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Thermal analysis during the formation of polyurethane and vinyl ester resin interpenetrating polymer networks*

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A vinyl ester resin (VER) with negligible carboxyl and hydroxyl groups was prepared from bisphenol A epoxy resin and α-methacrylic acid in combination with styrene. Simultaneous interpenetrating polymer networks (SINs) consisting of this VER and polyurethane (PU) could be obtained with negligible inter-component chemical binding between the two networks. The synthetic courses of these SINs were monitored with differential scanning calorimetry. While the amount of PU formation remained almost the same, the copolymerization of VER was greatly affected by temperature, by the composition of SINs and by the molecular crosslinking nature of both components. Furthermore, the thermal behaviour during the synthesis of SINs from VER containing hydroxyl groups was examined and showed that, when the secondary hydroxyl groups in VER were included for the metering of isocyanate in the feed for PU formation, inter-component chemical binding between the two networks should occur, resulting in a completely different molecular architecture of SINs.

(Keywords: IPNs; polyurethane/vinyl ester resin; d.s.c.)

INTRODUCTION

Interpenetrating polymer networks (IPNs), by their original definition[1], are composed of two (or more) chemically distinct components held together ideally and solely by their permanent mutual entanglements. Basically there are two methods for the production of IPNs, i.e. sequential and simultaneous formation[2]. Semi-IPN results from the bifunctional starting materials in one of the components, leading to a linear polymer in the network.

These IPN materials have been studied extensively as polymer alloys with synergistic physical properties of technological interest. Pernice and coworkers[3] first reported some simultaneous interpenetrating networks (SINs) composed of polyurethane (PU) and industrial unsaturated polyester resin or epoxy resin for application in reaction injection moulding (RIM) technology. Since then the interest of using IPNs as RIM material has increased. Most of these research works were related to SINs of PU and industrial unsaturated polyester resin[4–6]. In the previous papers[7,8], another SIN composed of PU and vinyl ester resin (VER) has been synthesized and studied for the RIM process. The experimental results showed that the mechanical properties of such SIN materials greatly depended on the rate of formation of PU and VER networks, as the reaction rate of the formation of these two networks had a strong effect on the morphologies of these materials. Thus, the study of reaction kinetics of such SINs for use in the RIM process is significant. However, the hydroxyl and carboxyl groups usually existing in commercial VER or unsaturated polyester resin should be paid more attention, because they can easily react with isocyanates and make the study of kinetics as well as the structure of SIN more complicated. In this article, a VER without pendent hydroxyl groups and only having negligible carboxyl groups was synthesized. The reaction kinetics of SINs prepared with PU and such a VER has been monitored by using differential scanning calorimetry. Comparable systems containing VER with pendent hydroxyl groups were also examined.

EXPERIMENTAL

Synthesis of vinyl ester resin

Vinyl ester resins were prepared by the reaction of 1 mol E-51 bisphenol A epoxy resin (supplied by Shanghai Synthetic Resin Plant) and 2 mol α-methacrylic acid under argon gas protection. When the acid number of the reaction system was below 6 mg KOH/g, the reaction continued under vacuum to reduce the acid number. Styrene, as comonomer, was then introduced into this vinyl ester oligomer (VEO). The resulting resin was designated as VERH, containing pendent hydroxyl groups. To obtain the so-called VERA resin, in which the pendent hydroxyl groups were capped with acetyl groups, a suitable amount of acetyl chloride was added in drops to VEO. The system was exposed to vacuum again to eliminate hydrochloride and finally combined with styrene.

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Table 1 Elastic component formulation

Designation	Ingredients	Parts by weight
CPU	Arco 5613 ($f = 3.0$)	56.0
(crosslinked	TDI	31.1
polyurethane)	1,4-BDO	12.9
	DBTDL	1×10^{-4}
LPU	Gaoqiao GE-220 ($f = 2.0$)	55.1
(linear	TDI	32.0
polyurethane)	1,4-BDO	12.9
	DBTDL	1×10^{-4}

Table 2 Rigid component formulation

Designation	Ingredients	Parts by weight
VERA	VEO without OH groups	68
(AN = 0.4 mgKOH/g	styrene	32
HN = 0 mgKOH/g)	AIBN	1
VERH	VEO with OH groups	64
(AN = 0.8 mgKOH/g	styrene	36
HN = 143.5 mgKOH/g)	AIBN	1

AN = acid number; HN = hydroxyl number

Materials

Trifunctional poly(oxypropylene) polyol (5613, hydroxyl number 54 mg KOH/g) and difunctional poly(oxypropylene) polyol (GE-220, hydroxyl number 64 mg KOH/g) were supplied by Arco Co. and Gaoqiao No. 3 Chemical Plant, respectively. Toluene diisocyanate (TDI, 80/20) was provided by Olin Co. All other chemicals used in this study were standard laboratory reagents obtained from various manufacturers.

