High Performance Semi-Interpenetrating Polymeric Networks Based on Acetylene-Terminated Sulfone. Part I. Cure and Thermal Characteristics

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SYNOPSIS

A series of semi-interpenetrating polymer networks (semi-IPN) have been prepared from acetylene-terminated sulfone (ATS-C) oligomer and high-performance thermoplastic (TP) blends. The cure characteristics and thermal properties of ATS-C and semi-IPNs are presented in this paper. The addition of thermoplastics has no effect on the mechanism of ATS-C cure reaction and thermal behavior of cured systems. The glass-transition temperature (T_g) and heat distorsion temperature (HDT) of thermoplastics are remarkably decreased with adding ATS-C. The higher the T_g and HDT of the thermoplastics, the more obvious the reduction of T_g and HDT. In the case of fully cured semi-IPNs, the T_g and HDT value of the TP phase are higher than or equal to the T_g and HDT of pure TP. The thermal stabilities of semi-IPNs decrease as the content of ATS-C oligomer increases.
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INTRODUCTION

Although the addition of small amounts of elastomers to brittle resin produces a significant rise in fracture toughness, the glass-transition temperature (T_g) and elastic modulus of modified systems become lower. Recently, the concept of semi-interpenetrating polymeric networks (semi-IPN) has been developed to obtain high-performance polymer systems comprised of an easy-to-process but brittle thermosetting polymer with a tough but difficult-to-process thermoplastic polymer. The combination leads to a high performance semi-IPN that could be processed like thermoset and have good toughness like thermoplastic.[1,2] This concept has been successfully applied to develop several semi-IPNs, including acetylene-terminated oligomers,[2–4] bismaleimide,[5–7] and epoxy-based materials.[8,9] Some of them show notable improvements in fracture toughness over the unmodified thermosetting polymers. Synergy in processability has also been realized[3,7]: the crosslinking component acts as a plasticizer for the linear thermoplastic and the linear thermoplastic, in turn, adds toughness to the brittle, crosslinked component.

Acetylene-terminated sulfone (ATS) oligomer has generated much interest as a candidate high-performance matrix resin for advanced composite materials.[10–12] Because the ATS oligomer has a structure similar to that of commercial polysulfone resin, it is not surprising that ATS resin has good moisture resistance. For this reason and low viscosity at temperatures below cure temperature range, ATS oligomer has significant potential as a high temperature/high humidity replacement for epoxies. Unfortunately, cured ATS resin is very brittle and has fairly low fracture toughness that limit its usefulness unless it can be improved. Thermoplastic polysulfone resin, on the other hand, is one of the useful high performance engineering thermoplastics with outstanding thermal and mechanical properties. Its high resistance to hydrolysis at elevated temperature is known.[13] However, these amorphous polymers exhibit poor organic solvent resistance, and in addition, they require a high processing temperature because of the high glass-transition temperatures. Some of these disadvantages can be improved by blending the thermoplastic with a reactive

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plasticizer with lower T_g that can react through thermal cure to form a network. Goldfarb and Sikka[14] have reported that addition of ATS to polyphenylsulfone (PPSF) lowered the T_g and viscosity of PPSF that in turn lowered the temperature requirement for processing. Fully cured ATS/PPSF blends show improved resistance to stress failure in the solvent environment. Fried and Lee[15] have studied the compatibility of two high temperature polysulfones with three acetylene-terminated oligomers by TICA and DSC. The uncured blends were compatible. The curing process leads to phase separation. Zeng and Mai[4] have shown that uncured blends of bisphenol A polysulfone and ATS-C oligomer were compatible systems and the T_gs of the uncured blends decrease with increasing ATS-C contents.

Using the semi-IPN approach, we have developed a series of semi-IPNs prepared from crosslinking ATS oligomer (more properly, *bis*[4-(4-ethynyl phenoxy) phenyl] sulfone and its higher oligomer), designated ATS-C, with thermoplastic bisphenol A polysulfone (PSF), polyethersulfone with cardo group (PES-C), and polyetherketone with cardo group (PEK-C), respectively. This synthesis is shown in Figure 1. Because the crosslinked ATS-C resin is the second one formed, it is defined as a semi-2-IPN. The purpose of our investigation was to develop a series of new high-performance resin matrixes for advanced composites by using a semi-IPN approach. In this paper, the cure characteristics of ATS-C oligomer and uncured blends, and thermal properties of cured ATS-C resin and their resulting semi-IPNs are presented. In a second paper, we will report the phase separation and phase morphology of the semi-IPNs.

