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Synthesis of novel maleimide-terminated thioetherimide oligomer and its bulk copolymerization with reactive solvents

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Abstract

This paper reports the synthesis of a novel maleimide-terminated thioetherimide oligomer and its copolymerization with reactive solvents bearing vinyl. Starting from 3-chlorophthalic anhydride and 4-chlorophthalic anhydride, 2,2′,3,3′-thiodiphenyl tetracaboxylic dianhydride (3,3′-TDPA) and 3,3′,4,4′-thiodiphenyl tetracaboxylic dianhydride (4,4′-TDPA) were synthesized. Thereby, a novel maleimide-terminated thioetherimide oligomer was prepared from. 3,3′-TDPA, 4,4′-TDPA, 3,3′-dimethyl-4,4′-diaminodiphenylmethane (DMMDA) and maleic anhydride. Binary and ternary copolymer resin were derived from corresponding binary and ternary homogeous solution consisting of thioetherimide oligomer, reactive solvent *N*-vinylpyrrolidone (NVP) or *N*,*N*′-dimethylacrylamide (DMAA) and divinylbenzene (DVB) as modifier, initiated either by gamma ray irradiation or by benzoyl peroxide (BPO). Thermal and mechanical properties of copolymer resin are determined and compared in terms of the kind of reactive solvent, addition of modifier DVB. The effect of initiation approach on property of final copolymer resin were studied. Phase separation and sub-transition of ternary copolymer resin induced by BPO are observed, which could be accounted for by thermal movement of DMAA molecules during thermal initiation. Structure-property relationship of copolymer resin was discussed. The effect of monomer molar ratio of 3,3′-TDPA and 4,4′-TDPA on thermal and mechanical properties were investigated.

Keywords: Maleimide-terminated thioetherimide oligomer; Reactive solvents; Isomeric effects

1. Introduction

Polyetherimides (PET) represented by Ultem 1000 have recently attracted great attention in fabrication of UF membrane [1,2], matrix composite [3,4], semi-IPN [5], branched polymer [6,7,9], microcellular foaming [8] and use as modifer of epoxy resin [10], hollow fiber [11], NLO materials [12]. The aromatic imide units of PEI provide high performance properties such as considerable mechanical strength, thermal stability and chemical resistance, while the flexible ether linkages provide good processability.

However, thioetherimides as an emerging class of PEI have not been fully researched. Compared with oxygen-connected ether linkage, sulfur-connected ether linkage is more flexible for the existence of 3d orbit of sulfur atom, and so thioetherimide demonstrated further-improved solubility and processability.

In this research, we synthesized two isomeric thioether dianhydride and thereby, prepared a novel reactive thioetherimide oligomer using maleic anhydride as endcapping agent. The thus-obtained maleimide-terminated thioetherimide oligomer exhibited very good solubility. Making use of the superior solubility, oligomer can be easily dissolved in reactive solvent bearing vinyl with solid content as high as above 60 wt%, to form homogenous system with good flow.

The use of reactive solvents in the processing of polymer with high T_g provide a possible solution to circumvent the compromise between regaining the intrinsic material properties and ease of processing. Thomas Fine et al. [13] has reported structures and rheological properties of reactive solutions of block copolymer P(S-*b*-MMA) and P(B-*b*-MMA) in liquid epoxy monomer. There has been a research [14] which investigated on using reactive solvent thermoplastic poly(urethane) (TPU) which reversibly (de)polymerize to facilitate the processing of poly(2,6-dimethyl-1,4-phenylene ether) (PPE). To the best of our knowledge, there have been no reports on curing polyimide via the copolymerization with reactive solvents except for some reports on

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modification of bismaleimide and its oligomer with reactive solvents [15–17]. Taking advantage of the reactivity of double bond of end group maleimide, thioetherimide oligomer can copolymerize with reactive solvent bearing vinyl. Compared with traditional hot-press thermal cure for PEI resin, this approach showed better processability, characteristic of homogeneous system capable of thermal initiation and irradiation hardening and nearly zero emission of volatile, which could be of potential industrial interest to electrical product encapsulating and chemical products that requires no emission of volatile, for instance, solventless paint. In addition, for the large quantity of chemically and thermally stable imide group existing in copolymer resin, this novel type of resin material could bridge up the gap of epoxy resin and BMI resin, which requires better processability than BMI resin and higher long-term service temperature (130 °C) than epoxy resin while retaining comparable mechanical properties and chemical stability.