The polyols were dried at 100°C under vacuum for 12 h, then treated with 4 Å molecular sieves for over one week before use. 1,4-Butanediol (1,4-BDO) was distilled under vacuum in the presence of sodium wire. Styrene was washed, dried and distilled under vacuum, and inhibited with 1,4-hydroquinone (10^{-4} g/g styrene). 2,2′-Azobisisobutyronitrile (AIBN) was filtered and recrystallized from hot 95 wt% ethanol, and dried under vacuum at room temperature.

Tables 1 and *2* show ingredients and their weights for the two components of SINs, respectively. The catalyst for PU, dibutyltin dilaurate (DBTDL), was used as received at a rather low content to facilitate d.s.c. operations (see *Table 1*).

Instrumentation and experimental routine

Infra-red (i.r.) measurements on a Nicolet 5SX were performed in the wavenumber range 4000–400 cm^{-1} at a resolution of 4 cm^{-1}. ^{1}H n.m.r. spectroscopy was recorded with $CDCl_3$ as solvent and tetramethylsilane (TMS) as reference on a Bruker WP-100SY.

A Perkin-Elmer PC series differential scanning calorimeter (PE PC Series DSC7) was employed to monitor the synthetic courses of all individual components and SINs. The instrument was left for stabilization with ice–water cooling media and dry nitrogen purge gas (24 ml min^{-1}). Ingredients of each component were weighed with a total weight from 10 to 20 g. All raw materials except TDI were then thoroughly mixed with a mechanical agitator at 1200 rev min^{-1} for about 30 s, and then TDI weighed in a syringe was quickly injected into the mixture, which was further stirred for 30 s. A homogeneous solution was thus assured, from which about 8 to 12 mg was transferred into a volatile sample pan as soon as possible. The pan was then sealed together with a volatile sample cover using a Perkin-Elmer volatile sample pan sealer. An empty pan and cover of equivalent weight was put in the reference pan holder.

The rate profile *versus* temperature of individual components was carried out in the scanning operation mode over a range of temperature from 10 to 250°C at a heating rate of 10°C min^{-1}. A second scanning run was performed to check the residual activity after the first scanning run and to check the validity of the baseline established previously. In all cases, no residual activity and no change in curvature and slope of the baseline were observed. As 250°C is far beyond the glass transition temperature of either phase, the total heat of reaction for individual components can be calculated from the area of the exothermic peak.

The reaction exothermic rate *versus* time of individual components as well as of all SINs were carried out in the isothermal operation mode, which took advantage of the rapid response of the DSC7. The isothermal run was terminated until a constant energy signal, representing a zero-activity baseline, was displayed or up to 120 or 180 min in some cases. A scanning run immediately after the isothermal run was carried out for the same isothermally cured sample from 10 to 250°C at a heating rate of 10°C min^{-1}. For further checking the residual activity of each component, a third scanning run was conducted. In this case, the residual activity of each component was not found. From the isothermal run and the following scanning run, the heat of reaction for individual components was calculated by adding the two areas of the exothermic peaks measured.

After the heat of reaction of each individual component was determined under different conditions, i.e. scanning run or isothermal run at several temperatures followed by a second scanning run, the temperature effect upon the synthetic course of PU/VERA SIN was investigated. The composition and crosslinking nature effects were then studied at a given temperature. Finally, the thermal behaviour of PU/VERH SINs was compared with that of PU/VERA SINs in an attempt to get insight into the inter-component chemical binding effect.

