Influence of Chemical Structure of Polyimide Prepolymer on Rheo-Mechanical Properties of Polyimide Foam Composites

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A study is reported of the effect of varying chemical composition of foam polyimide prepolymers (H-complex) on the structure and properties of foam polyimide resins and their composites with aromatic polyimide fiber felt. The melt rheological behavior of the H-complex was found to be strongly dependent on its chemical composition and structure reorganization in the melt which is akin to mesophasic structural transition states in liquid crystal polymers. Changing the diamine part of the H-complex from 4,4-methylene dianiline to 1,3-diaminobenzene led to decreased steady shear viscosity at temperatures and shear rates ranging between 95° and 105°C and 0.01 and 1 s⁻¹, respectively. Additionally, changing the dialkyl moiety from dimethyl to diethyl in 3,3',4,4'-benzophenonetetracarboxylic dialkyl ester (precursor to the H-complex) increased gelation time of the H-complex, enhancing processibility of the foam polyimide composites. The results indicate that novel, lightweight foam polyimide composites with enhanced thermomechanical properties for beneficial uses can be prepared through chemical modification of the H-complex prior to its thermal imidization in the presence of the aromatic polyimide fiber felt.

1. INTRODUCTION

In our previous papers (1, 2) we have shown that incorporating carbon or organic fiber felt into foam polyimide (FPI) matrix increases the strength and modulus of the foam composite approximately 100 to 1000 times over pure polyimide foams. The foam composite retains the low density, porosity and compressibility of the pure foam and fiber felt. The desirable characteristics of the foam composites imply the combination, in one material, of the benefits of load-bearing continuous fiber composites and the thermal and vibration insulation property of the pure foam materials, allowing new uses in a number of applications

where traditional continuous fiber composites or pure polyimide foam is not useable. Potential application areas for these FPI composites include aerospace, automotive, and medical prosthesis areas.

A nearly identical processing method is used in making the foam composites and traditional fiber-reinforced polymer composites. The process is a facile and environmentally friendly one that uses electrostatic powder prepregging, evaporating pure alcohol (methanol or ethanol) and water during molding of the composite. This processing method is made possible due to the thermal stability of the polyimide prepolymer (H-complex), which can be obtained as follows (1–5):

1) Esterification of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) in boiling alcohol gave 3,3',4,4'-benzophenonetetracarboxylic dialkyl ester (BTDE) according to the reaction:
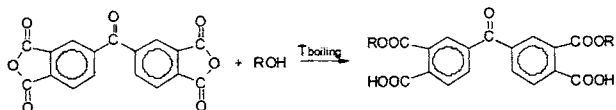
where R is -CH$_3$ or -C$_2$H$_5$. The BTDE obtained from the above reaction when methanol and ethanol are used is depicted as BTDMe and BTDEt, respectively.

2) The dissolution of diamines in an alcohol solution of the BTDE, leading to the spontaneous formation of complexes with hydrogen bonds (H-complexes) formed between the amino group of the diamine on the one hand and the carboxylic and ester groups of BTDE on the other according to the following reaction (3–6):
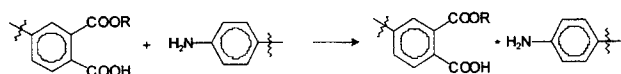
The high stability of the above H-complexes was confirmed by their low formation heat from their spontaneous formation when the components were mixed at the molecular level (6). Even in very dilute solutions, the H-complexes do not dissociate into individual molecules but exist in the form of di- or trimer oligomers (7, 8). Additional details on the current understanding on the chemistry of polyimide prepolymers can be found elsewhere (3–5).

In the molten state at temperatures ranging from 60°C to 80°C, the H-complex can be used for fiber felt impregnation as previously reported (1). The melt rheology of the H-complex is unknown and must be studied to accelerate efforts to develop optimal processing method for the foam polyimide composites. This paper discusses the chemical composition dependence on the melt rheology and structure evolution of the H-complex under conditions that the H-complex is likely to encounter during processing. The rheology behavior of the H-complex is also compared with the thermomechanical properties of the cured foam polyimide composite to find optimal chemical structure of the H-complex for foam composite processing.

## 2. EXPERIMENTAL

2.1. Processing of Foam Composite

2.1.1. H-complex

In this study, 4,4'-Methylenedianiline (MDA) and 1,3-Diaminobenzene (DAB) were used for the H-complex preparation. The BTDA was dissolved completely in absolute methanol or ethanol by stirring and refluxing for three to four hours. After cooling the resulting solution to room temperature, the MDA was added until complete dissolution was achieved. The dissolution process increased the reaction temperature by 50°C, and the resulting solution was maintained at this temperature for 5 to 10 minutes. A second diamine (DAB) was added to the reaction mixture after cooling the solution to room temperature. After a homogeneous solution was achieved, the temperature

was raised to 65°C, and the solution was kept at this temperature for 5 minutes. The solution was cooled, the excess methanol was removed under vacuum at 20°C, and the solid residue was powdered.
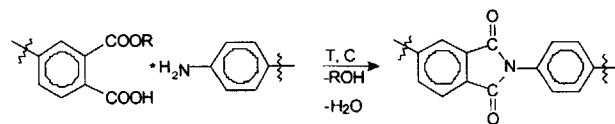
2.1.2 Fiber Felt

The commercial felt used in this study was based on Arimid® T polyimide fibers (Russian Scientific Center, Moscow) with the following chemical structures:
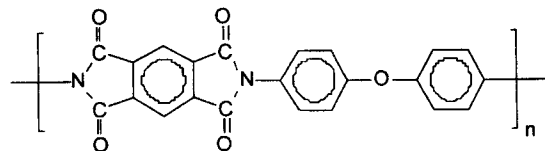
The density of the fiber felt is 0.045 kg/dm^3 and nominal thickness is 3 mm.