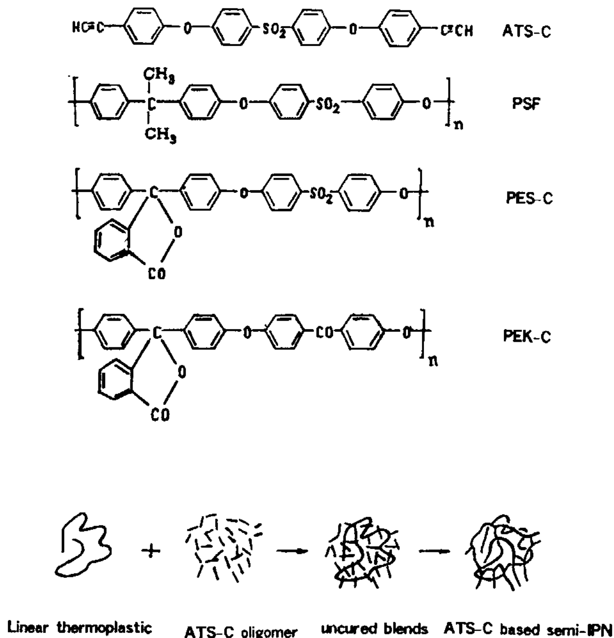

Figure 1 Synthesis of semi-interpenetrating polymeric networks.

EXPERIMENTAL

Materials

The PSF was obtained from Shuguang Chemical Factory, Shanghai. The PES-C, PEK-C, and ATS-C were provided by Changchun Institute of Applied Chemistry, Academia Sinica.

Resin Preparation

All of the blends were prepared by dissolving the thermoplastics and ATS-C in 1,2-dichloroethane to form a 10 wt % resin solution. The solution was cast on a glass plate. The solvent was evaporated at room temperature for 1 day and dried at 100–120°C for 5 h. The film was removed from the glass plate. These uncured ATS-C/thermoplastic (ATS-C/TP) blends (without solvent) are nontacky solids and have an infinite shelf life at room temperature. Cured samples were produced under different conditions described as follows.

Resin Characterization

The cure characteristics of ATS-C and uncured blends were investigated by means of a Perkin-Elmer DSC-2 in air. Dynamic DSC of ATS-C and uncured blends were carried out at four heating rates of 5, 10, 20, and 40°C/min, respectively. Cured samples were made at a 20°C/min heating rate. The degrees of cure were calculated by using the equation,

$$a(\%) = (\Delta H - \Delta H_r)/\Delta H \times 100 \quad (1)$$

ΔH, the heat of reaction of uncured specimen in dynamic curing at 20°C/min; ΔH_r, the heat of residual reaction of the corresponding cured specimen at 20°C/min. The activation energy (E) and the preexponential factor ($\ln A$) of cure reaction for ATS-C and uncured blends were estimated by Kissinger[16] and ASTM E698[17] methods. The T_g was determined by torsional braid analysis (TBA). After a glass braid coated with each specimen was cured

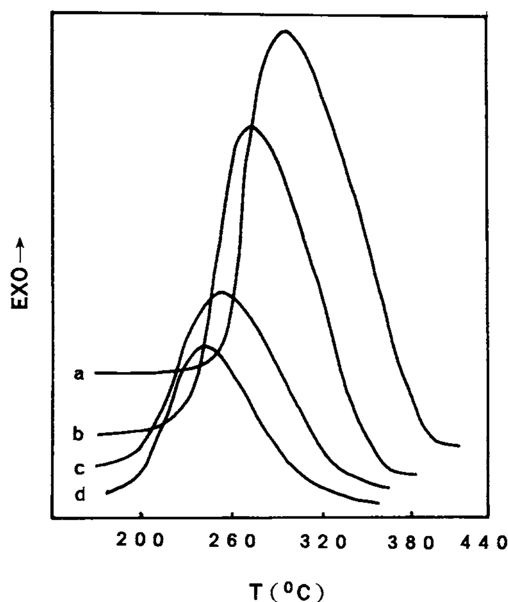

Figure 2 Dynamic DSC of ATS-C oligomer at different heating rates (°C/min): (a) 40; (b) 20; (c) 10; (d) 5.

at a given condition, it was cooled to room temperature. The TBA spectra (the damping and relative rigidity vs. temperature curves) were recorded at a heating rate of 3°C/min using a model NB-1 torsional braid analyser (Changchun Nonmetal Materials Test Instrument Factory). T_g was determined by the temperature of the peak of the damping curve of the TBA spectra. TGA data were obtained in nitrogen or air at a heating rate of 10°C/min using a Perkin–Elmer Model TGS-2 thermogravimetric analyser. The activation energy (E) and preexponential factor ($\ln A$) of thermal degradation were determined by method of Coats and Redfern.[18]

