

Semi- and Fully Interpenetrating Polymer Networks Based on Polyurethane–Polyacrylate Systems. XI. The Influence of Polymerization Temperature on Morphology and Properties

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SYNOPSIS

Polyurethane–poly(methyl acrylate) interpenetrating polymer networks (IPNs) of fixed composition (50/50) were prepared at 200 MPa and a range of temperatures. Decreased synthesis temperatures generally resulted in improved mixing of the two networks, although the sequence of formation of the two polymers was also important. No obvious improvements in physical properties resulted from the enhanced mixing. At high synthesis temperatures, the exothermic heat of polymerization of the methyl acrylate led to excessive temperatures, capable of degrading the already-formed polyurethane network. This resulted in a deterioration in tensile strength and a decrease in hardness of the IPN. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are a special class of polymer blends and have been the subject of a number of reviews.^{1–4} IPNs consist of two independent networks, of which at least one has been synthesized and/or cross-linked in the presence of the other. Ideally, the interpenetration is of a physical nature, with little or no chemical grafting between the two components.⁵ If only one polymer is cross-linked, the material is called a semi-IPN. A semi-IPN of the first kind (semi-1-IPN) results when the first-formed polymer is cross-linked.

There are two principal routes for preparing IPNs, namely, sequential and simultaneous polymerization of the two components.^{2,5} Sequential IPNs are generally prepared by swelling the first-formed network with the second monomer, which is then polymerized *in situ*. They may also be one-shot, two-stage processes in which the monomeric ingredients are all added simultaneously, but the temperature is kept low to enable the first network to form independently and then raised, after a suit-

able period, to form the second network.⁶ Simultaneous IPNs (SINs) are, of necessity, one-shot, one-stage processes. It should, however, be noted that true SINs are only formed if the rates of polymerization are at least similar for both components of the IPN. This requires careful selection of catalyst, initiator, temperature, and pressure, and, in practice, true SINs are seldom obtained.

IPNs, like most polymer/polymer systems, generally show phase separation as a consequence of the low entropy change on mixing, which results in a positive value for the Gibbs free energy of mixing.⁷ Generally, the monomeric ingredients are mutually soluble, and it is only upon polymerization that thermodynamic incompatibility occurs and the system starts to phase-separate. Wolf et al.^{8–10} have shown the decrease in miscibility with increasing molecular mass for certain oligomeric systems. The degree of separation observed will depend on the mobility of the polymer chains as well as on the time required for the networks to interlock. In other words, the extent of phase separation is a function of the synthesis procedure.

Most polymer blends exhibit lower critical solution temperatures (LCST), where the miscibility decreases with increasing temperature.^{11–16} Theoretical investigations by McMaster¹² and Sanchez and Lacombe¹⁷ also predict LCST behavior. In addition, the rate of separation will be greatly enhanced

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at elevated temperatures, as a result of the increased mobility of the macromolecular chains.¹⁸ The gelation time, on the other hand, will be reduced in accordance with the standard Arrhenius equation, thus opposing phase separation. Lee et al.^{18,19} showed that increasing the synthesis temperature of a polyurethane (PU)–polystyrene IPN led to a decrease in the degree of intermixing, suggesting that the decrease in gel time is the dominant factor.

This paper investigates the effect of synthesis temperature on the resultant morphology and properties of a PU–poly(methyl acrylate) (PMA) IPN of fixed composition.

EXPERIMENTAL

Materials

The isocyanate-terminated PU prepolymer, Adiprene L-100, supplied by DuPont, had a \bar{M}_n value of 2000 g/mol and a polydispersity of 2.1. Trimethylolpropane (TMP), supplied by Aldrich Chemical Co., was used as the cross-linking agent, giving a theoretical mass between cross-links (\bar{M}_c) of 2090 g/mol. In practice, \bar{M}_c is likely to be higher as a result of the diluting effect of the methyl acrylate.²⁰ The NCO : OH ratio was 1.1, since this gives a network with the lowest \bar{M}_c and best properties.²¹ Dibutyl tin dilaurate (1.04% w/w of Adiprene L-100) was added as a urethane catalyst. The methyl acrylate contained 1 mol % of ethylene glycol dimethacrylate as network former yielding a theoretical \bar{M}_c of 8600 g/mol. Azobisisobutyronitrile (AIBN) (0.2% w/w of methyl acrylate) was used to initiate the free radical polymerization.