2.1.3. Prepregging and Composites Curing

Prepreg was obtained by impregnating the Arimid T fiber felt with the H-complex melt. Using electrostatic powder deposition, the powdered H-complex was uniformly deposited on the felt following the method previously reported (1). Subsequently, the felt with the deposited powder was rolled on calenders at 100°C for 10–15 s to achieve uniform wetting of the fiber felt with the H-complex melt. The resulting prepreg is a flexible composite material with felt and H-complex contents of about 1:5 by weight. Subsequently, the H-complex was directly transformed into the FPI via thermal imidization at temperatures ranging from 110°C to 250°C without the formation of polyamic acid intermediate (6):

Evaporation of the alcohol and water during this reaction in a closed mold (50 × 20 × 15 mm dimensions) containing the desired amount of the H-complex/fiber felt prepreg resulted in formation of the FPI composite. The mold and its contents were heated in a bake oven (without the application of pressure) at 200°C for one hour, followed by post-curing at 250°C for two hours.

2.2. Measurements

A strain-controlled dynamic rheometer (ARES, Rheometric Inc.) was used to measure the steady shear viscosity of H-complex under steady shear flows near their melt processing temperature in the cone and plate configuration following standard procedures. The diameter of the plate was 25 mm and the cone angle was 0.04 rad. The reproducibility of the measured parameters was tested with a minimum of three samples of the same composition and the results obtained are identical to the ones reported in this paper.

The foam composite samples were fabricated into rectangular bars (60 mm length, 10 mm width, and 7 mm thick) for flexural tests in a three-point bending test at room temperature using a standard tensile testing machine. Cylinders of foam composites (8 mm diameter × 10 mm length) were loaded under compression at a rate of 1 mm/min. Because of the foam structure of the composites and the compressibility of the fiber felt used, the FPI composites did not fracture under the test conditions used in this study and so compression strength and strain-to-failure could not be determined.

A Scanning Electron Microscope (SEM, Cambridge S-200) was used to examine the fracture surface of the foam composites. An optical microscope (BH-2, Olympus Co.) equipped with an automatic video capture system and a heating table was used to monitor the melting process of the H-complex.

Dynamic Mechanical Analysis (DMA), thermogravimetric Analysis (TGA), and differential Scanning Calorimetry (DSC) curves were recorded with a comprehensive Perkin-Elmer thermal Analysis 7 system. The DMA three-point bending measurements were conducted on samples (15 mm length, 5 mm width, and 1.5 mm thick), that were machined from the molded samples. A frequency of 1 Hz, heating rate of 5°C/min, static force of 110 mN, and dynamic force of 100 mN gave reproducible results and were used throughout. The TGA measurements were conducted using 5 to 10 mg samples contained in a platinum crucible with a heating rate of 20°C/min under a nitrogen atmosphere. DSC was performed on 7.5 ± 2.5 mg samples contained in a platinum crucible with a heating rate of 10°C/min under a nitrogen atmosphere.

Wide-angle X-ray diffraction measurements on the as-received and cured H-complex powder were conducted on an X-ray diffractometer (Model XDS-2000) supplied by Scintag Inc. Gas Chromotography - Mass Spectrometry experiments were performed using the Finnigan TSQ 700 (Finnigan MAT, San Jose, Calif.). The system was configured in the electron impact ionization mode. The first quadrupole was used as the analyzer and scanned from a mass to charge (m/z) ratio of 10 to 100 with a rate of 0.5 s per scan. The second and the third quadrupoles were kept at RF only mode. Unit mass resolution was achieved using perfluorotributylamine (FC43) as calibration and tuning reference. Oven temperature was maintained at 35°C for 1 min and increased to 300°C at a rate of 10°/min. A blank experiment was effected before sample analysis. Sample was deposited in a steel container and connected to 1m DB-1 column. Injector and transfer line temperatures were maintained at 250°C.