RESULTS AND DISCUSSION

Cure Characteristics

Dynamic DSC thermograms of ATS-C samples at different heating rates in air are shown in Figure 2. The increase of the heating rate shifts the thermograms to high temperature and also broadens the temperature of range of curing. When the sample of ATS-C was cooled from 350°C to room temperature and rescanned at a heating rate of 20°C/min, no exotherm was found because of the formation of crosslinked thermoset. According to the mechanism proposed for the crosslinking reaction of ATS,[19] the polymerization proceeds via a free radical propagation of an acetylene functionality to form a linear conjugated polyene that then acts as a crosslinking site. Table I compares the DSC results of dynamic cure for ATS-C and uncured blends under different heating rates. T_i, T_p, and T_f denote the initial, the peak, and the final temperature of the cure reaction, respectively. It can be seen from Table I that the reaction temperature increases with increasing heating rates because of the kinetic nature of the reaction. The increase in T_i of ATS-C by adding thermoplastics becomes more and more significant at higher heating rates because of the rise in viscosity of the blend systems. However, the DSC thermograms for various blends are not influenced by the thermoplastics, indicating that thermoplastics do not effect the cure behavior of ATS-C. It was found

Table I Dynamic DSC Results for Cure of ATS-C and Uncured Blends

	B (°C/min)	T_g (°C)	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
ATS-C	5	73	149	238	298	256
	10	75	162	248	308	255
	20	78	172	266	330	249
	40	83	187	279	349	240
ATS-C/PSF = 50/50	5	130	158	232	278	285
	10		167	257	327	260
	20		185	266	328	231
	40		216	279	359	214
ATS-C/PES-C = 50/50	5	150	158	227	279	246
	10		163	248	314	226
	20		185	260	329	217
	40		197	277	349	195

Table II Kinetic Parameters for Cure of ATS-C and Uncured Blends

	E (kJ/mol)	s	ln/A	n
Kissinger				
ATS-C	105.3	0.994	23.43	1.5
ATS-C/PSF = 50/50	92.3	0.965	20.31	1.4
ATS-C/PES-C = 50/50	87.7	0.991	19.47	1.4
ASTM E698				
ATS-C	108.7	0.995	23.61	
ATS-C/PSF = 50/50	96.2	0.971	20.55	
ATS-C/PES-C = 50/50	91.8	0.993	19.73	

that the T_p of uncured blends is slightly lower than that of ATS-C at lower heating rates (heating rates <5°C/min). It can be also seen from Table II that the addition of thermoplastics slightly lowers the activation energy (E) and the preexponential factor ($\ln A$) of cure reaction for ATS-C. These cure kinetic parameters of ATS-C and uncured blends were obtained from the methods of ATSM E698[17]:

$$\ln B = Z - 1.05E/(R \cdot T_p) \quad (2)$$

$$\ln B = \ln[R \cdot T_p^2/E - E/(R \cdot T_p)] + \ln A \quad (3)$$

and of Kissinger[16]:

$$\ln(B/T_p^2) = \ln(A \cdot R/E) - E/(R \cdot T_p) \quad (4)$$

where B is the scan rate, T_p is the peak temperature of the DSC curve, A is the preexponential factor, E is the activation energy, R is the gas constant, Z is a constant. The ATS-C oligomer in this paper has higher activation energy (E) and lower heat of reaction (ΔH) than that of ATS-G[20] because the oligomer of ATS-C may be of higher molecular weight. Addition of thermoplastics decreases the activation energy of ATS-C reaction, implying an increase in the rate of cure. Chartoff and Askins[10] found that the presence of residual palladium catalyst would tend to increase reaction rate and decrease the heat of reaction and exothermic peak temperature. The increase in viscosity of ATS-C/thermoplastic blend systems, which lowers the rate of termination of the growing macromolecular chain radical, also increases the rate of cure. As the heating rate increases, the effect of temperature variation on the cure reaction of ATS-C in blend is more remarkable. In this case, the addition of thermoplastics decreases the concentration of ATS-C and the reaction of ethynyl group is diffusion controlled. The rate of cure and heat of reaction for ATS-C in blends are lower than that of the pure ATS-C with increasing heating rates. It is possible that the residual uncured ethynyl group exists after the first run at the fast heating rate because of the presence of the thermoplastics. Although there are some variations in the reaction temperature for the cure exotherm in the case of various blends, it does not show a significant effect on the cure characteristics. FTIR studies also show that no reaction is present between ATS-C and thermoplastics. These results indicate that no chemical interaction between the components takes place during the semi-IPN synthesis and thermoplastics have no significant effect on the mechanism of cure reaction for ATS-C.