Synthesis

The requisite amounts of Adiprene L-100 and TMP were dissolved in methyl acrylate in order to give

an IPN containing 50% by weight of PU. The solution was carefully degassed and any volatilized methyl acrylate replaced. The remaining ingredients were added and mixed before final degassing. The mixture was carefully poured into an aluminum foil bag lined with polyethylene. This bag contained three parallel stainless-steel plates separated at the corners by silicone rubber spacers. The bag had previously been flushed with nitrogen. It was then sealed and placed in the chamber of a hydraulically operated high-pressure vessel. Heating was effected by submersing the entire vessel in a thermostated oil bath. The pressure in the vessel chamber was raised to an initial value of 200 MPa. Because of the volume contraction on polymerization, the pressure dropped by about 30 MPa during the course of the reaction.

Experiments were conducted at 45°C for 95 h, 55°C for 69 h, 71°C for 18.5 h, 90°C for 18 h, and 120°C for 17 h. Isothermal temperatures were approached at rates approximately equal to those shown in Table I. For the experiment at 45°C, the initiator concentration was raised to 0.6% w/w of methyl acrylate, and for the polymerization at 120°C, it was lowered to 0.14%. After polymerization, the bag was cut open and the sheets of material recovered from between the metal plates by freezing the "sandwich" in liquid nitrogen. The samples were dried to constant mass under vacuum at 20°C.

Characterization

Transmission electron micrographs were obtained using a Hitachi electron microscope (model HU-11B). Prior to microtomy, the samples were hardened and stained with osmium tetroxide vapor.

Dynamic mechanical analysis was performed with a Polymer Laboratories dynamic mechanical thermal analyzer in the dual cantilever mode. The frequency was 1 Hz and the heating rate was 2°C/min.

A J. J. Lloyd tensile tester (type T5002) was used

Table I DSC Data for the Polymerization of Methyl Acrylate at a Range of Temperatures

Sample No.	Synthesis Temperature (°C)	[AIBN] (wt %)	Heating Rate (°C/min)	ΔH (kJ/mol)	Induction Time (min)	Peak Temperature (°C)
1	45	0.6	1.25	72	134	45
2	55	0.2	1.25	74	268	55
3	71	0.2	1.25	73	60	71
4	90	0.2	1.25	73	44	85
5	120	0.14	2.5	75	24	91

to obtain stress-strain data on samples of 25 mm gauge length. The crosshead speed was 20 mm/min, and the temperature, 20°C.

A Perkin-Elmer DSC-II was used for the differential scanning calorimetry studies. Samples were heated from 26°C at the rate shown in Table I and then held at the appropriate isothermal temperature until polymerization was complete. Nitrogen was used as a purge gas.

RESULTS AND DISCUSSION

Extent of Mixing

Transmission electron microscopy of the PU-PMA IPN synthesized at 71°C showed an extremely fine structure in which the dark OsO₄ stained PU regions form a fine network in the light-colored PMA matrix. Close inspection indicated that both components were present as continuous phases, as would be expected for 50-50 wt % IPNs.

Damping curves for the IPNs synthesized at different temperatures are presented in Figures 1-3.

The complete $\tan \delta$ vs. temperature plots are presented in Figure 1, while Figure 2 is an expanded view showing only the PU component transition. As the synthesis temperature decreases, the transition due to the PMA component of the IPN shifts to lower temperatures and decreases in magnitude. At the same time, the PU peak shifts to higher temperatures and increases in magnitude. The transition temperature for the two samples prepared at low temperature is unclear because of the absence of a well-defined peak. Loss modulus vs. temperature plots (Fig. 3), however, confirm the trend of the PU transition shifting to higher temperatures at lower synthesis temperatures. They also show that, with decreasing synthesis temperature, the PMA loss modulus transition shifts to lower temperatures and merges with the PU transition. The merging of the peaks at lower synthesis temperatures indicates improved mixing.