3. RESULTS AND DISCUSSION

3.1 Structure of H-complex

In their initial solid state, H-complexes exist in the form of thin, slightly crystalline (*Fig. 1*, curve 1) powder. By using optical microscopy equipped with a heating table, it was possible to estimate the melting point (mp) of the H-complex. The temperature at the start of reaction (T_s) of the H-complex was found to be about 120°C and identical to the onset temperature for alcohol and water evaporation as measured by TGA analysis (*Fig. 2*). *Table 1* shows the difference between melting points and T_s for some of the H-complexes used
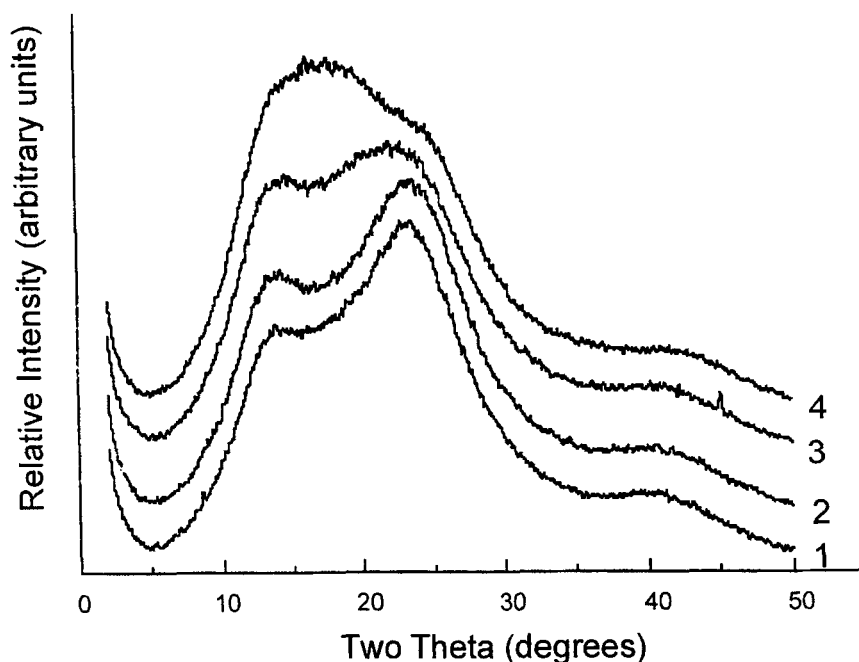
Fig. 1. Wide-angle X-ray scattering patterns for: (1) as-received BTDMe-MDA-DAB H-complex; (2) after rheology measurements at 95°C for 15 min; (3) cured (partially imidized) H-complex at 130°C for 1 hr; and (4) post-cured H-complex at 250°C for 1 hr.
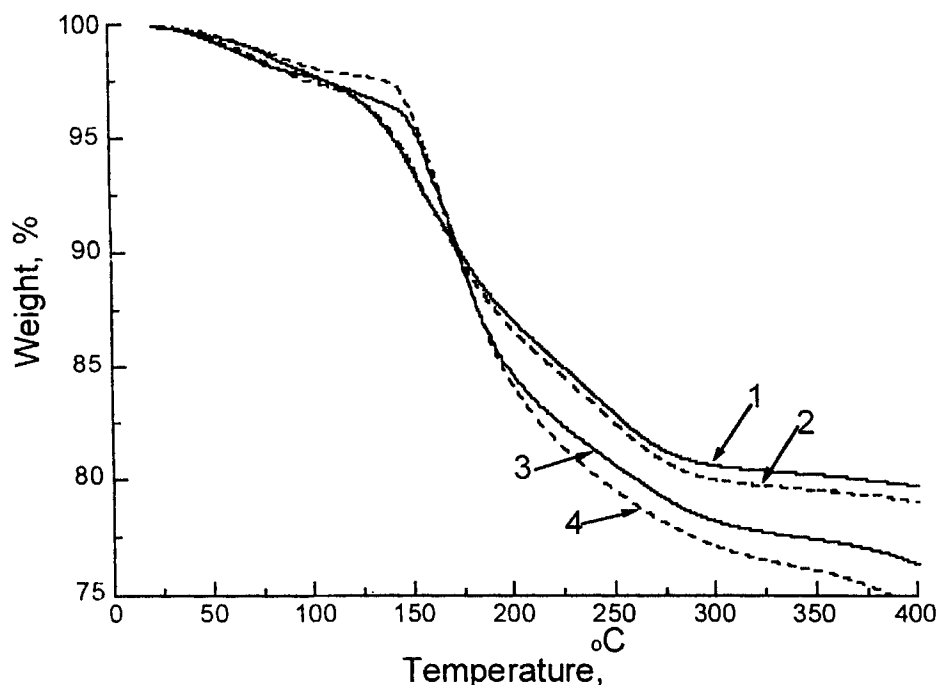
Fig. 2. TGA scans for H-complexes based on (1) BTDMe-MDA, (2) BTDMe-MDA-DAB, (3) BTDEt-MDA, and (4) BTDEt-MDA-DAB discussed in the text.

here. According to these data, the H-complex is a liquid at temperatures ranging from 70°C–120°C for the methanol-based complex and at 80°C–140°C for the ethanol-based complex. Within these temperature ranges, it is possible to evaluate the melt rheology behavior of the H-complex as will be shown later.

Detailed investigation of melting behavior of the H-complex at 95°C for 15 min did not reveal destruction of the slightly crystalline (or mesomorphic) structure (Fig. 1, curve 2) present in the H-complex. The mesomorphic structure is thought to gradually transform to a disordered (amorphous) structure during thermal imidization of the H-complex at temperatures higher than 120°C (Fig. 1, curves 3 and 4). Therefore, the rheology of the H-complex is expected to be strongly affected by mesomorphic structure especially in the temperature range of 70°C–120°C as will be demonstrated in the next section.

DSC analysis of H-complex shows that a melting peak occurs in the 60°C–90°C temperature range (Fig. 3). This peak disappears after additional heating, transforming into a heat capacity increase that is remarkably

similar to a glass transition process at high temperatures (Fig. 3, curves 2–4). In this case, it would be more correct to say that the H-complex has softened (not melted) because the mesomorphic structure was not destroyed according to X-ray analysis (see Fig. 1, curve 2).

This DSC peak at 60°C–90°C can be attributed to the evaporation of 3%–4% of water and residual methanol or ethanol as shown by the total ion chromotograms of H-complexes (Fig. 4). For both BTDMe-MDA and BTDEt-MDA the peak I-1 (1-2) with the maximum at 83°C is connected with evaporation of absorbed water (Fig. 5a). The peak II-1 at a temperature range of 110°C–180°C for BTDMe-MDA correspond to the production of water and methanol from the imidization reaction (Fig. 5b). The Peak II-2 that was observed at a temperature range of 130°C–200°C for BTDEt-MDA correspond to the production of water and ethanol from the imidization reaction (see Fig. 5c). The small peak III-2 occurring at temperatures ranging from 105°C to 125°C is probably connected with evaporation of residual ethanol that was used for H-complex

Table 1. Rheology Characteristics of H-Complexes.