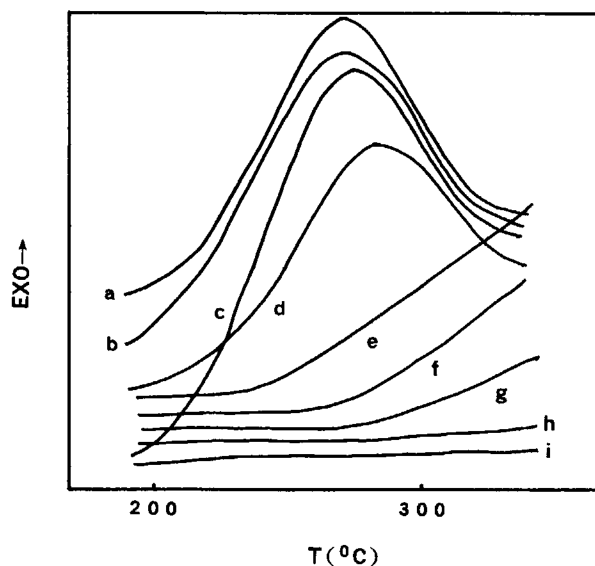

Figure 3 DSC of ATS-C resin cured dynamically at a heating rate of 10°C/min, T_{max} (°C): (a) 200; (b) 220; (c) 240; (d) 260; (e) 280; (f) 300; (g) 320; (h) 340; (i) 400.

Thermal Characteristics

The thermal behavior of cured ATS-C resin and the resulting semi-IPNs depends upon the cure conditions. Dynamic cure samples were prepared by heating from room temperature to dynamic cure temperature, T_{max}, at 10°C/min in the DSC apparatus, removing them from the DSC apparatus, and cooling at room temperature. The dynamic cured samples was rescanned at 20°C/min. The DSC thermogram of ATS-C resin cured dynamically at various T_{max} are shown in Figure 3. The thermal thermograms of the resulting semi-IPNs are similar to that of cured ATS-C resin, indicating that thermoplastics do not