Half-peak widths of $\tan \delta$ peaks can also be used as a measure of the level of mixing of the components in a phase-separated polymer system. Provided the two peaks have not yet merged, the half-peak width

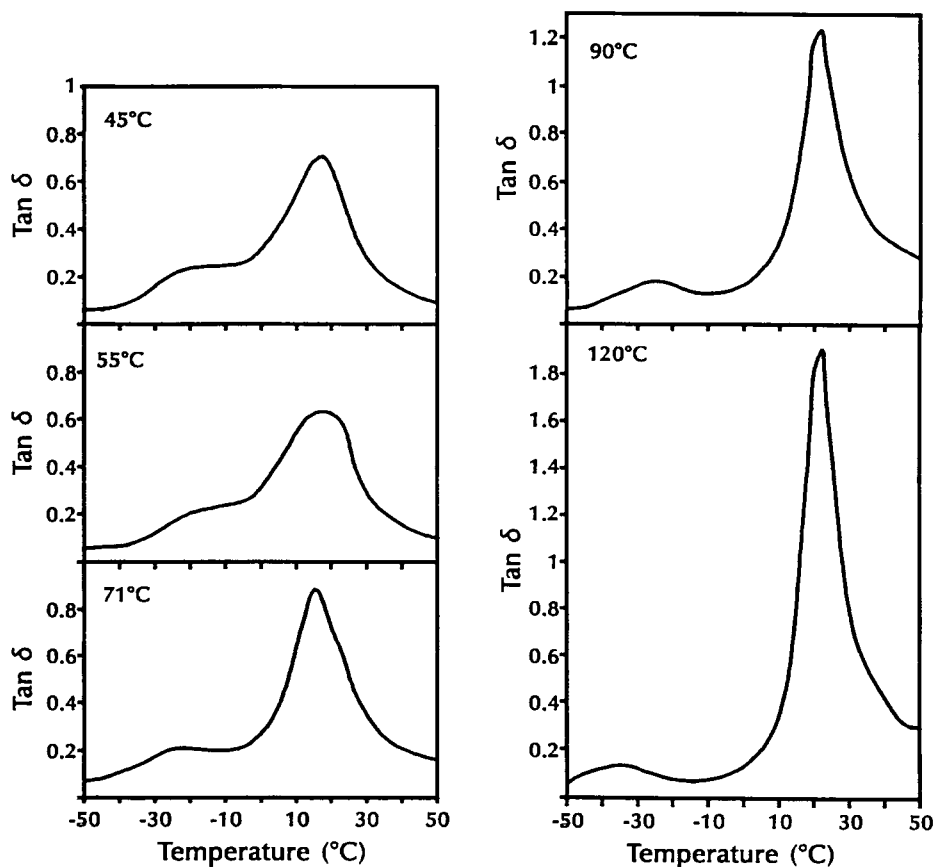


Figure 1 $\tan \delta$ vs. temperature plots for samples synthesized at 45, 55, 71, 90, and 120°C.

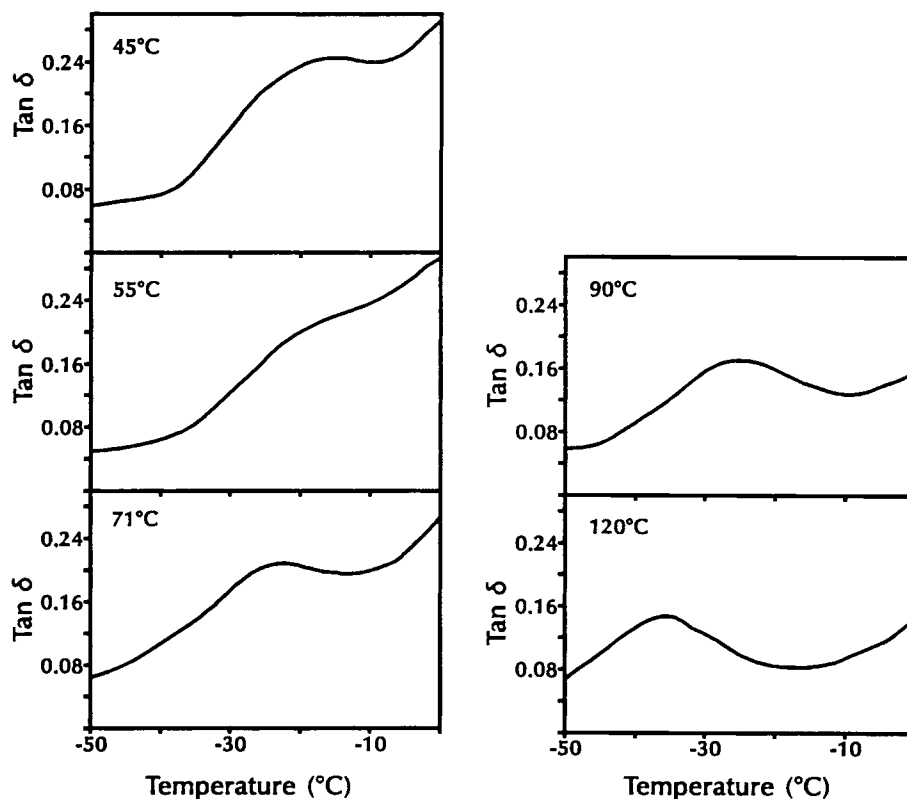


Figure 2 Expanded $\tan \delta$ vs. temperature plots for samples synthesized at 45, 55, 71, 90, and 120°C, showing the PU transition.