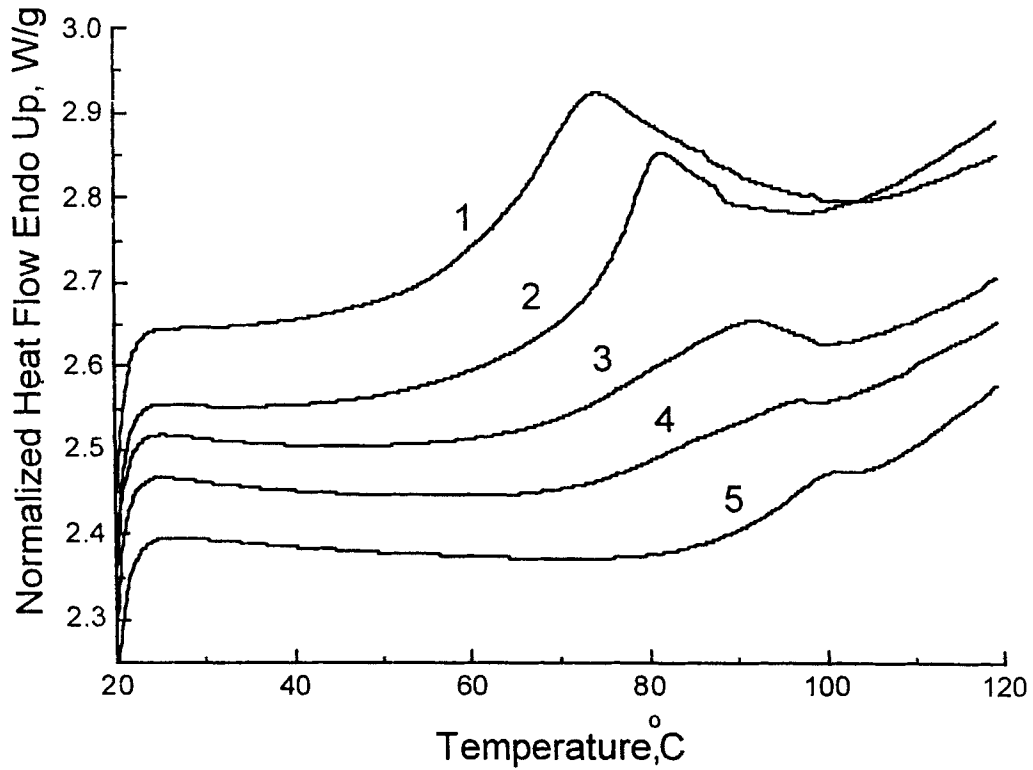| No.	Chemical Structure of H-Complex			mp, °C	Ts, °C	η at 0.013 s^{-1}, Pa·s T = 95°C	η at 0.013 s^{-1}, Pa·s T = 105°C	n
	Diester	Diamine	Diamine					
1	BTDMe	MDA	no	70	120	$1.5 \cdot 10^5$	$3.0 \cdot 10^4$	0.1
2	BTDMe	MDA	DAB	75	120	$6.0 \cdot 10^4$	$1.5 \cdot 10^4$	0.18
3	BTDMe	DAB	no	65	120	$2.5 \cdot 10^4$	$1.0 \cdot 10^4$	0.25
4	BTDEt	MDA	no	87	150	$1.0 \cdot 10^5$	$1.6 \cdot 10^4$	—
5	BTDEt	MDA	DAB	73	140	$8.0 \cdot 10^3$	$4.0 \cdot 10^3$	—

Fig. 3. DSC scans for H-complex based on BTDMe-MDA-DAB for (1) as-prepared and annealed at (2) 65°C, (3) 75°C, (4) 85°C and (5) 100°C.
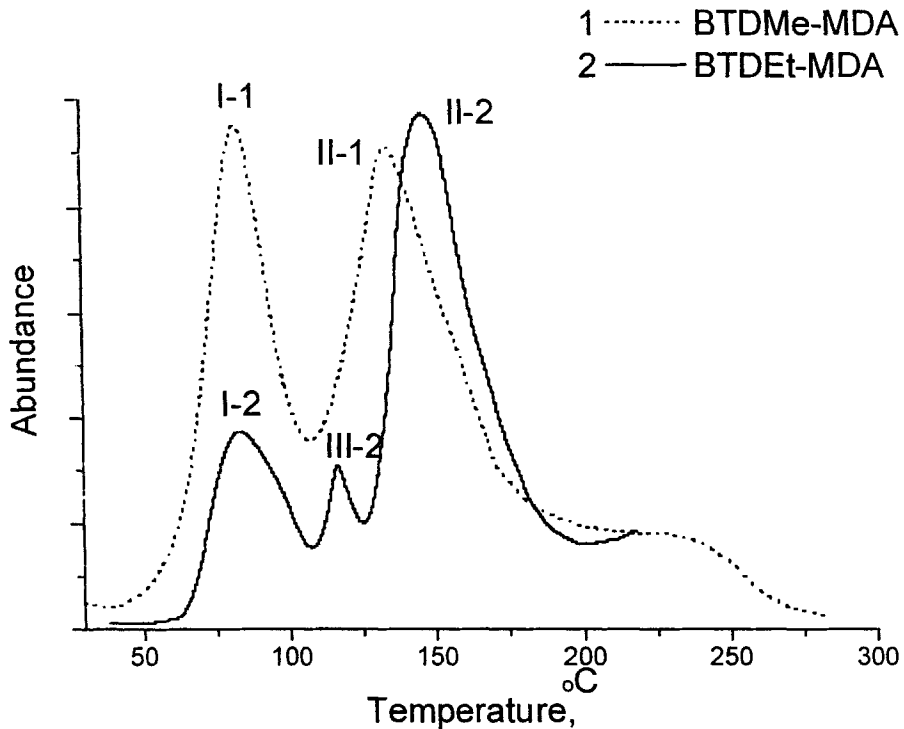

