

POLYIMIDE MOLECULAR COMPOSITE UTILIZING REACTIVE OLIGOIMIDE

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ABSTRACT

Polyimide molecular composite (MC) was prepared by blending a rigid polyimide and a reactive oligoimide that contain reactive acetylene units in the backbone at the stage of polyamide acid. The polyimide MC had exotherm due to the reaction of internal acetylene units on DSC. Viscoelastic analyses of the polyimide MC films showed that the crosslinking of the acetylene units gave polyimide that have very high glass transition temperature. Tensile measurements revealed that tensile modulus of the MC utilizing reactive oligoimide is higher than that of the MC utilizing reactive polyimide.

INTRODUCTION

In the fiber reinforced plastics, the presence of interface between the fiber and the matrix often causes problem. It is also known that defects of fibers prevent the composites from exhibiting the expected mechanical properties. Molecular composite (MC), in which a rigid polymer is dispersed in a flexible polymer at molecular level, could be an ultimate composite material. Two representative examples of MC are *p*-terephthalamide / nylon system¹⁾ and poly-*p*-phenylenebenzobisthiazole / poly-2,5 (6)-benzimidazole system.²⁾ The problem is that rigid polymers used as reinforcement are hard to dissolve and susceptible to aggregate, making molecular dispersion very hard. Block and graft polymers have been used to overcome this problem.

Polyimide / polyimide MC also were developed.³⁾ It has advantages in that the problem of segregation is easily avoided owing to the excellent miscibility between the two polyamide acids, and that high modulus and high strength MC films can be easily prepared by cold-drawing the cast film obtained from the blend solutions followed by imidization. Processability as laminate was realized by utilizing reactive polyimide having internal acetylene unit in the backbone as one component of MC.⁴⁾ In this study, reactive oligoimide was utilized as one component of MC, and the property of MC was compared with that of MC utilizing reactive polyimide.

EXPERIMENTAL

Materials

3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA), pyromellitic dianhydride (PMDA), oxydianiline (ODA), and *p*-phenylenediamine (PDA) were purified by recrystallization and sublimation. 3,3'-diaminodiphenylacetylene (*m*-intA) was prepared following the reported procedure.⁵⁾ N-Methylpyrrolidone (NMP) was purified by distillation.

Preparation of polyamide acid and polyimide

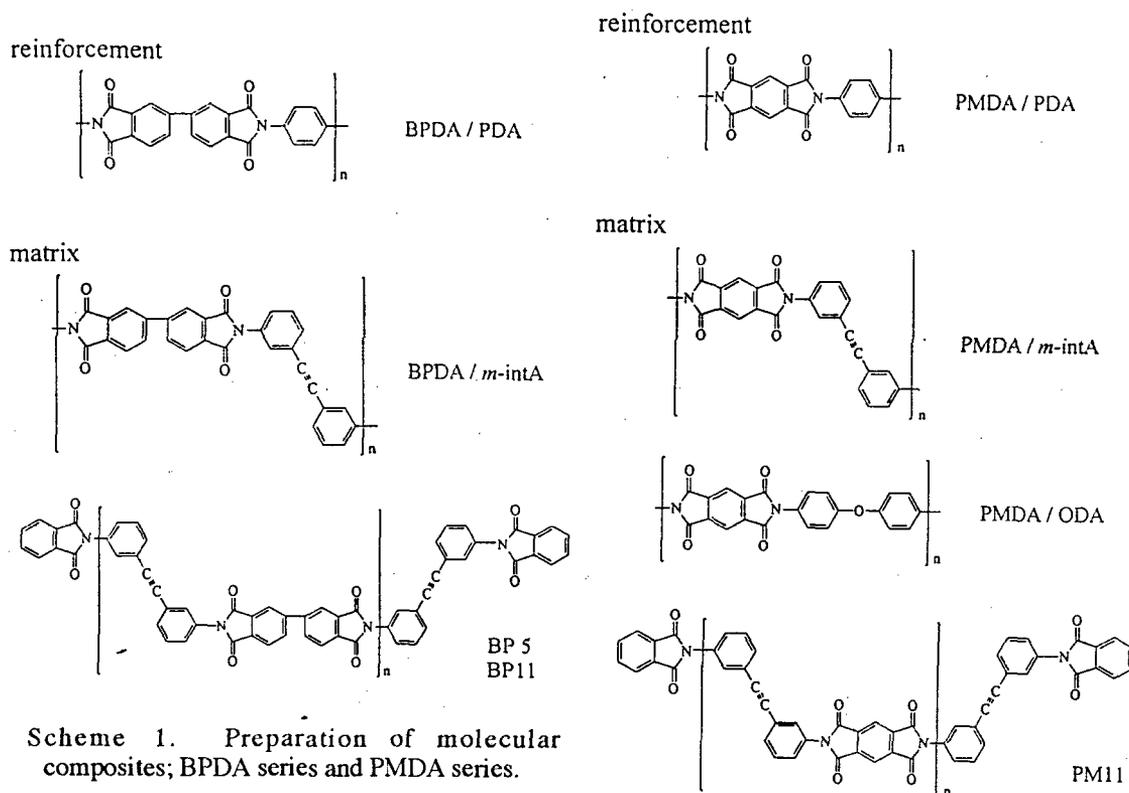
Polyamide acid was prepared by the reaction of diamine and dianhydride in NMP. Films were prepared by casting the solution and then drying at ambient pressure at 50°C for 2h. and then at reduced pressure for 16h. Imidization was carried out thermally.