increases as the extent of mixing increases. Table II shows that decreasing the synthesis temperature produces more intimately mixed IPNs down to a temperature of 55°C, but that the IPN synthesized at 45°C is less well mixed. This is supported by other data in Table II, which show that the loss modulus maximum temperature for the PU component reaches a maximum (of -25°C) for the sample synthesized at 55°C, as well as the PMA $\tan \delta$ maximum temperature and magnitude, which show minimum values for the samples synthesized at 71 and 55°C, respectively.

The storage modulus vs. temperature plot (Fig. 4) also shows improved mixing for samples synthesized at lower temperatures. Two distinct drops in modulus are evident for the sample synthesized at 90°C, whereas the 55°C sample shows an essentially continuous and broad transition from glassy to rubbery behavior.

Thus, all the dynamic mechanical analysis results indicate improved mixing as the synthesis temperature decreases from 120 to 55°C, but slightly poorer mixing in the IPN synthesized at 45°C. The extent of mixing can be quantified with the aid of the Fox equation²² below:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where T_{g1} and T_{g2} are the glass transition temperatures of the PU and PMA homopolymers, respectively, and w_1 and w_2 represent their respective weight fractions. If the T_g of PU is taken as -29°C and that of PMA as 30°C,²³ then the mass fraction of PU in the PMA phase is 20% for the IPN synthesized at 55°C. Similarly, it can be shown that there is 24% PMA present in the PU phase.

A number of questions still remain to be answered. First, why does the sample synthesized at 45°C show poorer mixing than expected, and, second, why is the glass transition temperature of the PU component in the IPN synthesized at 120°C so low? The PU homopolymer has a glass transition temperature of -29°C,²³ whereas the IPN synthesized at 120°C has a PU glass transition at -36°C.

DSC data was obtained for the AIBN-initiated polymerization of methyl acrylate and is presented in Figure 5 and Table I. Time-temperature profiles were chosen to match actual conditions in the IPN synthesis as closely as possible and the concentration of initiator was identical. Note that for samples