Fig. 4. Total ion chromatorgams of H-complexes based on BTDMe-MDA (1) and BTDEt-MDA (2).
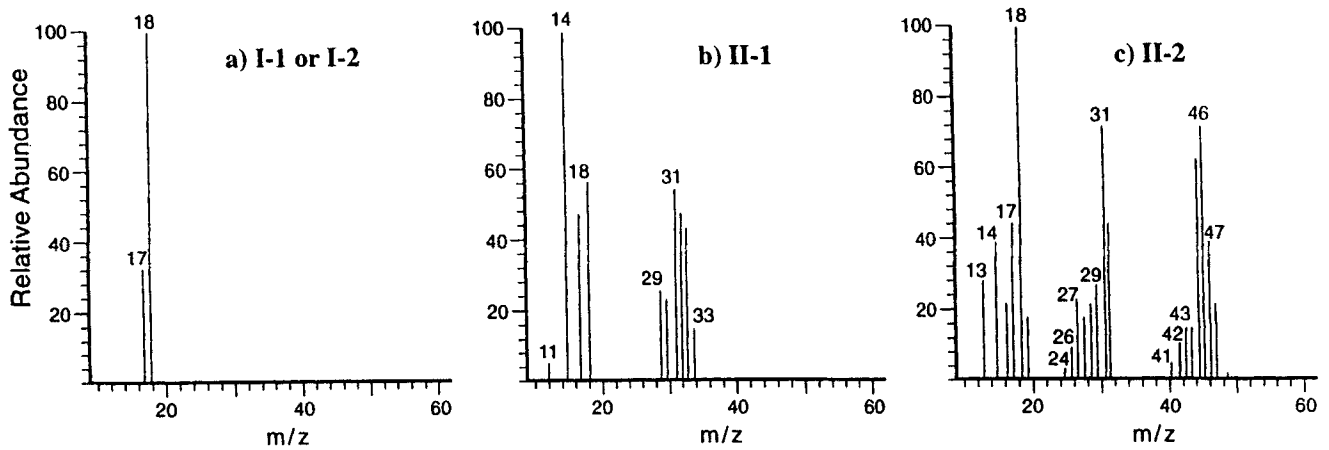
Fig. 5. Electron impact mass spectrum of: a) peak I-1 (I-2); b) peak II-1 showing the presence of methanol; c) peak II-2 showing the presence of ethanol.

preparation. Clearly, only pure water with residual methanol or ethanol could be evaporated at the temperature range of 60°C–110°C. The amount of this water evaporated was found not to exceed 4% (w/w) from the TGA data shown in *Fig. 2*. The evaporation of the reaction products in the case of BTDEt-MDA is slightly shifted to high temperatures (*Fig. 4*), which is also in good agreement with the TGA data (*Fig. 2*).

3.2 Melt Rheology Behavior of H-Complex

Figure 6 shows time dependencies of steady shear viscosity at shear rate of 0.013s⁻¹ and at temperatures

of 95°C and 105°C for BTDMe-MDA-DAB (sample #2, *Table 1*) and BTDEt-MDA-DAB (samples #5, *Table 1*) H-complexes. The critical time (or gelation time) for transformation from the liquid H-complex to rigid foam polyimide is shorter at both temperatures for BTDMe-MDA-DAB than for BTDEt-MDA-DAB as evidenced by the corresponding times to the viscosity rise in *Fig. 6*. This observation substantiates our previous results concerning the velocity constant K for the imidization reaction at 125°C of BTDMe-MDA-DAB (K = 0.5 × 10⁻⁴ s⁻¹) and BTDEt-MDA-DAB (K = 0.1 × 10⁻⁴ s⁻¹) H-complexes (6). The viscosity of the
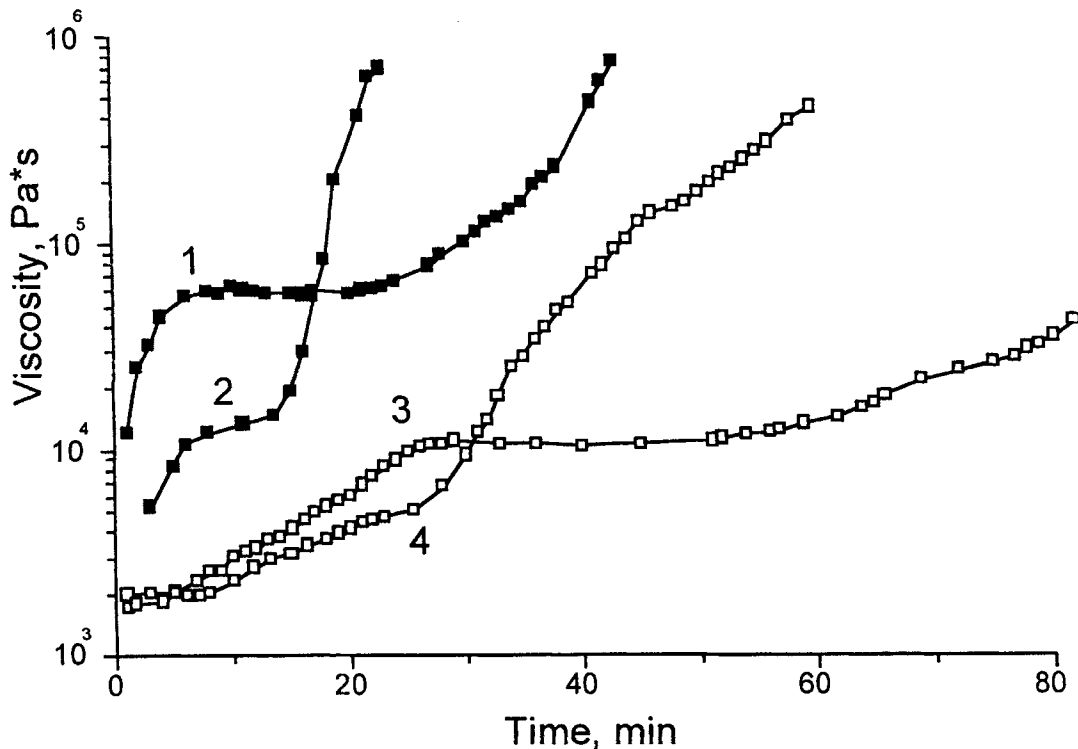