RESULTS AND DISCUSSION

Characterization of vinyl ester resin

Infra-red (i.r.) spectra for vinyl ester resin, VERA and VERH, are illustrated in *Figure 1*. It can be observed that the i.r. absorption peak of hydroxyl groups at about 3480 cm^{-1} was strong for VERH, while VERA shows almost no absorption at this area, indicating the hydroxyl groups have been capped with acetyl groups. *Figure 2* shows the ^{1}H n.m.r. spectra of VERA and VERH, where the peaks around 4.0 ppm were assigned to the hydrogen atoms connected with oxygen atoms. The disappearance of these peaks for VERA can be attributed to the elimination of hydrogen atoms from pendent hydroxyl groups. Both i.r. and n.m.r. spectra show that the characteristic peaks of ester group are enhanced for VERA after esterification at about 1730 cm^{-1} and 2.0 ppm, respectively. All these observations are

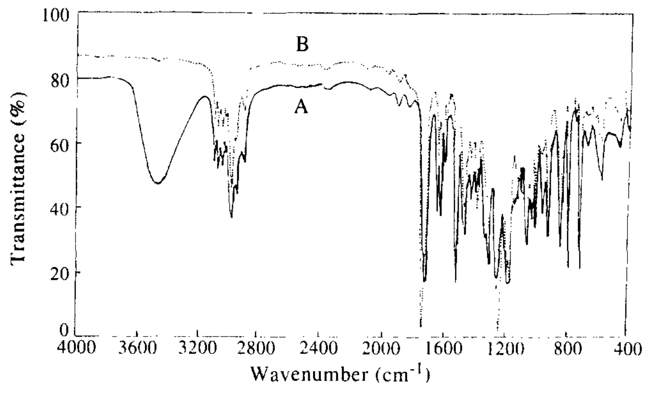

Figure 1 Infra-red spectra for vinyl ester resin: (A) VERH; (B) VERA

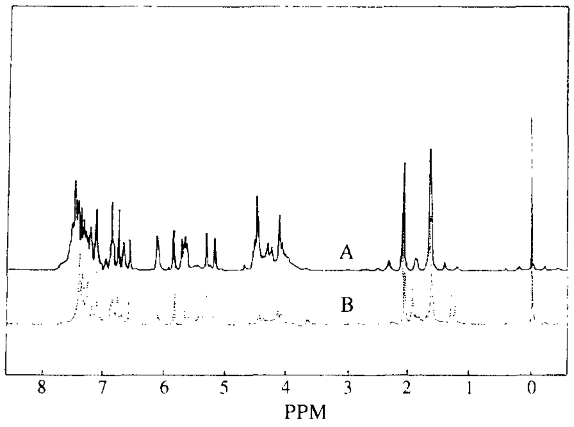

Figure 2 ^{1}H n.m.r. spectra for vinyl ester resin: (A) VERH; (B) VERA

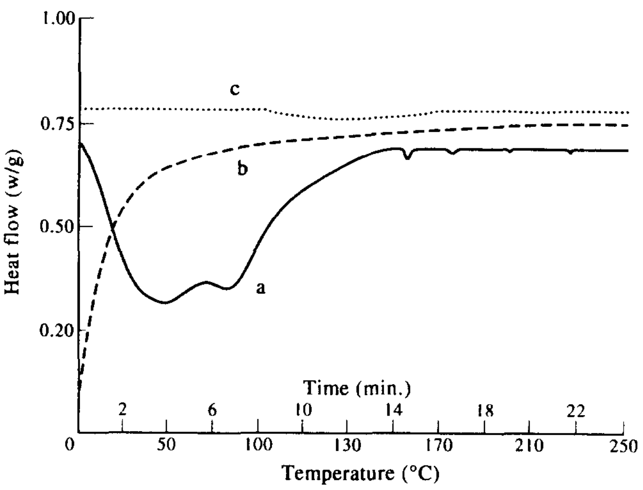

Figure 3 CPU reaction rate profile: (a) rate vs. temperature, scanning run; (b) rate vs. time, isothermal run at 80°C; (c) rate vs. temperature, scanning run following isothermal run at 80°C