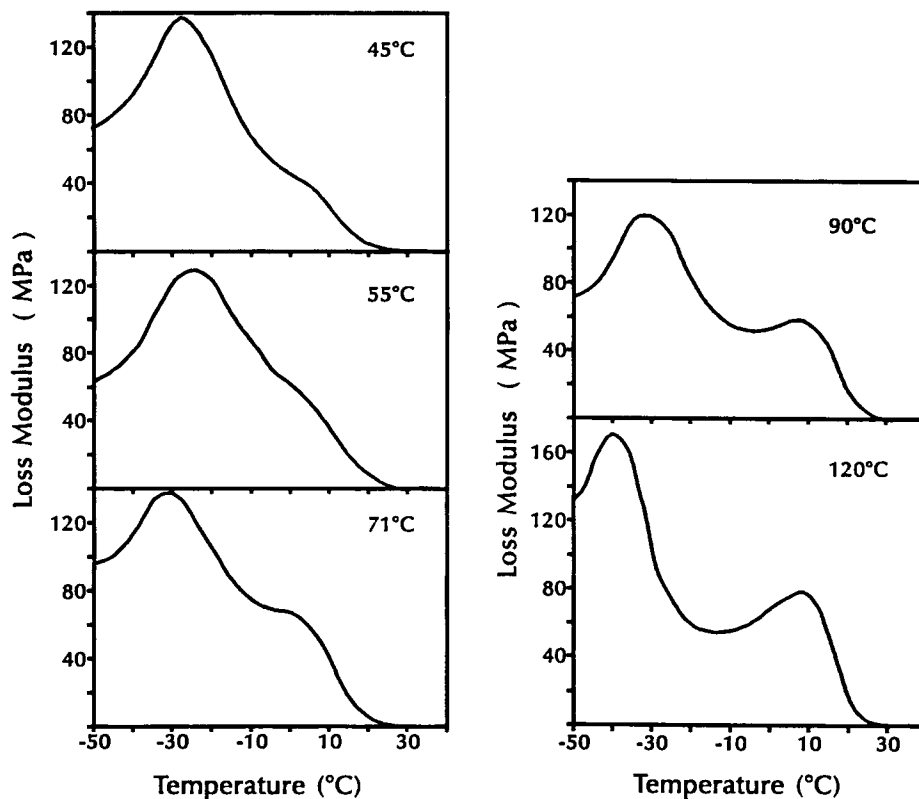


Figure 3 Loss modulus vs. temperature plots for samples synthesized at 45, 55, 71, 90, and 120°C.

4 and 5 the polymerization reaches its maximum rate prior to attaining isothermal conditions (Table I). As expected, decreasing the polymerization temperature causes a decrease in the height of the exothermic peak as well as greater induction periods. Increased levels of initiator in sample 1, however, have reduced its induction period so that it polymerizes sooner than sample 2, albeit at a slower rate in accordance with its lower temperature. Well-de-

finer curing exotherms for PU were difficult to obtain because of the low heat of polymerization, but DSC results suggest that the reaction peaks at about 60°C and that it is complete at 80°C when heated at 2.5°C/min. Thus, for IPNs prepared at 120, 90, and 71°C, the PU would cure first, followed by the methyl acrylate. The lower the temperature, the lower the mobility of the separating polymer, and, hence, demixing occurs to a lesser extent. At 55°C,

Table II Dynamic Mechanical Data for the IPNs Synthesized at a Range of Temperatures

Sample No.	Synthesis Temperature (°C)	PU Transition			PMA Transition		
		Tan δ Max		E'' Max	Tan δ Max		
		Temperature (°C)	Magnitude	Temperature (°C)	Temperature (°C)	Magnitude	Half-Peak Width (°C)
1	45	-14	0.24	-28	18	0.70	25
2	55	-17	0.21	-25	18	0.63	32
3	71	-21	0.21	-31	16	0.87	21
4	90	-25	0.17	-31	22	1.23	16
5	120	-36	0.14	-40	23	1.90	13

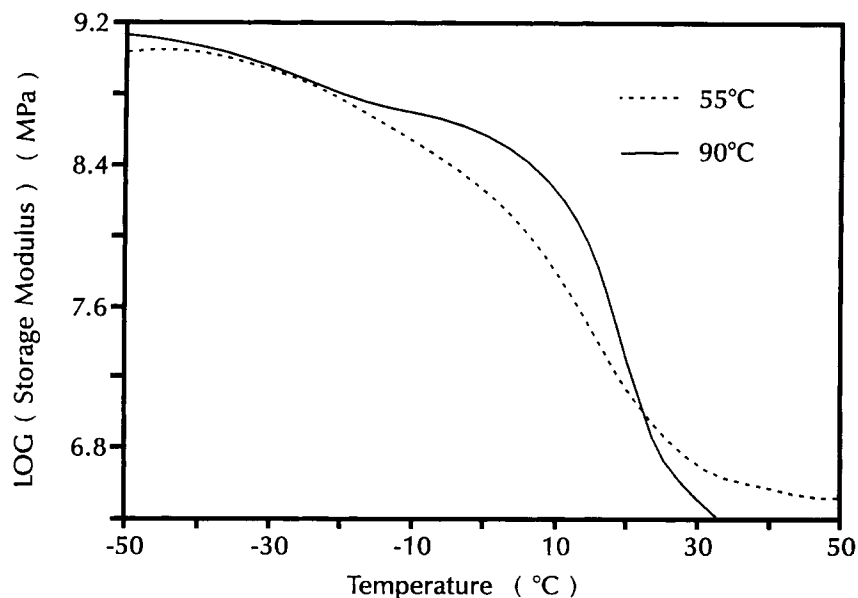


Figure 4 The storage modulus vs. temperature plots for samples synthesized at 55°C (----) and 90°C (—).

the PU should still be able to cure in the 268 min before the addition polymerization commences. However, at 45°C, the PU reaction rate will be much slower, while increased initiator reduces the induction period of the methyl acrylate polymerization so that it is likely to gel before the PU network forms. This implies that PU would be the separating phase, and since it has a glass transition some 60°C below

that of PMA, it would be more mobile. Consequently, demixing would be greater.