2. Experimental

2.1. Materials

N-Vinylpyrrolidone (NVP), *N*,*N*′-dimethlyacrylamide (DMAA) were purchased from Aldrich and used without further purification. *N*,*N*′-dimethylacetylamide (DMAc) was dried over P_2O_5 and distilled under vacuum. 3,3′-Dimethyl-4, 4′-diamino-diphenylmethane (DMMDA) and benzoyl peroxide (BPO) were recrystalized with ethanol twice before use. Maleic anhydride was recrystalized with toluene and acetic anhydride (1:2). All other materials commercially available are used as received.

2.2. Instruments

FTIR spectra were recorded on a Nicolet AVATAR360 FTIR spectrometer. ^{1}H NMR spectra were obtained from AVANCE 500 MHz Bruker spectrometer in $CDCl_3$ solution using tetramethylsilane as an internal reference.

Flexural strength and impact strength of copolymer resin were determined according to State Standard (PRC) GB-1843-80 and GB-1042-92 on INSTRON 1121 with a crosshead of 100 mm/min and JIYI impact strength tester at room temperature. At least five specimens were tested to generate the data in each case.

Irradiation was performed at a cobalt source ($7\times10^4 w$) with dose rate of 8.31 Gy/s at room temperature.

Glass transition temperature of copolymer resins was derived by dynamic mechanical thermal analysis (DMTA) experiments on a Rheometric Scientific DMTA-V system at a heating rate of 3 °C/min with single frequence of 1 Hz.

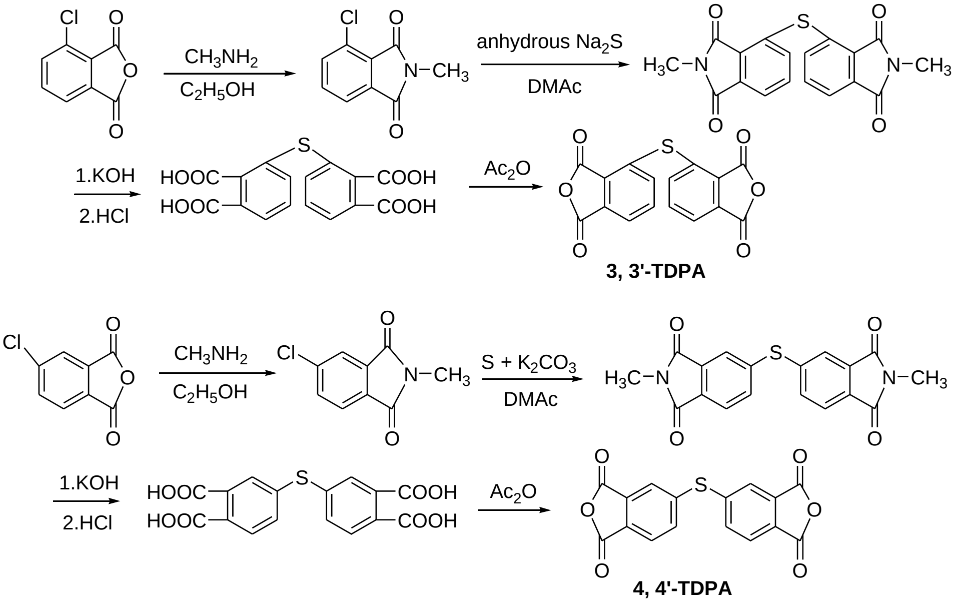
Thermogravimetric analyses were obtained at a heating rate of 10 °C/min in N_2 with a Perkin–Elmer TGA-2 thermogravimetric analyzer.