Preparation of reactive oligoimide

By adjusting the stoichiometry of dianhydride and diamine monomers, amine-terminated oligoamide acids having various degrees of polymerization (DP=3, 5, and 11) were prepared, and then end-capped with phthalic anhydride. Thermal imidization gave oligoimides containing internal acetylene units.

Preparation of polyimide/polyimide MC films

Rigid polyimide and reactive oligoimide were blended in 7:3 weight ratio at the stage of amide acid solutions in NMP. The clear blend solution was cast on a glass plate. The cast films were then cold-drawn and imidized to give polyimide/polyimide MC films.



Scheme 1. Preparation of molecular composites; BPDA series and PMDA series.

RESULTS AND DISCUSSION

Preparation of polyimide/polyimide MC films

Polyimide/polyimide MC was prepared according to the Scheme 1. As the reinforcement, rigid polyimide such as BPDA/PDA or PMDA/PDA were utilized. As the matrix component, reactive oligoimide were used. Reactive polyimide and polyimide without reactive site were also used for comparison. It was found that viscosity of the MC with reactive oligoimide, at the stage of amide acid, is lower than that with reactive polyimide.

Crosslinking of internal acetylene units

It is expected that reactive oligoimide in MC crosslink by thermal treatment to give MC with high glass transition temperature. The crosslinking behavior of the reactive oligoimide were measured using DSC. In the case of BPDA/m-intA series, the onset of exotherm due to the reaction of acetylene units were observed at 345 - 378°C depending on the degree of polymerization as shown in Fig. 1. Exotherm disappeared after 400°C treatment. Similar exothermic behavior was observed with PMDA/m-intA (Fig. 2).

Neat resin was melt-processed to examine the melt-processability. Melt flow was not so good and brittle films were obtained. It was confirmed from viscoelastic analyses (Fig. 3) that the melt-processed films had high Tg; 389°C from the E'' and above 400°C from $\tan\delta$. The modulus was maintained to high temperature up to 400°C.

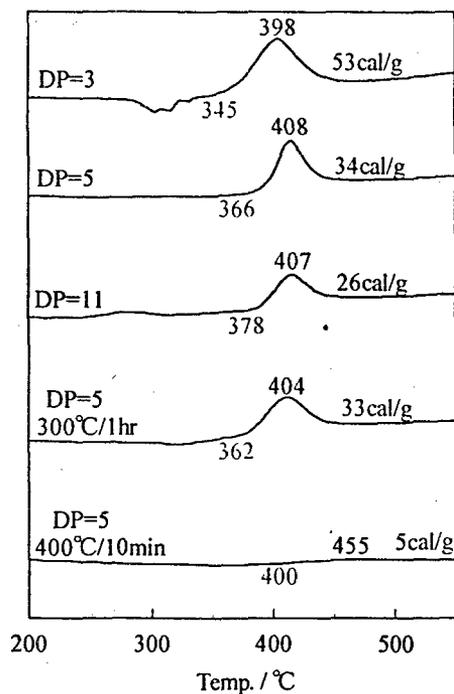


Fig. 1 DSC of BPDA/m-intA oligomer.