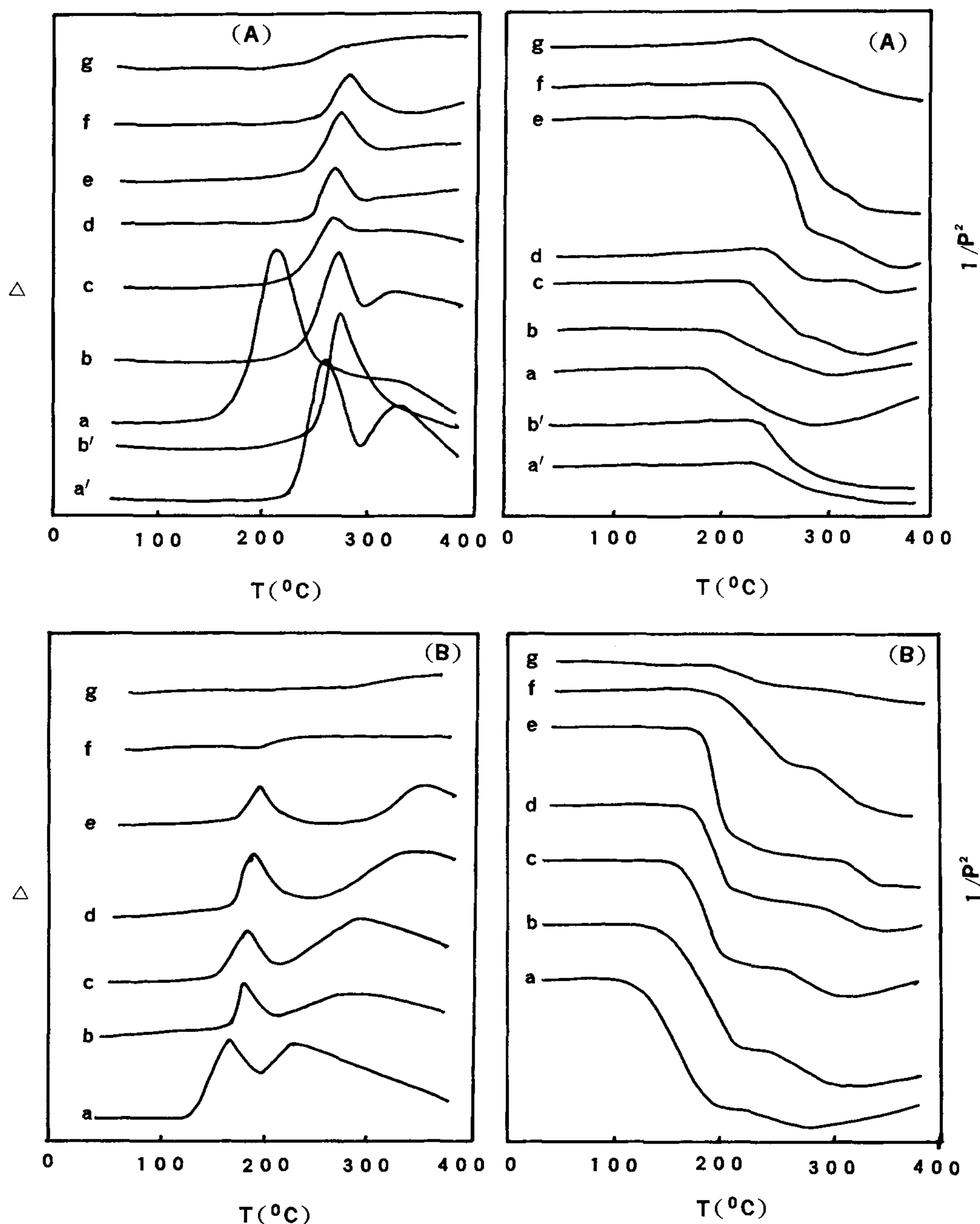

Figure 4 Torsional braid analysis of (A) ATS/PES-C = 50/50 and (B) ATS/PSF = 50/50 semi-IPNs cured at different conditions, T_{max}: (a) 270°C; (b) 300°C; (c) 330°C; (d) 330°C, 1 h; (e) 360°C, (f) 2nd scanning for sample (e); (g) 400°C. (a') PES-C, RT to 330°C; (b') PES-C, 400°C, 1 h.

Table III T_gs **of the Resulting Semi-Interpenetrating Polymer Networks**

	T_{max} (°C)							
	270		300		330		360	
	T_{g1}	T_{g2}	T_{g1}	T_{g2}	T_{g1}	T_{g2}	T_{g1}	T_{g2}
ATS-C				265		285		365
PSF			190					
ATS-C/PSF = 50/50	175	240	190	275	190	300	200	365
PES-C					260			
ATS-C/PES-C = 50/50	210		265		265	320	270	365

Table IV Degrees of Cure of Isothermal Cured ATS-C Resin and Semi-IPNs

Cure Condition			ATS-C/PSF	ATS-C/PES-C		
T_{iso} (°C)	t (h)	ATS-C	50/50	25/75	50/50	75/25
150	2	47.1	48.1		24.9	59.7
	5	59.2	53.4	37.0	44.8	71.6
	8	68.2	56.3			
	18	87.1	74.6	39.9	56.1	83.4
	40	90.4	81.8	55.7	67.2	89.7
165	8	82.6	82.5	53.0	63.0	80.1
	18	91.6	82.8	53.7	70.0	88.3
	40	91.8	93.0	78.3	86.6	92.0
180	1	78.0	78.8	57.5	71.6	86.9
	2	81.9	79.2	61.7	79.3	90.0
	5	92.8	91.7		78.5	94.4
	8	96.4	94.4		81.2	92.0
200	0.5	74.7	82.0	42.1	79.7	85.0
	1	89.1	87.6	69.9	82.0	96.4

Table V Thermogravimetric Characteristic

	T (°C) for 5% Wt. Loss	Wt. Loss, Percent at		T_{max1} (°C)
		400°C	500°C	
Air				
ATS-C	428	3.0	16.9	539
PSF	510	0.4	2.8	536
PES-C	500	1.1	4.8	530
PEK-C	455	3.3	9.4	525
ATS-C/PEK-C = 50/50	455	2.6	8.6	546
N2				
ATS-C	461	1.7	9.6	555
PSF	522	0.3	2.0	551
PES-C	514	0.8	3.2	546
PEK-C	512	0.5	3.7	541
ATS-C/PES-C = 50/50	468	1.7	9.4	545
ATS-C/PEK-C				
70/30	459	1.8	9.9	534
50/50	471	1.6	8.5	537

effect the thermal behavior of cured ATS-C resin. At T_{max} < 270°C, a residual exotherm is observed on scanning of cured ATS-C resin and the semi-IPNs caused by the presence of the remaining ethynyl group. TBA results (Fig. 4) also show that the ATS-C resin phase in semi-IPN cured at T_{max} < 270°C has plasticization for thermoplastics. The T_g of the thermoplastic phase is lower than that of pure thermoplastic (Table III) and the resulting semi-IPN is a partial compatible system. As T_{max} increases, the ATS-C react completely. Cured samples have no residual exothermic peak. T_g of the thermoplastic phase in semi-IPN is equal to or higher than T_g of pure thermoplastic. The semi-IPN is an incompatible system, but a continuous exotherm is presented at the high temperature region. Stevenson et al.[20] pointed out that it may be a result of thermal isomerizations of the polyene crosslink

