvent
m_c: weight of dry sample
V_s: specific volume of solvent
V_c: specific volume of sample

The values of V_s and V_c are listed in *Table 5* (given as densities).

Furthermore, some solubility parameters were determined either according to Small's method[5], or by a swelling method[6].

RESULTS AND DISCUSSION

Effect of PUR content

IPN's containing between 5 and 50% by weight of PUR were prepared (*Table 1*). Obtaining IPN's with very low contents in either phase is not clear cut, as the swelling behaviour intervenes. Thus the equilibrium degree of swelling of the PUR network in the methacrylic monomer mixture is $Q_v = 5.22$, thereby setting a limiting superior value of 81% PAc in the PUR network (PUR/PAc : 19/81). For higher amounts of methacrylic monomers, syneresis occurs, or the PUR network will not form completely. An important syneresis was never observed for IPN's (less than 5% of the total initial volume); incompletely crosslinked PUR networks (NCO/OH < 1) do not show any syneresis as their actual swelling degree is in fact higher. *Table 1* shows also that the time to reach gelation, t_{gel}, decreases with increasing PUR content. As the catalyst concentration is kept constant ($C_0 = 1.45\%$) the niticeable acceleration is due to the increased probability of encounter between the PUR precursors as already emphasized[3], a 5% concentration in the latter does not yield a network for the same reason. Due to a higher initial viscosity, air bubbles are sometimes included in the 50/50 IPN's.

However, the increasing content of methacrylic monomers produces an important acceleration of the copolymerization of the PAc system. Thus, the operating conditions had to be adjusted: the AIBN concentration was decreased, and the temperature was kept at 56°C instead of being raised up to 75°C. Note that for the 5/95 composition also, a solid sheet was obtained, though only a semi-IPN can be formed.

From the above discussions, it is clear that in the 5 to 50% PUR range, only the intermediate compositions are formed without some additional problems. Therefore, the influence of the other compositional parameters was studied on 34/66 PUR/PAc IPN's.

IPN's containing 34% PUR

Unless otherwise posted, the reactive mixtures contain: 1.45% OcSn, 1% AIBN, a NCO/OH ratio of 1.07 and 5% TRIM.

Effect of the catalyst concentration. This effect on the formation of the PUR network appears in *Table 2*. The first column shows the slowing down of the gelation rate with decreasing OcSn concentration; OcSn was added

Table 2 Time to gel for PUR network at various catalyst concentrations

% OcSn (C_0 units)	Time to gel (min)		
	OcSn added directly	OcSn added in solution in MMA (1/10)	PUR in ethyl acetate
C_0	22	37	21
$C_0/4$	45	75	45
$C_0/8$	90	120	185
$C_0/16$	300	600	365

C_0 = 1.45%; room temperature

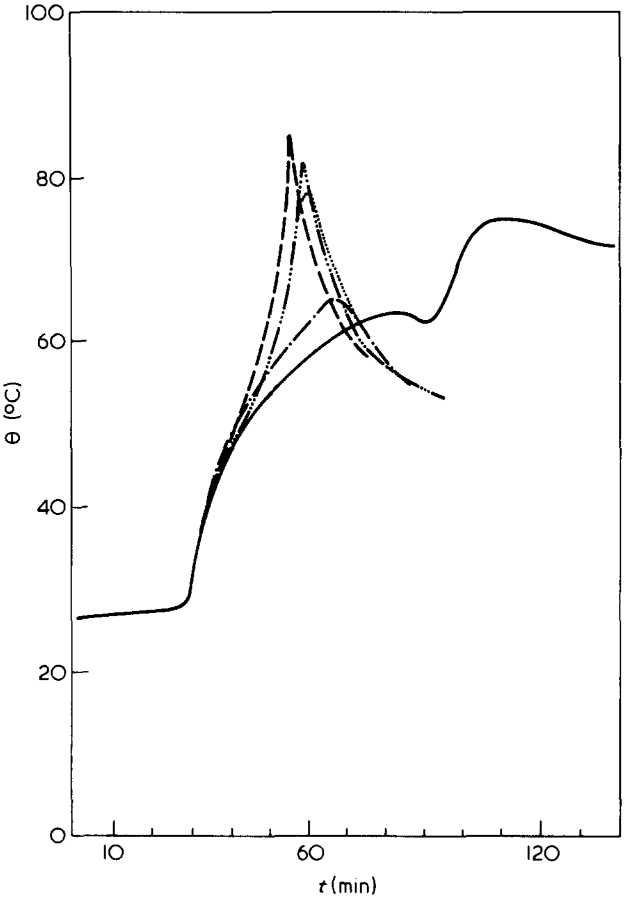

Figure 1 Time *versus* temperature curves at various initiator contents, for the copolymerization of the methacrylic monomers. % AIBN: (–––), 2; (–···–···–), 1.5; (.....), 1; (–-–-–), 0.5; (–), 0.25