Effect of Exothermic Heat of Polymerization

Since the addition polymerization is generally occurring in the already-formed PU network, and since all polymers are good thermal insulators, it was felt

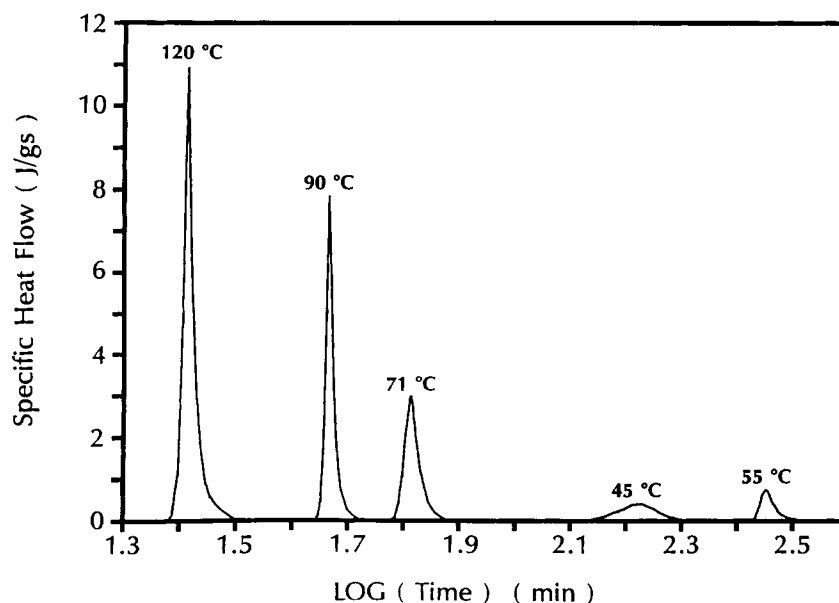


Figure 5 DSC scans of the AIBN-initiated polymerization of methyl acrylate at a range of temperatures.

that it would be instructive to calculate the temperatures reached during the IPN synthesis. The calculation is approximate, requiring a number of assumptions, but nevertheless gives a good indication of the magnitude of the temperature increase that can be expected.

Heat is gained as a result of the exothermic heat of polymerization of methyl acrylate and is lost by conduction to the surrounding oil bath. Since the rate of loss of heat is dependent on the difference between the sample and its surroundings, it is necessary to make a number of calculations at small time intervals. This was done by dividing the reaction exotherm up into small time intervals (θ) and calculating the heat energy evolved for each time interval (ΔH_{in}). The temperature increase for the n th time interval (ΔT_{in}) is given by eq. (2):

$$\Delta T_{in} = \frac{\Delta H_{in}}{2mc} \quad (2)$$

where m is the mass of methyl acrylate in the IPN, $\Delta H_{in}/m$ is the specific heat of polymerization evolved during the n th time interval, c is the specific heat of the IPN taken, nominally, at $2 \text{ Jg}^{-1} \text{ K}^{-1}$, and the factor 2 takes account of the fact that only 50% by weight of the IPN is generating heat.

The temperature drop as a result of conduction can be calculated, using an infinite plane as a model and ignoring the steel plates (i.e., assume all heat

is lost through the major face of the sample and none through the ends and edges, or by conduction via the steel plates). The heat lost due to conduction in the n th time interval (ΔH_{cn}) is given by eq. (3):

$$\Delta H_{cn} = Q\theta = \frac{kA(T_{in} - T_0)\theta}{L} \quad (3)$$

where Q is the rate at which heat is lost; k , the coefficient of thermal conductivity; A , the surface area of the face of the sample; θ , the time interval; L , half the sample thickness; T_0 , the temperature of the surrounding medium; and T_{in} , the temperature of the IPN at the end of the n th time interval just prior to cooling. Note that eq. (3) assumes that the surface of the sample is always T_0 , which is a good assumption provided ΔT_{in} is not too large. The cooling during this interval is given by eq. (4):

$$\begin{aligned} \Delta T_{cn} &= \frac{\Delta H_{cn}}{2mc} = \frac{kA(T_{in} - T_0)\theta}{2Lmc} \quad (4) \\ &= \frac{kA(T_{in} - T_0)\theta}{\rho AL^2 c} \\ &= \frac{\alpha\theta(T_{in} - T_0)}{L^2} \quad (5) \end{aligned}$$

where α (equal to $k/\rho c$) is the thermal diffusivity of the IPN and ρ is its density. Thus, using eqs. (2) and (5), the temperature at the end of the n th time interval can be calculated after heating (T_{in}) and after cooling (T_{cn}):

$$T_{in} = T_{c(n-1)} + \Delta T_{in} \quad (6)$$

and

$$T_{cn} = T_{in} - \Delta T_{cn} \quad (7)$$

where $T_{c(n-1)}$ is the temperature after cooling at the end of the $(n-1)$ th interval. For $n=1$, $T_{c(n-1)} = T_0$.