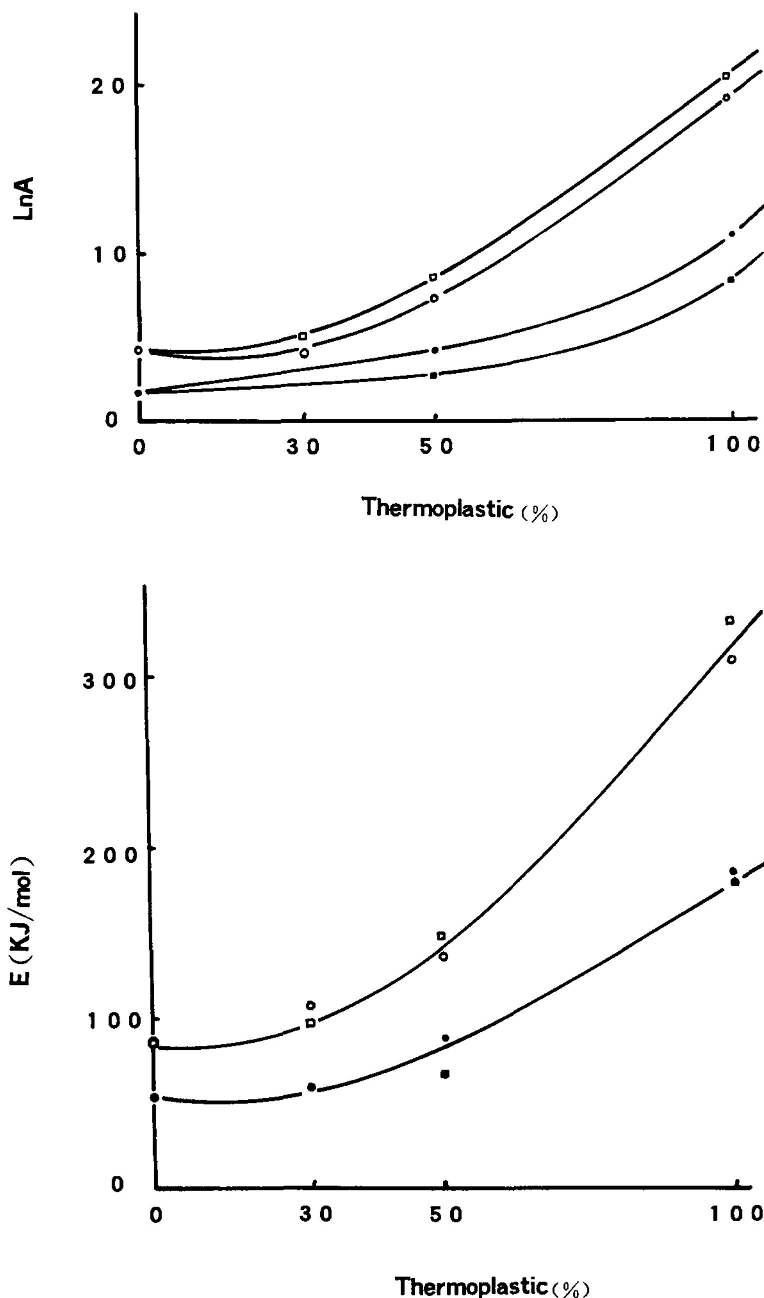

Figure 5 Kinetic parameters of thermal degradation, air (–●–) N2 (–○–) ATS-C/PEK-C = 50/50; air (–■–) N2 (–□–) ATS-C/PES-C = 50/50.

to a more stable configuration. It may also be a result of a partial cyclization of the polyene network. It is also confirmed by increasing the relative rigidity of TBA. In all cases, the reaction temperatures (T_i, T_p, and T_f) of the residual exothermic peak and the degree of cure for cured samples increase with increasing the T_{max}. Compared with ATS-C resin, the T_i and T_p of residual exothermic reaction and the degree of cure for semi-IPN cured dynamically are higher, and T_i of semi-IPN is increased more remarkably when increasing the T_g of thermoplastics. One reason is that the decrease in activation energy of the cure reaction and the increase in viscosity of the systems increase the rate of cure by addition of thermoplastic. The degree of cure increases significantly at temperatures above 240°C because of the rapid increase of the rate of cure at high temperature.

Isothermal DSC data were taken at different temperatures in the range 150–200°C. The DSC thermogram of semi-IPN cured isothermally is also similar in shape to that of cured ATS-C resin. The residual exothermic peak shifts to high temperature and finally disappears with the increasing cure temperature, T_{iso}. It can be seen from Table IV that fully cured systems could not be obtained even in the case of extremely long cure times at temperatures below 180°C. This is a result of the thermal motion of the growing macromolecules being continuously hindered as the T_g and viscosity of the system are increased. The reactions are probably diffusion-controlled at high conversions.[10,11] Although T_gs of uncured blends are lower than the cure temperature because of the plasticization of ATS-C oligomer, as the reaction proceeds, the increase in viscosity and T_g of the cured system could decrease the rate of cure and stop the reaction. It is confirmed that the degree of cure for semi-IPN decreases when increasing the content of PES-C and the T_g of thermoplastics.