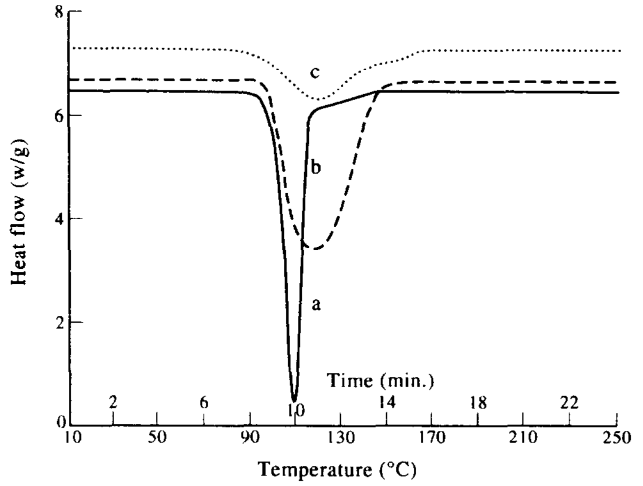

Figure 4 VERA reaction rate profile: (a) rate vs. temperature, scanning run; (b) rate vs. time, isothermal run at 80°C; (c) rate vs. temperature, scanning run following isothermal run at 80°C

Table 3 Heat of reaction of individual component

Code	Operation mode	Heat of reaction (J g^{-1})
CPU	isothermal at 80°C + scan	155.42
	isothermal at 70°C + scan	157.13
	isothermal at 60°C + scan	157.44
	scan	160.64
LPU	scan	166.36
VERA	isothermal at 90°C + scan	352.94
	isothermal at 80°C + scan	352.16
	isothermal at 70°C + scan	353.86
	scan	352.22
VERH	scan	378.08

consistent with the chemical analysis of hydroxyl number for these two VERs (see *Table 2*).

Therefore, SINs composed of PU and VERA can be considered as ideal ones with negligible chemical bonds between the two networks.

PU/VERA SIN

Figures 3 and *4* show both scanning and isothermal reaction rate profiles for crosslinked PU (CPU) and VERA reaction measured by d.s.c., respectively. The DSC7 presents thermograms with endotherms shown as upward deviations from the baseline in the scanning operation mode, or from the zero-activity baseline in the isothermal operation mode. Thus, the downward peak shown on d.s.c. plots is indicative of exothermic activity in the sample. In general, for a step-growth polymerization, the maximum reaction rate occurs at the beginning of the reaction in the isothermal mode, and then decays for the consumption of functional groups. For a chain polymerization, however, the reaction starts only after a certain period of induction time, and passes through a maximum. It is clear that the formation of CPU and the copolymerization of VERA follow the step-growth and free-radical polymerization, respectively, as shown in *Figures 3* and *4*, but the scanning of the isothermally cured samples, especially in the case of VER, indicates that the conversion is incomplete. Numerical data for the total heat of reaction for individual components are summarized in *Table 3*. As mentioned previously, DBTDL used for PU was at a rather low concentration, so the reaction during the sample preparation and loading period could be minimized. Furthermore, it only took about half a minute to heat samples, which retain a fixed temperature in the isothermal mode, so that the heat of reaction measured from isothermal runs at different temperatures followed by a scanning run are very close to that from the scanning run of fresh samples. Thus, the total heat of reaction measured from the

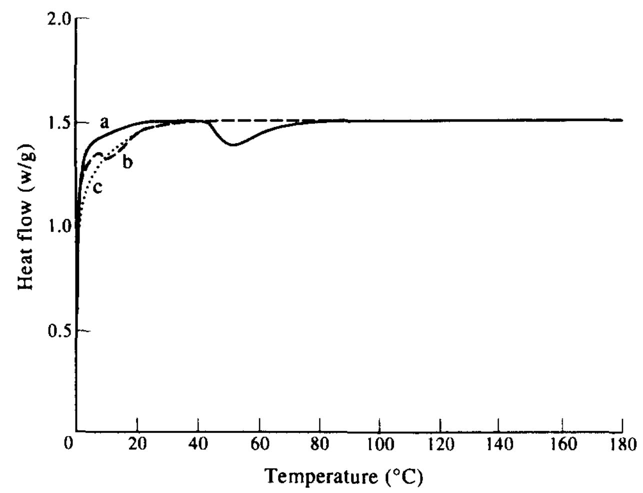

Figure 5 Reaction rate profiles of CPU/VERA (50/50) SIN at different temperatures: (a) isothermal run at 80°C; (b) isothermal run at 90°C; (c) isothermal run at 100°C