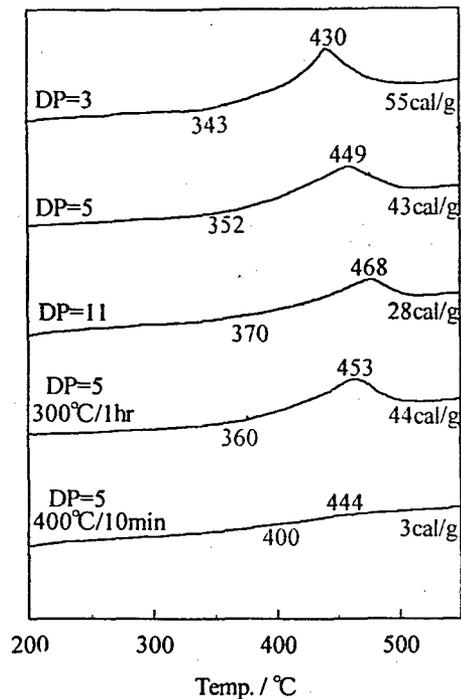


Fig. 2 DSC of PMDA/m-intA oligomer.

Tensile properties of MC films

From the tensile measurement, it was observed that tensile modulus of MC films utilizing reactive oligoimide is higher than that utilizing reactive polyimide for 20 - 30 % (BPDA series in Table 2). Similar results were obtained from PMDA series

CONCLUSION

1. Polyimide/polyimide MC was prepared by physically blending a rigid polyimide and reactive oligoimide having acetylene units.
2. The acetylene units crosslinked to give a MC film that have very high T_g.
3. Tensile modulus of the MC film that utilize reactive oligoimide was higher than that utilize reactive polyimide.

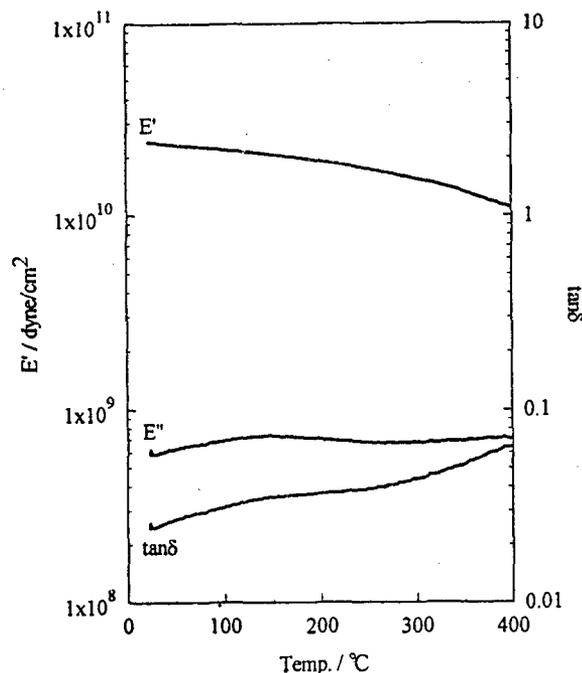


Fig. 3. Viscoelastic analyses of BP11

Table 2. Tensile properties of MC films.

	Treatment / °C	E / GPa	σ / GPa	elongation / %
(BPDA/PDA) / (BPDA/m-intA)	300	4.9	0.15	7.8
"	350	5.3	0.18	3.8
"	400	4.5	0.09	2.2
(BPDA/PDA) / BP5	300	5.9	0.03	0.5
"	350	5.5	0.15	2.7
"	400	6.4	0.11	1.8
(BPDA/PDA) / BP11	300	5.4	0.16	4.2
"	350	5.9	0.19	3.9
"	400	5.9	0.12	2.7

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