Water uptake was determined by immersing specimens in distilled water until equilibrium amount of water was absorbed, then taking out to remove the surface free water with filter paper and directly weighed. The water uptake was calculated as: $(w-w_0)/w\times100\%$, w_0 and w refer to initial weight and the weight after absorbing water.

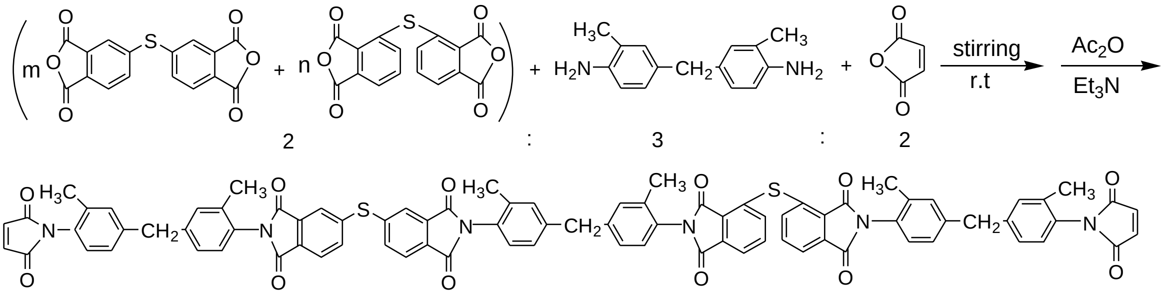
Specimens obtained from impact test were coated with gold and examined under an XL-30 ESEM FEG Scanning Electron Microscope (FEI COMPANY) to study the fracture surface morphological behavior.

2.3. Synthesis of thioether dianhydrides

Two isomeric thioether dianhydrides 2,2′,3,3′-thiodiphenyltetracaboxylic dianhydride (3,3′-TDPA) and 3,3′,4,4′-thiodiphenyltetracaboxylic dianhydride (4,4′-TDPA) were prepared starting from 3-chrolophathalic anhydride and 4-chrolophathalic anhydride according to reported literatures



Scheme 1. Synthetic route of 3,3′-TDPA and 4,4′-TDPA.



Scheme 2. Synthesis of maleimide-terminated thioetherimide oligomer. Varying value of *m*/*n* is 1:0, 3:2,1:1, 2:3 and 0:1, respectively.

with some modifications [18–21]. The synthetic routes are illustrated in Scheme 1. 3,3′-TDPA was obtained as a yellowish crystalline solid in total yield of 35%; mp: 247–248 °C (lit. [20] 240 °C, lit. [21] 245–247 °C). ^{1}H NMR 8.07–8.04 ppm (d, 2H), 7.94–7.98 ppm (t, 2H), 7.75–7.73 ppm (d, 2H). 4,4′-TDPA was obtained as off-white crystalline solid in total yield of 40%; mp: 199–201 °C (lit. [20] 202 °C, lit. [21] 202–203 °C). ^{1}H NMR 8.13–8.11 ppm (d, 2H), 8.04 ppm (s, 2H), 8.00–7.98 ppm (d, 2H).

2.4. Synthesis of maleimide-terminated thioetherimide oligomer

To a stirred solution of DMMDA in DMAc, mixture of thioether dianhydride 3,3′-TDPA and 4,4′-TDPA with molar ratio of 1:0, 3:2, 1:1, 2:3, 0:1, respectively, was added under nitrogen atmosphere at room temperature. Eight hours later, maleic anhydride as endcapping agent was incorporated and the whole molar ratio of DMMDA and mixed thioether dianhydride and maleic anhydride was 3:2:2. Stirring continued for another 4 h. After that, acetic anhydride and triethyl amine were added to complete chemical imidation in 10 h. The resulting purple solution was poured into ethanol and precipitate was washed with 5% $NaHCO_3$ solution, distilled water and heated ethanol sequentially, and dried under vacuum at 60 °C. Off-white product was obtained in yield no less than 80%. The general synthetic route is shown in Scheme 2. The calculated molecular weight of the obtained maleimide-terminated thioetherimide oligomer is 1419. IR spectra: 1715, 1775 cm^{-1} (C=O), 1110, 1140 cm^{-1} (Ar–S).