The dynamic TGA results carried out in air and nitrogen atmosphere are presented in Table V for cured ATS-C resin, thermoplastics, and the semi-IPN, respectively. The temperature at 5% weight loss and the weight losses at 400°C and 500°C indicate that the thermal stability of semi-IPN is governed by the concentration of the less stable cured ATS-C resin. The TGA results point out that the thermal stabilities of cured ATS-C resin were increased with increasing cure temperatures. The thermal stabilities of ATS-G resin is also shown to be increased with increasing crosslinking density in the cured resin.[20] For cured ATS-C resin and thermoplastics, the degradation is a two-stage process in air and is essentially a single-stage reaction in

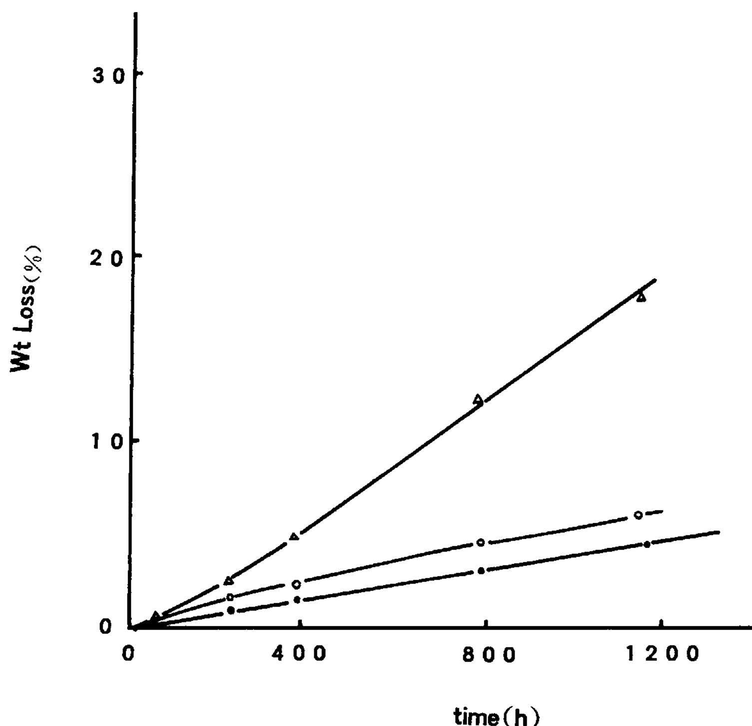

Figure 6 Isothermal weight loss at 250°C. ATS-C/PSF: (–●–) 0/100; (–○–) 25/75, (–△–) 75/25.

nitrogen. The derivative plots indicate that the primary peak in air is a thermal degradation and the latter one represents oxidative degradation of the material. The thermal stabilities of the phenolphthalein group in PEK-C and PES-C, and the isopropyliene group in PSF are lower than that of other groups. The heat resistance of the semi-IPN is dramatically influenced by the content of ATS-C oligomer. Lowering the content of thermoplastics reduces the thermooxidative stability of semi-IPN. But no weight loss is observed until about 300°C. Therefore, it is desirable to keep the ratio of thermoplastic to ATS-C oligomer as high as possible in order to obtain optimum thermooxidative stability.

As shown in Figure 5, the E and the $\ln A$ obtained by the method suggested by Coats and Redfern[18] for thermal degradation in nitrogen are higher than that obtained in air. E and $\ln A$ of cured ATS-C resin depend on the cure conditions. The addition of ATS-C decreases E and $\ln A$ of thermoplastics. These observations are consistent with the results of weight loss experiments. PEK-C and PES-C give similar values of E and $\ln A$ because of the similar chemical structure. Weight loss of isothermal aging also