Fig. 6. Time dependencies of steady shear viscosity at 0.013 s⁻¹ and temperatures 95°C (1, 3) and 105°C (2, 4) for H-complexes based on (1)-(2) BTDMe-MDA-DAB and (3)-(4) BTDEt-MDA-DAB.

BTDMe-MDA-DAB H-complex at 95°C is independent of time for a time span of about 3 minutes until the gelation time is reached 15 minutes after the start of the viscosity measurements. The evaporation of water or residual solvent and formation of H-complex can explain the initial increase in viscosity during the first 3–4 minutes of the viscosity-time measurements from the monomers. The viscosity of the H-complexes is approximately constant for about 10–15 minutes (*Fig. 6*). For comparative purposes, the viscosity at gelation time of the H-complexes are also shown in *Table 1*. It can be seen from this table that incorporating DAB to the H-complex decreases the viscosity of methanol- and ethanol-based complexes.

Figure 7 shows the shear rate dependencies of viscosity of BTDMe based H-complexes at 95°C and 20 minutes after the start of melting of the H-complex. The figure shows a strong dependence of the viscosity on shear rate and viscosity decrease with increasing shear rate in the range 0.02 to 1 s^{-1} with incorporation of DAB to H-complex. The slope of the lines 1 to 3 in *Fig. 7* changes with the chemical structure of the H-complex. We applied the power-law equation to the data of *Fig. 1* to obtain the power-law index, n according to the following equation [9]:

$$\eta = K\gamma^{n-1} \tag{1}$$

The values of n (obtained from the slopes of the lines in *Fig. 7*) for the H-complexes based on BTDMe and different diamines are listed in *Table 1*. The table shows that n increased from 0.1 to 0.25 when the diamine part of

the H-complex was changed from MDA to DAB. This change in n together with increased viscosity suggest a strong dependence of structural organization on the chemical composition of the H-complexes. The generally low value of n for the H-complexes indicate some structural organization of the melt. This hypothesis is supported by the x-ray measurements performed on the H-complex ten minutes after the rheology experiments at 95°C (see curve 2, *Fig. 1*).

As mentioned earlier, the structural organization in the H-complex melt is of the mesomorphic type, which is analogous to that exhibited by liquid crystal polymers in their mesophasic transition temperature range (10). It would appear from the results of this study that the fluidity (low viscosity) can be obtained by changing the chemical structure of the H-complex—for example, from MDA to DAB—and/or applying high shear rates.

3.3. Thermomechanical Properties of Foam Composites

The flexural strength σ_f, flexural modulus E, and compression modulus E_c at room temperature of the Arimid T fiber-reinforced foam polyimide composites are shown in *Table 2*. The composites based on the BTDMe-DAB H-complex (sample #3, *Table 2*) showed the lowest mechanical properties of the three samples shown earlier in *Table 1*. Using a mixture of DAB and MDA in the H-complex (sample #2, *Table 2*) was found to significantly improve the mechanical properties of the foam polyimide composites. This improvement in
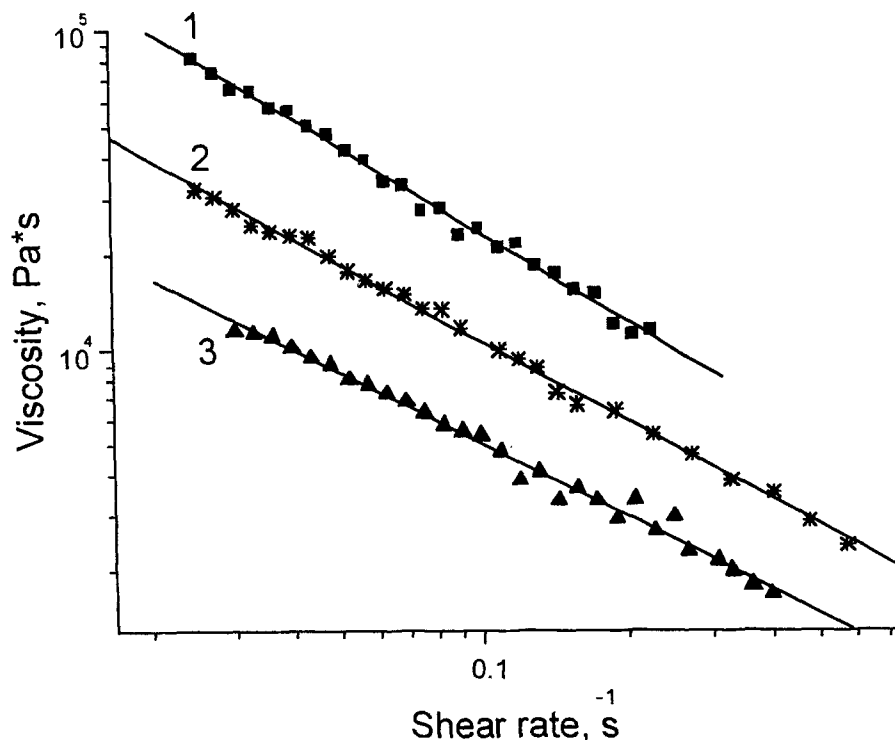

Fig. 7. Viscosity versus shear rate dependence of the H-complexes based on (1) BTDMe-MDA, (2) BTDMe-MDA-DAB, and (3) BTDMe-DAB at 95°C.