2.5. Fabrication of homogeneous system involving maleimide-terminated thioetherimide oligomer and reactive solvents and its bulk copolymerization procedure

Under mechanical stirring at 50 °C, oligomer was thoroughly dissolved in reactive solvent (NVP or DMAA) with solid content of 60 wt% to form yellow transparent solution with good flow. In this process, modifier divinylbenzene (DVB 5 wt%) and radical initiator BPO were incorporated or otherwise. Homogeneous solution was degassed under vacuum and then poured into glass plate to induce bulk copolymerization via gamma ray irradiation or by heating in the air-circulated oven in the presence of BPO (0.3%). For the case of gamma ray induced copolymerization, BPO was not included. Irradiation dose was 100 K Gy and subsequent thermal treatment proceeded at 120 °C (2 h), 140 °C (2 h). For the case of BPO initiated copolymerization, pre-copolymerization took place at 80 °C for 48 h, and post-copolymerization was performed at 100 °C (4 h), 110 °C (2 h), 120 °C (2 h), 140 °C (2 h).

3. Results and discussion

3.1. Characterization of thioether dianhydrides and maleimide-terminated thioetherimide oligomers

Fig. 1 shows IR spectra of 3,3′-TDPA and 4,4′-TDPA. It is found that C=O absorption appears at 1785±10 and 1855±5 cm^{-1}, absorption of Ar–S at 1115±5 and 1160±10 cm^{-1}. The influence of sulfur atom linking position can be observed by the shape difference of Ar–S absorption band and C=O absorption band between 3,3′-TDPA and 4,4′-TDPA. In addition, characteristic Ar–H absorption at 3100 cm^{-1} of 3,3′-TDPA appears more distinctively than 4,4′-TDPA. This may be due to stronger P-π conjulation effect of 3,3′-TDPA than that of 4,4′-TDPA, because sulfur atom of 3,3′-TDPA is ortho-linked to carbonyl group in each aromatic ring. In contrast, sulfur atom is meta-linked to carbonyl group in each aromatic ring in the molecule of 4,4′-TDPA, so P-π conjulation effect of is weaker.

^{1}H NMR spectrum of oligomer shows the absorption of methyl hydrogen attached to phenyl ring at 2.13±0.05 ppm, absorption of methylene hydrogen between two phenyl ring at 3.99±0.03 ppm, absorption of aromatic hydrogen in phenyl ring linked by $–CH_2–$ at 7.15±0.05 ppm, absorption of aromatic hydrogen in phenyl ring linked by sulfur atom at 7.6±0.1, 7.7±0.1, 7.9±0.1 ppm and absorption of double

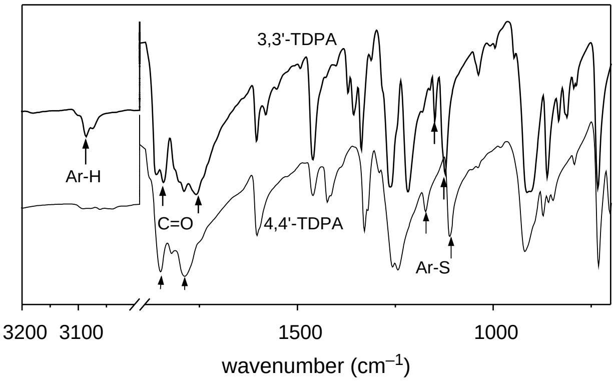


Fig. 1. IR spectra of 3,3′-TDPA and 4,4′-TDPA.