Using eqs. (6) and (7), the time-temperature profile for the IPNs synthesized at various temperatures was calculated. (Note that where the reaction occurs prior to reaching the isothermal temperature, a value of T_0 was used coinciding with the temperature at which the rate of polymerization was a maximum.) Table III lists the data for the IPN prepared at 90°C using a time interval of 30 s. The value of α used was $3.75 \times 10^{-6} \text{ m}^2/\text{min}$. This value was calculated from typical values of k , ρ , and c for

Table III Calculated Increase in T_i and T_c with Time for the IPN Synthesized at 90°C

Time (min)	ΔT_i ($^\circ\text{C}$)	T_i ($^\circ\text{C}$)	ΔT_c ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)
0.5	0.7	85.7	0.0	85.7
1.0	3.4	89.1	0.3	88.8
1.5	13.1	101.9	1.3	100.6
2.0	33.2	133.8	3.7	130.1
2.5	52.8	182.9	7.3	175.6
3.0	44.9	220.5	10.2	210.3
3.5	25.1	235.4	11.3	224.1
4.0	14.6	238.7	11.5	227.2
4.5	8.3	235.5	11.3	224.2
5.0	5.2	229.4	10.8	218.6
5.5	3.5	222.1	10.3	211.8
6.0	2.4	214.2	9.7	204.5
6.5	1.8	206.3	9.1	197.2
7.0	1.2	198.4	8.5	189.9
7.5	0.8	190.7	7.9	182.8
8.0	0.5	183.3	7.4	175.9
8.5	0.3	176.2	6.8	169.4
9.0	0.1	169.5	6.3	163.1

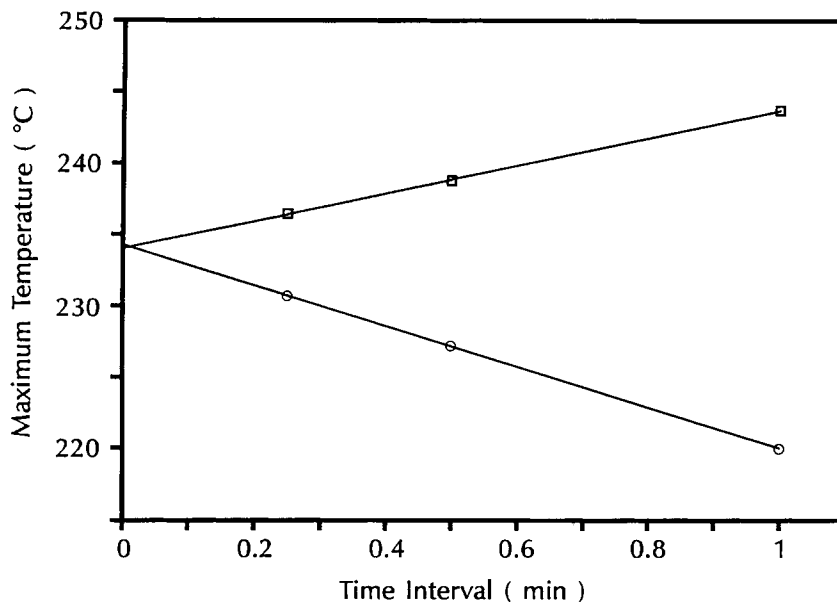


Figure 6 Calculated values of (□) $T_{i(\max)}$ and (○) $T_{c(\max)}$ for different time intervals.

a rubber.²⁴ L was taken as 5 mm. Clearly, both T_i and T_c increase to a maximum, as expected. $T_{i(\max)}$ and $T_{c(\max)}$ differ by about 12°C, but as the time interval is reduced, the two maxima come closer together and, within experimental error, they merge on extrapolation to zero-time interval (Fig. 6). Figure 7 shows these maximum temperatures plotted against the synthesis temperature of the IPNs.