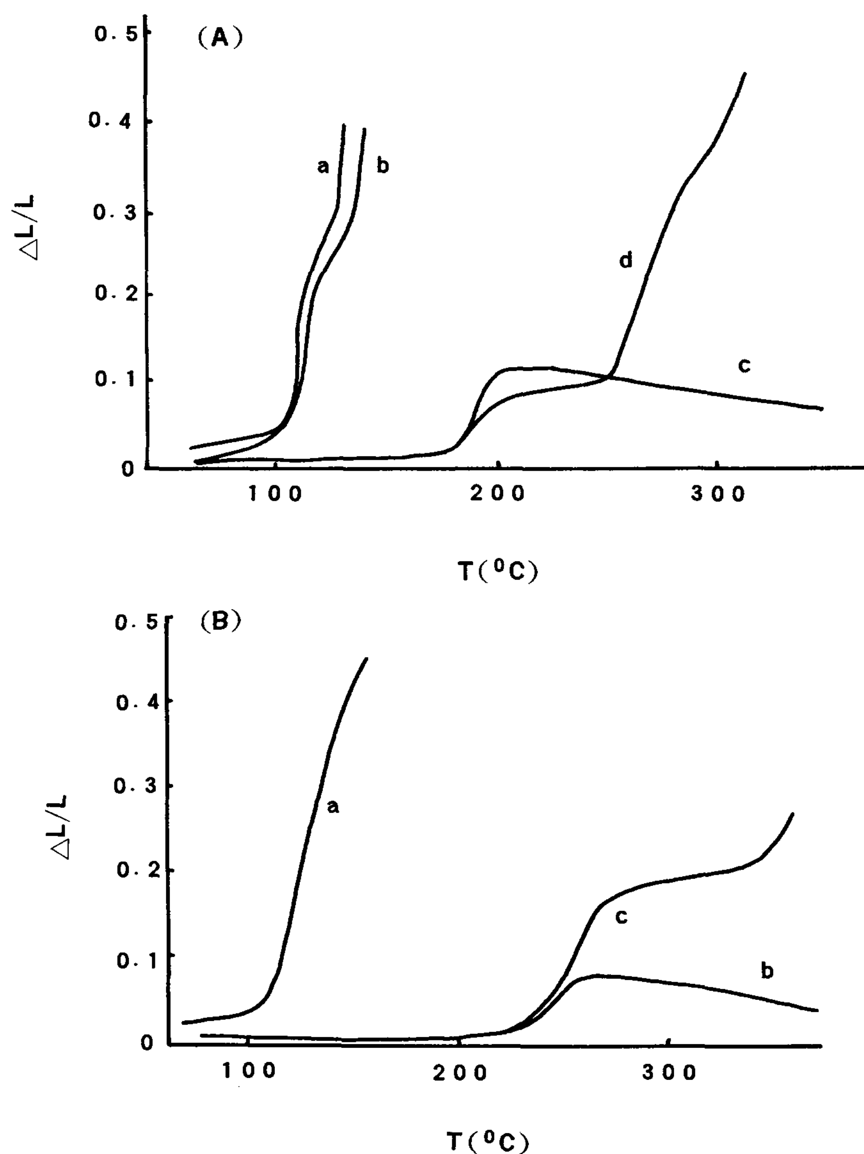

Figure 7 Thermomechanical analyses. (A) ATS/PSF = 50/50: (a) RT to 180°C; (b) RT to 150°C, 6 h to 190°C; (c) RT to 240°C, 0.5 h to 360°C; (d) PSF RT to 300°C. (B) ATS/PES-C = 50/50: (a) RT to 180°C; (b) RT to 240°C, 0.5 h to 360°C; (c) PES-C RT to 340°C.

indicates that the thermal stability of semi-IPN decreases as the content of ATS-C oligomer increases, more remarkably with increased aging time (Fig. 6).

The heat distorsion temperature (HDT) of linear thermoplastics, uncured blends, and their semi-IPNs were measured using the penetration technique on the thermal mechanical analyser. It can be seen from Figure 7 that there is significant effect of ATS-C on the thermomechanical properties of thermoplastics and the HDT of thermoplastics is remarkably decreased by adding ATS-C oligomer. It was found that the decrease in HDT of uncured blends with high HDT thermoplastic is larger than that of uncured blends with low HDT thermoplastic. The HDT of the uncured blends ATS-C/TP = 50/50 is about 105°C and that of PSF, PEK-C, and PES-C are 175, 210, and 245°C, respectively. For fully cured semi-IPNs, HDT values of the thermoplastic phase is increased up to the HDT of pure thermoplastic and no HDT of the cured ATS-C resin phase is present. It is evident that the addition of ATS-C oligomer significantly increases the flow property of thermoplastic, offering advantages in processability and wetting reinforcements. It was confirmed that the melt index (MI) of uncured blends decrease with increasing ATS oligomer content. End-use temperature does not decrease. The creep resistance at high temperature and solvent resistance are improved, which is different from commercial plasticized systems.

CONCLUSIONS

A series of semi-IPN were prepared from ATS-C oligomer and high performance thermoplastics: PSF, PEK-C, PES-C blends. The addition of ATS-C results in a dramatic reduction in T_g and HDT and improvement in the melt processability of thermoplastics. The reduction in T_g and HDT of uncured blends with thermoplastic of high T_g and HDT is larger than that of uncured blends with low HDT thermoplastic. The uncured blends are compatible. Thermoplastics have no effect on the mechanism of ATS-C cure reaction and thermal behavior of cured systems. In the process of cure, phase separation occurs. For fully cured semi-IPNs, the T_g and HDT value of the TP phase are higher than or equal to the T_g and HDT of pure thermoplastics. The thermal stabilities of semi-IPNs decreases as the content of ATS-C oligomer increases.

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