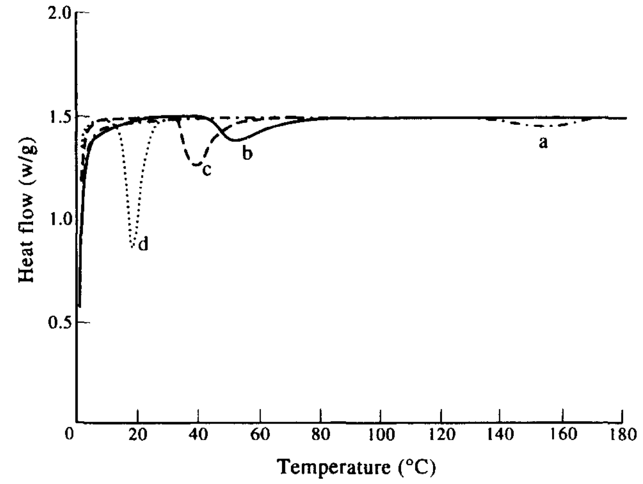

Figure 6 Isothermal exothermic profiles at 80°C of CPU/VERA SIN with different composition: (a) CPU/VERA, 60/40; (b) CPU/VERA, 50/50; (c) CPU/VERA, 40/60; (d) CPU/VERA, 20/80

scanning run of fresh samples can be used to calculate the limiting conversion of specimens. It should be pointed out that the real conversion of functional groups in cured thermosetting resins is usually lower than the so-called limiting conversion, which were only used here to compare all systems studied. Other components in *Table 3* exhibit similar behaviour.

Reaction rate profiles *versus* time in the isothermal mode at different temperatures for CPU/VERA (50/50, weight ratio) SIN are presented in *Figure 5*. At lower temperature such as 80°C, the d.s.c. curve could be divided into two parts, one for CPU and the other for VERA, respectively. With increasing temperature, the VERA peak moves to shorter induction time period. At 90°C the VERA peak appears as a shoulder overlapped with the CPU peak. Only a single combined peak is observed at even higher temperature such as 100°C. The temperature of 80°C was thus selected for further study. The other consideration for this temperature is that the mould temperature of PU RIM production is typically set at 80°C. *Figure 6* shows the effect of SIN composition on the thermal behaviour at 80°C. The two exothermic peaks due to the step-growth and free-radical polymerization are separated from each other, and the PU formation reaction remains almost the same over the range of compositions. The VER reaction peak, however, moves to the right on the d.s.c. plot and becomes broader and smaller in height with increasing PU content in SINs. It indicates a longer reaction time for VER in SIN system containing higher PU content. As an extreme case, much longer induction time (more than 180 min) for CPU/VERA (80/20) was observed (this d.s.c. curve was not shown in *Figure 6*). All these experimental data are listed in *Table 4*.

It is well known that the concentration of reactants will greatly affect the rate of polymerization for free-radical chain polymerization or step-growth polymerization. However, *Table 4* shows that over a range of CPU/VERA compositions (40/60 to 0/100), the limiting conversion of VERA is not affected appreciably by

Table 4 Composition effect for CPU/VERA SIN at 80°C

Operation mode	CPU/VERA (weight ratio)						
	100/0	80/20	60/40	50/50	40/60	20/80	0/100
CPU formation							
H1	152.64	154.21	154.34	157.38	158.25	153.45	–
H2	2.78	0	0	0	0	0	–
H1 + H2	155.42	154.21	154.34	157.38	158.25	153.45	–
LC	0.97	0.96	0.96	0.98	0.99	0.96	–
VERA formation							
H1	–	[a]	16.45	67.64	252.65	285.58	314.59
H2	–	[a]	108.60	76.75	41.13	19.34	37.57
H1 + H2	–	[a]	125.05	144.39	293.78	304.92	352.16
LC	–	0.17[a,b]	0.36	0.41	0.83	0.87	0.89
Peak time (min.)	–	[a]	154.32	52.78	38.24	18.39	10.72
Peak width (min.)	–	[a]	59.43	47.07	38.12	27.34	13.56

H1: exothermic area from isothermal run at 80°C
H2: residual heat from scanning run following isothermal run at 80°C
LC: limiting conversion based on heat of reaction from fresh sample scan
[a] Not observed within 180 min at 80°C
[b] Calculated from scanning run after isothermal cure at 80°C for 180 min

composition of SINs (0.83–0.87), although the limiting conversion of VERA increases with the increase of the content of VERA in SIN first (CPU/VERA, 100/0–50/50). However, for the system having lower amount of VERA (CPU/VERA, 80/20) the limiting conversion of VERA is quite low. Furthermore, the limiting conversion of PU is almost the same and maintains a high level (0.96–0.99) over all range of SIN compositions. Thus, all these abnormal kinetic phenomena could be attributed to the strong diffusion effect existing in these highly viscous systems, since the structures (crosslinkage of networks, entanglement and interpenetration between the two networks) and morphologies of the SINs will be changed progressively during the polymerization.