Even allowing for the approximations in the

above calculations, the magnitude of the maximum temperature reached is surprising, being 272°C for a 5 mm-thick IPN prepared at 120°C. Assuming a thinner sample (L equal to 4 mm) still results in a maximum temperature greater than 250°C. The thermal diffusivity is not too critical a parameter either, since a 20% change in α yields only a 2% change in the maximum temperature. The calculations leading to the maximum temperatures as

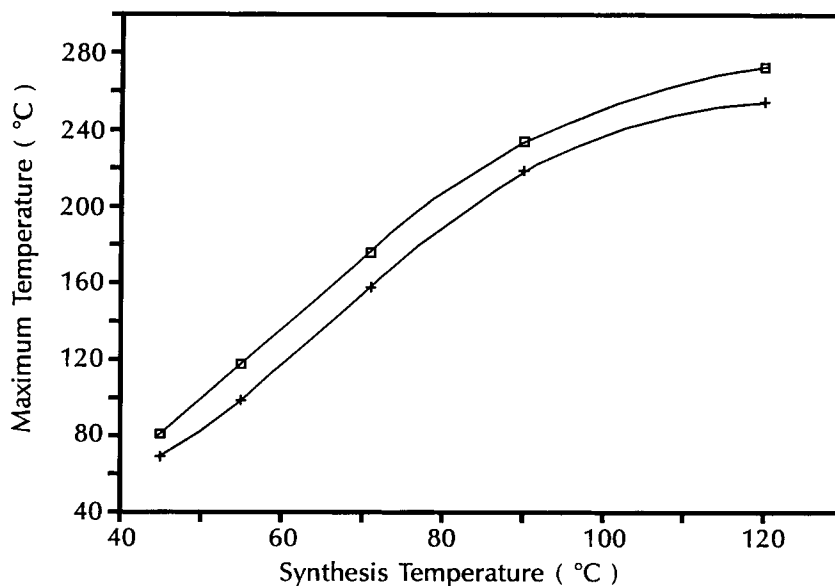


Figure 7 Calculated maximum temperatures reached in the IPNs, as a function of their synthesis temperature. Sample thickness: (□) 5 mm and (+) 4 mm.

Table IV Tensile, Hardness, and Swelling Data for IPNs Synthesized at a Range of Temperatures

Sample No.	Synthesis Temperature (°C)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	ν_r (%)	Extracted Material (wt %)
1	45	3.6	340	54	35	1
2	55	1.8	185	61	36	0
3	71	1.2	185	57	34	2
4	90	1.6	315	56	27	7
5	120	0.6	255	43	17	33

shown in Figure 7 are all based on reactions at atmospheric pressure. At 200 MPa, the rate of reaction will be about three times greater,²⁵ leading to potentially still higher temperatures.

Thermogravimetric analysis showed that the PU starts to volatilize at 280°C in nitrogen. Hence, thermal damage of the PU network is a distinct possibility. The DBTD may contribute to the thermal instability, as it has been shown to accelerate the thermal degradation of PU.²⁶ Swelling and extraction studies (Table IV) show constant cross-link density, with negligible extractable material, for the samples synthesized at lower temperatures. For the sample synthesized at 90°C, there is a slight drop in cross-link density, as reflected by the lower equilibrium volume fraction of rubber in the swollen sample (ν_r). The sample synthesized at 120°C has only 17% polymer in the swollen sample compared with 35% in the sample synthesized at 45°C. In addition, 33% of the IPN is extractable in toluene, confirming that the cross-linked network has been severely damaged. Thermogravimetric analysis of the sample after extraction indicates that it is the PU component that is being degraded. The presence of degraded PU would also explain the very low glass transition temperature of the PU component (Figs. 1 and 2.)

Physical Properties

The effect of synthesis temperature on the physical properties of the IPNs is also shown in Table IV. There are no obvious trends in hardness, tensile strength, or elongation at break as a result of enhanced mixing, although there is clear evidence that lower synthesis temperatures result in IPNs with higher tensile strength. This is most likely a result of subtle changes in the exact chemical nature of the PU network. It is well known²⁷ that the physical properties of PUs are very sensitive to the temperature of synthesis. The IPN synthesized at 120°C,

which has the most phase-separated structure, does have very poor tensile strength, but this is very probably a consequence of thermal damage to the PU network, rather than any phase separation. The reduced hardness for this sample is consistent with the presence of low molecular mass material as suggested by the large amount of extractable material (Table IV).

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