directly to the reaction mixture in these experiments. At least at the higher catalyst concentrations, the difference between MMA and ethyl acetate as reaction media is negligible (column 3). When very small amounts of OcSn were used, solutions of the latter in MMA were prepared in order to increase the accuracy. However the middle column in *Table 2* shows clearly the increase in gelation time due to the already mentioned interaction between MMA and OcSn[3]. This justified the somewhat excessive concentration of PUR catalyst used here. However, this introduction mode of OcSn was not used further. Usually, the mould is at room temperature for 30 min before its transfer into the heating oven. It seemed interesting to examine the influence on the IPN formation of an immediate heating soon after all reagents are mixed. *Figure 1* shows that heating the mould up to 56°C requires about 20 min, the actual gelation time of the PUR component at room temperature. Consequently, the PUR gel is always formed before the onset of the radical copolymerization. As a matter of fact, gelation is already terminated only 5 min after introducing the mould into the oven. The resulting IPN has the same appearance as those prepared in the usual way, but this does not signify that its properties would be identical.

Copolymerization with respect to the acrylic system, at a given temperature, is dependent on the concentration of the radical donor, AIBN. Other parameters play a role in the kinetic process, but do not vary: the viscosity of the reaction medium, which is that of the PUR gel, and the amount of crosslinker[3,7], 5% TRIM. *Table 3* and *Figure 1* show the variation of t_{max}, the time to reach the maximum of the exothermic peak, with the AIBN %. As expected, t_{max} increases when less initiator is added to the system. For 0.25% AIBN, the temperature has to be raised up to 75°C in order to obtain complete copolymerization, and a second small peak appears. The upwards slope of the exotherms, proportional to the propagation rate, increases with the AIBN concentration; however, due to the many factors involved, an appropriate kinetic law governing the present system has not yet been established.

The degree of crosslinking of the individual networks and the overall crosslink density are important parameters for materials like the IPN's. Therefore PUR/PAc IPN's with various NCO/OH ratios (K=0.7–1.3) and TRIM percents (0–7%) were prepared; only their physical characterization is given hereafter; the influence of crosslink density on their mechanical behaviour will be examined in a following paper.

Characterization of some IPN's

Solvent extraction. Though all the linear species entrapped in a network cannot always be removed[8], it is nevertheless important to carry out extraction tests on IPN's in order to determine the degree of fixation of the various reagents onto their respective network. *Table 4* shows that with a few exceptions, the amount of soluble species varies between 3% and 8%. Usually, in similar experiments, a value of 3% to 5% is found[9], so that the results are reasonable considering the complicated reaction medium. The values around 8% correspond to IPN's where at least one of the networks has been formed rather quickly, and therefore incompletely, for example: IPN 50/50; IPN with 2% AIBN. Also IPN's with a deficit in isocyanate ($K = NCO/OH < 1$) release more soluble

Table 3 Time to maximal temperature in the copolymerization of the PAc system, at various initiator concentrations

% AIBN	Time to maximal temperature (min)	Maximal temperature (°C)	Slope of exotherm (°C/min)	Number of exothermic peaks
2	7.5	86	6.13	1
1.5	10.4	83	4.56	1
1	10.8	79	3.12	1
0.5	16.7	66	0.53	1
0.25	27.5/57.5	64/76	0.24	2

Table 4 Solvent extraction of PUR/PAc IPN's

IPN sample	Parameter varied			Soluble extract (%)
	K = NCO/OH	% TRIM	% AIBN	
34/66	0.77	5	1	11.4
	0.89	5	1	7.7
	1.07	5	1	4.2
	1.07	7.5	1	5.2
	1.07	1	1	5.7
	1.07	5	0.5	2.9
	1.07	5	2	8.2
15/85	1.07	5	0.25	2.9
25/75	1.07	5	1.00	6.0
40/60	1.07	5	1.00	8.5
50/50	1.07	5	1.00	8.8