**Table 2. Thermal Mechanical Characteristics of Foam Composites Based on
Arimid T Fiber Felt and FPI Prepared From Different H-Complexes.**

| No. | Chemical Structure of H-Complex | | | Density, kg/dm³ | σ_f, MPa | E', GPa | E_c MPa | Tg °C |
	Diester	Diamine	Diamine					
1	BTDMe	MDA	no	0.55	30 ± 5	1.2	160	260
2	BTDMe	MDA	DAB	0.50	35 ± 4	1.3	190	280
3	BTDMe	DAB	no	0.50	15 ± 3	0.5	100	290

the mechanical properties is ascribed to the low viscosity of the BTDEtMe-MDA-DAB H-complex (see *Table 1*), which leads to enhanced wetting and impregnation of the fiber felt with the H-complex. These results show that the chemorheological behavior of the H-complex is an important factor that must be designed and controlled prior to its thermal imidization in the last stage of the composite fabrication stage to produce foam polyimide composites with maximal mechanical properties.

Microscopic evidence (*Fig. 8*) supporting the comparatively poor mechanical characteristics of foam composites based on FPI sample #3 (*Table 2*) was obtained by comparing SEM photographs of fracture surface of this sample with that of the foam composite based on the FPI sample #2 in *Table 2* (i.e., mixture of MDA and DAB). In the case of FPI sample #2, we see good dispersion of the Arimid T fibers in the matrix (*Fig. 8b*), good wetting and very good adhesion between the fibers and the matrix at higher magnifications (*Fig. 8c, d*). In the
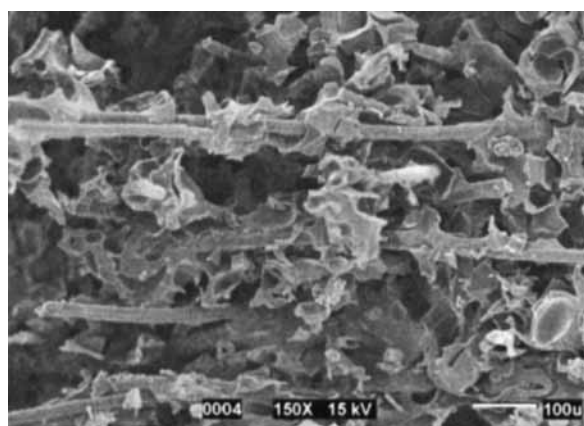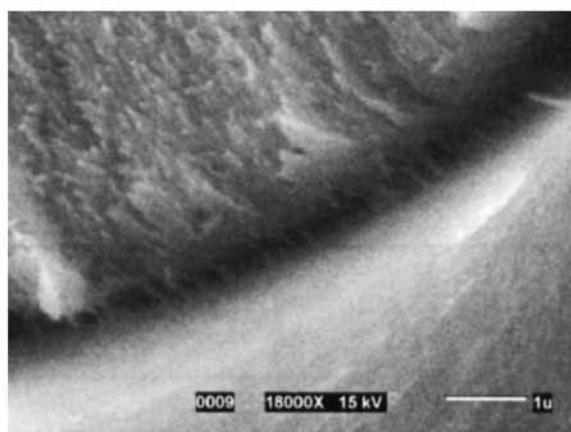

(a)
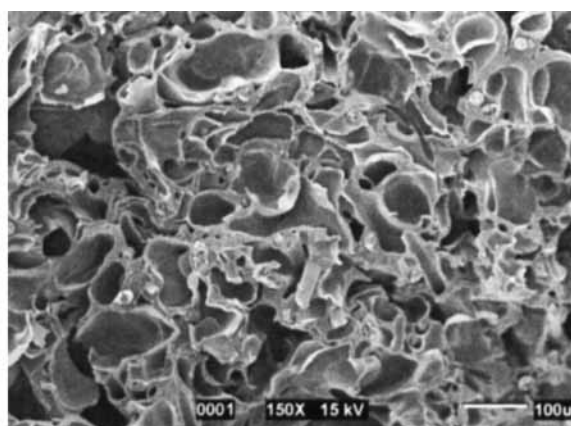
(b)
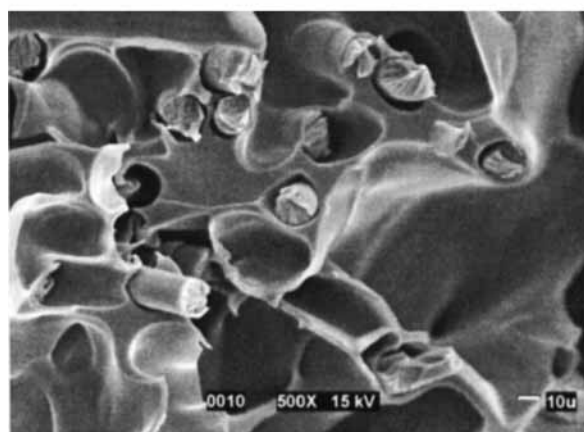
(c)