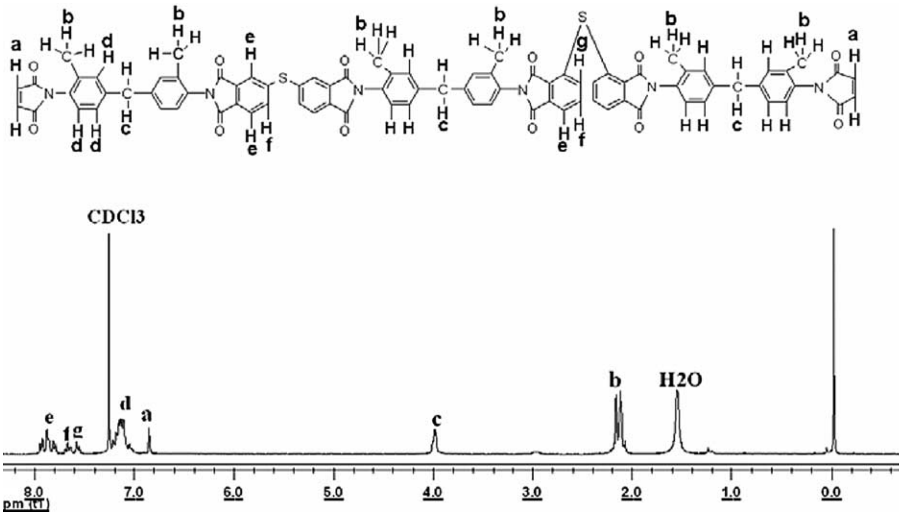


Fig. 2. ^{1}H NMR spectrum of maleimide-terminated etherimide oligomer.

bond hydrogen in maleimide ring at 6.86 ± 0.02 ppm, as illustrated by ^{1}H NMR spectra of oligomer in Fig. 2.

3.2. *IR spectra analysis of copolymerization of maleimide-terminated thioetherimide oligomer and reactive solvents*

The copolymerization mechanism of maleimide-terminated etherimide oligomer and reactive solvents is like that of bismaleimide oligomer and NVP, which we have reported previously [16]. Copolymerization of oligomer and reactive solvents could be revealed by comparison of IR spectrum before and after copolymerization. Fig. 3 is a typical IR spectra which compares the characteristic absorption change of binary homogeneous system consisting of oligomer and NVP before and after copolymerization. It is found that after copolymerization characteristic C=C stretch absorption 1629 cm^{-1} and out-plane bending vibration absorption of H–C= at 985 cm^{-1} was greatly diminished. Fig. 4 is about the case of binary homogeneous system consisting of oligomer and DMAA. It is found that after copolymerization out-plane bending vibration absorption of H–C= of DMAA at 981 and 955 cm^{-1} was greatly diminished.

3.3. *Effect of reactive solvent on general properties of binary copolymer resin induced by gamma ray irradiation*

As entry a and b in Table 1 show, mechanical properties of binary copolymer resin based on NVP is better than that based on DMAA, however, copolymer resin based on DMAA has higher glass transition temperature, 5% weight loss decomposition temperature and lower water uptake than that based on NVP.

3.4. *Effect of modifier DVB and water uptake on general properties of copolymer resin induced by gamma ray irradiation*

In order to enhance mechanical properties while maintaining thermal properties of copolymer resin involving DMAA, DVB was introduced to attain this aim. It is found that after the introduction of 5 wt% DVB, mechanical properties of copolymer resin induced by gamma ray irradiation increased a lot, meanwhile, water uptake was inhibited and thermal properties was maintained, as shown by entry c in Table 1. It can be attributed to ameliorated copolymerization of ternary system resulted from higher copolymerization reactivity by introducing DVB to bridge up the polymerization reactivity

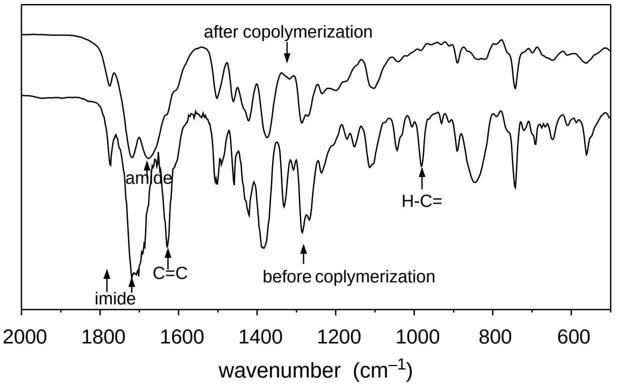


Fig. 3. IR spectra of binary homogenous system involving NVP and oligomer before and after copolymerization induced by gamma ray irradiation.