Extraction with ethyl acetate, over 12 days

Table 5 Physical properties of PUR/PAc IPN's

Sample	Refractive index, n_D^{20}	Density (g ml^{-1})	Equil. swelling degree, Q_v, in:		Solubility parameter (cal$^{1/2}$/cm$^{3/2}$)
			Ethyl acetate	Methanol	
PUR	1.491	1.093	4.54	2.82	9.4
L 75	1.533	1.17	–	–	–
POPG	1.451	1.00	–	–	7.7
PMMA crossl.	1.492	1.190	2.03	1.29	9.2
TRIM	1.471	1.065	–	–	–
Ethyl acetate	1.373	0.901	–	–	9.15
Methanol	1.329	0.792	–	–	14.2
K: 1.28	1.496	1.164	–	–	
1.13	1.494	1.161	2.75	1.67	
1.07	1.493	1.161	2.87	1.73	
0.89	1.492	1.157	3.04	1.78	
0.77	1.491	1.153	3.09	1.80	
% TRIM: 7.5	1.495	1.164	2.48	1.63	
5	1.496	1.161	2.58	1.73	
1	1.493	1.164	2.87	1.74	
% AIBN: 2	1.494	1.160	2.88	1.67	
1	1.494	1.161	2.87	1.73	
0.5	1.494	1.163	2.88	1.65	

species. The complete analysis of the extract is proving difficult. Using i.r. spectroscopy, absorptions belonging to both methacrylic and PUR phases appear. However, traces of stannous octoate and non-identified impurities (about 10% of the total extract) are present[10], thus limiting the amount of extract coming from the networks.

Optical properties. PUR/PAc IPN's are usually transparent materials (90% transmission for 3.5 mm thick sheets at 600 nm), with regular and smooth surfaces. Their transparency is due to the nearly identical refractive indices of the two components, PUR and PAc (*Table 5*); hence, no indication of the degree of phase dispersion can be drawn from the absence of turbidity. The transparency is lower (85%) when $K < 1$: in this case, several free or pendent POPG chains segregate into domains and as the refractive index of POPG is different from that of the surrounding matrix, slight turbidity results. For all the other IPN's listed in *Table 5*, only the third decimal varies; the variation is random and may be ascribed to experimental error.

Equilibrium swelling degree The volume equilibrium swelling degree, Q_v, is reported in *Table 5*. By swelling in ethyl acetate, a good solvent for both phases, the volume of the samples roughly increases threefold, and in methyl alcohol, times 1.7. Either solvent causes a cloudiness which is important in the latter. The partial loss of transparency may be due to some structural heterogeneity in which the solvent is gathered, and revealed by the difference in refractive indices. This effect is more pronounced in IPN's where $K < 1$, for the same reason as stated above. By evaporating the solvent, all the samples again become transparent, so that swelling does not induce any permanent morphological change. It should be pointed out that contrary to the IPN's, the individual networks always remain transparent upon swelling. Finally, when either K or % TRIM are increased, Q_v decreases, thereby indicating that more crosslinks can effectively be created, which is not clear in a 'compact' reaction medium such as the present one.

CONCLUSION

The previously established general preparation scheme is well adapted for the synthesis of PUR/PAc IPN's containing between 5 and 50% by weight of PUR. It yields reproducible sheets with high transparency and excellent surfaces. However, obtaining IPN's with low PUR content is limited by the equilibrium swelling degree of the PUR network in the methacrylic monomers. In the present system, the minimum PUR content is 19%. Another limiting factor is the probability of encountering of the PUR precursors, which decreases with their concentration. These facts do not preclude the study of such materials which can no longer be called IPN.

The rate of polymerization of each network may be adjusted by the catalyst, and the initiator concentration respectively. A too rapid gelation yields incompletely formed networks and bad sheets; when the network formation is too slow, incompatibility problems arise which may cause some turbidity in the IPN's.

The loss of transparency of solvent swollen IPN's indicates some morphological heterogeneity arising from the interpenetrated phases, the degree of dispersion of which, is perhaps rather low. The actual morphology of PUR/PAc IPN's is presently being examined by electron microscopy and small angle X-ray diffraction.

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