(d)

Fig. 8. SEM micrographs of the fracture surface of the foam composites based on FPI matrices prepared from a) BTDMe-DAB H-complex and b)-d) BTDMe-MDA-DAB H-complex. Magnification: a) and b) × 150; c) × 500; and d) × 1800.

case of foam composite based on the FPI sample #3, we see clear evidence for poor adhesion between the fibers and the matrix (relatively smooth surface of Arimid T fibers in *Fig. 8a*), which is largely responsible for the relatively low mechanical properties. While low viscosity of H-complex based on only DAB is desirable for good impregnation of the fiber felt, the fiber-matrix adhesion must be improved to obtain foam composites with optimal mechanical properties. Addition of a chemically compatible chemical coupling agent that will not inhibit the thermal imidization reaction might be useful in enhancing the mechanical properties of foam polyimide composite based on the BTDMe-DAB H-complex. This is a matter for further investigation.

The DMA data (*Fig. 9*) show that incorporating DAB to polyimide structure can also increase the thermal stability of the foam composite as evidenced by the 20°C shift to higher temperature of the loss modulus maximum corresponding to the glass transition temperature (curves 1" and 2", *Fig. 9*). Therefore, facile modification of the chemical structure of H-complex (as in this study) can be used to enhance the processability as well as the thermomechanical properties of the final foam structure, making it possible to produce foam polyimide composites with beneficial properties for a number of applications.

4. CONCLUSIONS

The following conclusions can be drawn from the present study:

1. Chemical alterations to the diamine part of the polyimide prepolymer (H-complex) by reacting the dialky ester (BTDE) with MDA, DAB, and MDA-DAB mixtures can significantly alter the steady shear viscosity at 95°C by a factor of 10 (viscosity) over a range of shear rates of 0.01 to 1 s^{-1} and the power-law index from 0.1 to 0.25.

2. Preliminary investigation of H-complex structure together with its melt rheology behavior suggest the presence of a mesomorphic structure in the H-complex melt that may be analogous to liquid crystallinity exhibited by liquid crystal polymers. The observed structure and strong shear thinning behavior of the H-complex melt suggest that applying high deformation rates may lead to better impregnation and consolidation of H-complex during prepregging of the fiber felt.

3. The gelation time of the H-complex may be increased by varying the type of alcohol used in step two of the FPI binder synthesis, leading to varying reaction velocity constants for the transformation of the H-complex to the polyimide resin.

4. Using only DAB as the diamine part in H-complex improves the fiber felt impregnation, but yields a very brittle matrix in the foam polyimide composite after thermal imidization. The brittlenes of the matrix can be overcome and the thermomechanical properties of the composite enhanced by using mixtures of DAB and MDA instead of using the DAB alone.
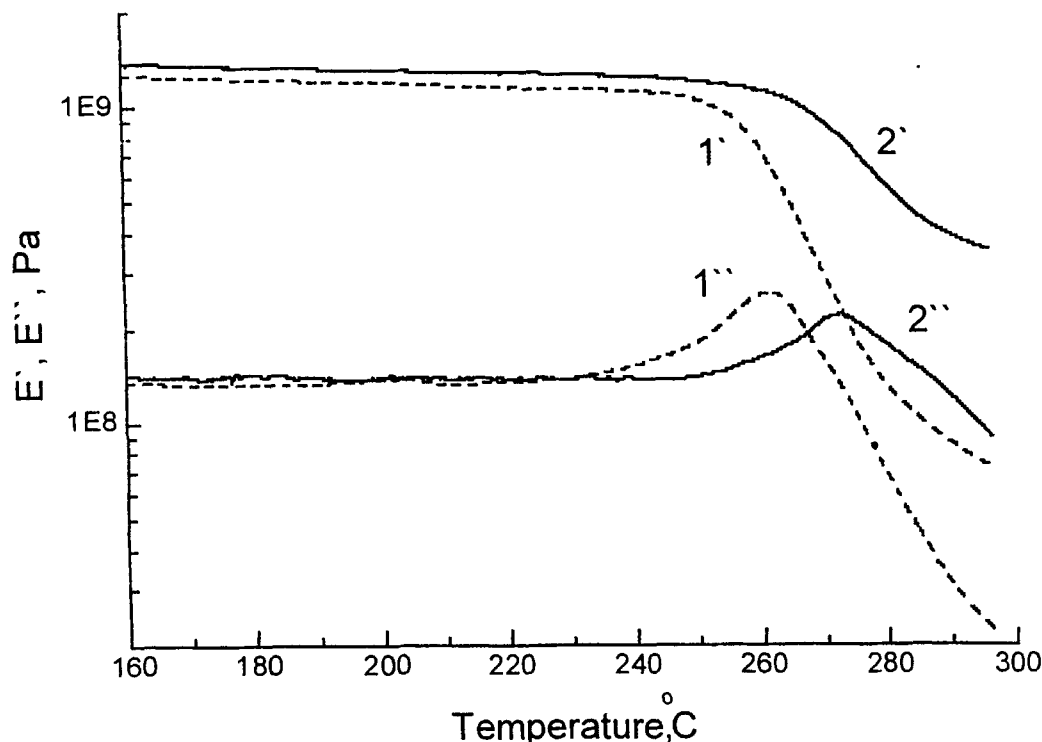

Fig. 9. Temperature dependencies of storage (1', 2') and loss (1", 2") moduli for the foam composites based on Arimid T fibers and FPI matrix prepared from BTDMe-MDA H-complex 1', 1") and BTDMe-MDA-DAB H-complex (2', 2") discussed in the text.

5. ACKNOWLEDGMENTS

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