The lowering of rate for VER network formation with the increase of PU content may be attributed first to the change of morphologies of SINs during the synthesis process. Huang and coworkers[8] have prepared similar PU/VER SINs, in which the PU networks were certainly formed earlier than the VER one, and found that the morphologies of phase separation between these two networks progressively changed with the composition of the systems. For SINs containing lower content of VER, the VER phase existing as domains were well dispersed through the PU matrix. As the size of these domains decreased with increasing content of VER, a phase inversion took place in the ratio of PU/VER around 50/50. Thus, the quite low limiting conversion for CPU/VERA (80/20) SIN listed in *Table 4* must result from the much stronger diffusion effect of copolymerization in the VERA. In this case, styrene as a comonomer must diffuse through the PU network into domains formed by the VER phase. When the amount of VERA in the composition of SIN is more than that of PU, the VERA exists as the matrix. This suggests that the diffusion of styrene in such a system should be much easier, so it reveals high conversion of VERA reaction. In order to verify this explanation, we measured the limiting conversions for some comparable SINs prepared with linear PU (LPU) at the composition of 50/50 (weight ratio), as listed in *Table 5*. It is clear that the comparable SIN including LPU and VERA shows shorter induction period and rather higher limiting conversion (0.87 *versus* 0.41) for copolymerization of VERA, since the diffusion barrier of monomer caused by the LPU is greatly reduced. Another comparable SIN prepared with CPU and methyl methacrylate/styrene (50/50, weight ratio) copolymer (MMAST) also exhibits high limiting conversion. In this semi-IPN, the compatibility between the two phases may be improved[9], and the two monomers may be easy to diffuse through the two phases, so it gives rise to high conversion.

Table 5 Molecular structure effect for 50/50 SINs

Operation mode	CPU/VERA	LPU/VERA	CPU/MMAST
CPU formation			
H1	157.38	162.48	159.14
H2	0	0	0
H1 + H2	157.38	162.48	159.14
LC	0.98	0.98	0.99
VERA formation			
H1	67.64	263.74	297.31
H2	76.75	42.74	30.86
H1 + H2	144.39	306.43	328.17
LC	0.41	0.87	0.79
Peak time (min)	52.78	33.11	69.86
Peak width (min)	47.07	30.95	66.76

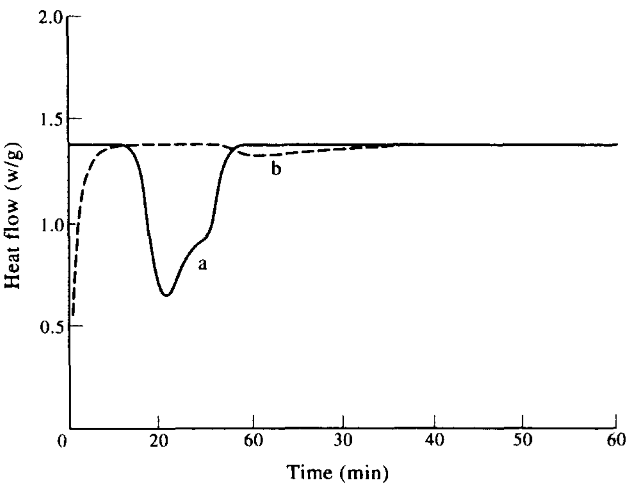

Figure 7 Isothermal exothermic profiles of VERH systems at 80°C: (a) pure VERH; (b) VERH/TDI mixture

Table 6 Inter-component chemical binding effect for 50/50 SINs

Operation	VERH	VERH/TDI	CPU/VERH	CPU/VERH/TDI	LPU/VERH	LPU/VERH/TDI
Urethane formation						
H1	–	114.40	157.93	127.10	162.18	130.29
H2	–	0	0	0	0	0
H1 + H2	–	114.40	157.93	127.10	162.18	130.29
LC	–	1.00	0.98	0.97	0.97	0.95
Free-radical reaction						
H1	327.01	49.31	108.35	[a]	200.82	[a]
H2	48.02	96.92	31.50	[a]	62.66	[a]
H1 + H2	375.03	146.23	139.85	[a]	263.48	[a]
LC	0.99	0.39	0.37	0.15[a,b]	0.70	0.38[a,b]
Peak time (min)	10.64	21.22	72.53	[a]	38.16	[a]
Peak width (min)	13.41	25.87	84.50	[a]	42.72	[a]

[a] Not observed within 120 min at 80°C

[b] Calculated from scanning run after isothermal cure at 80°C for 120 min

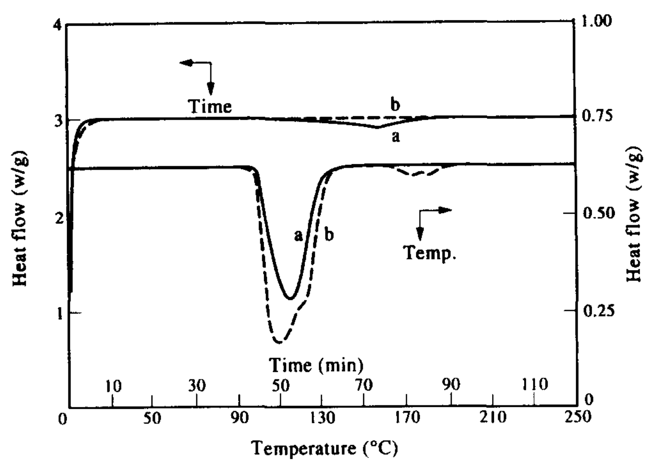

Figure 8 Reaction rate profiles of CPU/VERH (50/50) SINs: (a) CPU/VERH; (b) CPU/VERH/TDI. Upper curves: isothermal run at 80°C *versus* time. Lower curves: scanning run followed *versus* temperature

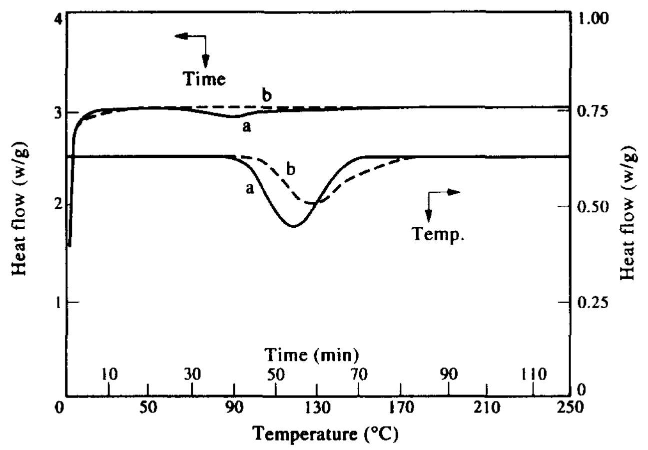

Figure 9 Reaction rate profiles of LPU/VERH (50/50) SINs: (a) LPU/VERH; (b) LPU/VERH/TDI. Upper curves: isothermal run at 80°C *versus* time. Lower curves: scanning run followed *versus* temperature

The increase of VERA content in the composition of SIN, however, has no significant effect on the formation of PU network quantitatively, although the concentration of reactants for forming PU decreases in these systems. This unusual kinetics cannot be related to the phase separation condition between the two networks as the PU network is formed earlier (see *Figure 6*), and may result from the 'solvent effect' of VERA containing styrene as indicated by Lee and cowokers[4,5], who studied PU and commercial unsaturated polyester resin SINs and found similar behaviour.

PU/VERH SIN

All SIN reactions discussed before have been considered to be ideal with only negligible chemical bonds between the two components. Then it is of interest to examine the SINs prepared with VERH, which is closer to the industrial product.

We first conducted isothermal runs at 80°C for pure VERH, as well as for VERH and TDI mixture (designated as VERH/TDI for simplicity hereafter), in which the amount of TDI corresponding to the amount of hydroxyl groups in VERH and DBTDL was added as catalyst (1×10^{-4} phr). *Figure 7* displays the exothermic curves for these two systems. The results are listed in columns 1 and 2 of *Table 6*. The pure VERH shows a quite similar copolymerization behaviour to that of VERA (see *Figure 4*), but the VERH/TDI system reveals a completely different profile of exothermic curve from that of pure VERH. The early part of the exothermic curve for VERH/TDI is very similar to that of CPU (see *Figure 3*). It is clear that, in the case of VERH/TDI, TDI should react with OH groups existing in VERH to form so-called 'unsaturated linear PU' first, and then the copolymerization between this linear PU containing double bonds and styrene takes place. In such a case, the viscosity of the reaction medium is much higher than that of the pure VERH system at the early reaction stage and the diffusion effect of styrene through this highly viscous medium must be very strong, giving rise to longer peak time, smaller exothermic peak height and broader peak duration as well as much lower limiting conversion, as shown in *Figure 7* and *Table 6*.

Figures 8 and *9* exhibit the d.s.c. curves of CPU/VERH and LPU/VERH with or without adding extra TDI, whose amount corresponds to the amount of the OH groups in VERH. The numerical data of these experimental results are also listed in *Table 6*. For CPU/VERH and LPU/VERH, the conversion of urethane formation was calculated according to the heat of reaction of CPU ($160.64\,\mathrm{J\,g^{-1}}$) and LPU ($166.36\,\mathrm{J\,g^{-1}}$), respectively (see *Table 1*). However, for CPU/VERH/TDI or LPU/VERH/TDI system, the conversion of urethane formation was calculated from the heat of reaction of CPU or LPU together with the heat of reaction of VERH/TDI system ($114.40\,\mathrm{J\,g^{-1}}$) according to their weight fractions in SINs.

It can be seen in *Table 6* that the free-radical copolymerization of VERH is greatly prohibited for both CPU/VERH and LPU/VERH systems, as compared with CPU/VERA and LPU/VERA SIN, respectively, although the conversions of urethane formation still maintain a high level (0.97–0.98). The same consideration for prohibiting the copolymerization in VERH/TDI system could therefore be applied to explain the low conversion of copolymerization in these two systems without adding extra TDI, as competitive reactions between TDI and polyol, extender as well as the OH groups in VERH should exist during the reaction process. In this case, the perfect structure of CPU or LPU could not be formed, since some VEO have been incorporated into polyurethane chains.

The copolymerization of VERH in both systems of CPU/VERH/TDI and LPU/VERH/TDI is much more difficult, so they do not show any exothermic peak within 120 min at 80°C, and the conversion of urethane formation also decreases to some degree (0.97–0.95) as shown in *Figures 8* and *9* and *Table 6*. This indicates that the unsaturated CPU or LPU may be formed very fast at early reaction times in these SINs, which could exert greater restriction upon the diffusion of styrene through the quite highly viscous medium as mentioned before. Thus the structures of these SINs should be obviously rather hybrid.

It is clear that the kinetics of the two components and the structure of SINs for these two extremes, i.d. PU/VERH and PU/VERH/TDI, are quite different from each other. In consequence, differences between the morphologies as well as the mechanical properties for these two systems could be expected. It is generally accepted that the commercial products of VER contain some OH groups. In order to synthesize IPNs with excellent physical properties, the amount of isocyanates consumed should take account of those OH groups in VER. This consideration may also be important for using industrial unsaturated polyester resins, as there are more OH and COOH groups existing at the ends of polyester chains. The effects of stoichiometric composition of isocyanates on physical properties of PU/VER IPNs are now being studied and will be given in the near future.

Finally, it should be pointed out that the Trommsdorff–Norrish effect is usually observed in many free-radical polymerizations, where the polymerization rate increases with time, especially for highly viscous systems. This phenomenon is also related to diffusion-controlled termination reaction for chain radical. For SIN systems described in this study, the Trommsdorff–Norrish effect for copolymerization of VERA or VERH may exist, but this was difficult to examine as the relationship between conversion of monomers (VEO and styrene) and reaction time was not explicit. Recently, however, the kinetics of the same SINs is being studied by using *FT*i.r. The experimental data show that the conversion–time curves are not typical autoacceleration plots and the rates of copolymerization are nearly the same over a wide range of conversions (up to around 60%) for VERA and VERH[10]. Thus, for the SINs studied here, such unusual kinetic behaviour should be studied further.

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