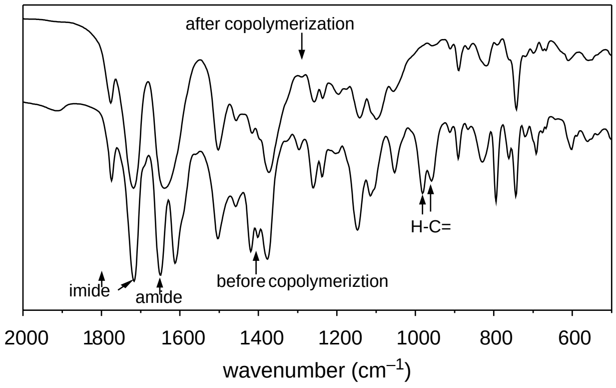


Fig. 4. IR spectra of binary homogenous system involving DMAA and oligomer before and after copolymerization induced by gamma ray irradiation.

Table 1
General properties of copolymer resins involving maleimide-terminated thioetherimide oligomer prepared from mixture of 3,3′-TDPA and 4,4′-TDPA with molar ratio of 1:1

Entry	Reactive solvent	Modifier	Initiation approach	Flexural strength (Mpa)	Flexural modulus (MPa)	Impact strength (kJ/m^2)	Water uptake (wt%)	$T_{5\%}$ (°C)	T_g (°C)
a	NVP	–	Gamma ray	97.8	3.56	4.83	20.4	253	144
b	DMAA	–	Gamma ray	50.6	3.42	0.41	13.7	265	173
c	DMAA	DVB	Gamma ray	103.4	3.51	8.88	8.8	278	177
d*	DMAA	DVB	Gamma ray	86.2	2.04	5.68	–	–	–
e	DMAA	DVB	BPO	79.6	3.01	5.60	8.8	266	166

Sample d* refers to immerging sample c in water until maximum water is absorbed and then taking out for mechanical properties measurement.

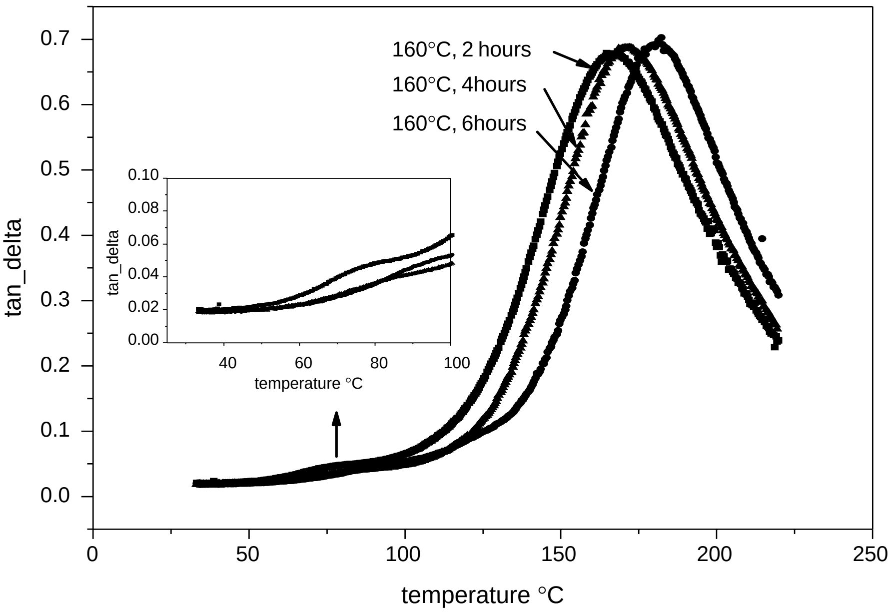


Fig. 5. Effect of thermal treatment at 160 °C with different time duration on T_g of ternary copolymer induced by BPO. T_g is 168.2, 170.3 and 179.8 °C, respectively. A sub-transition near 85 °C appears for all cases.

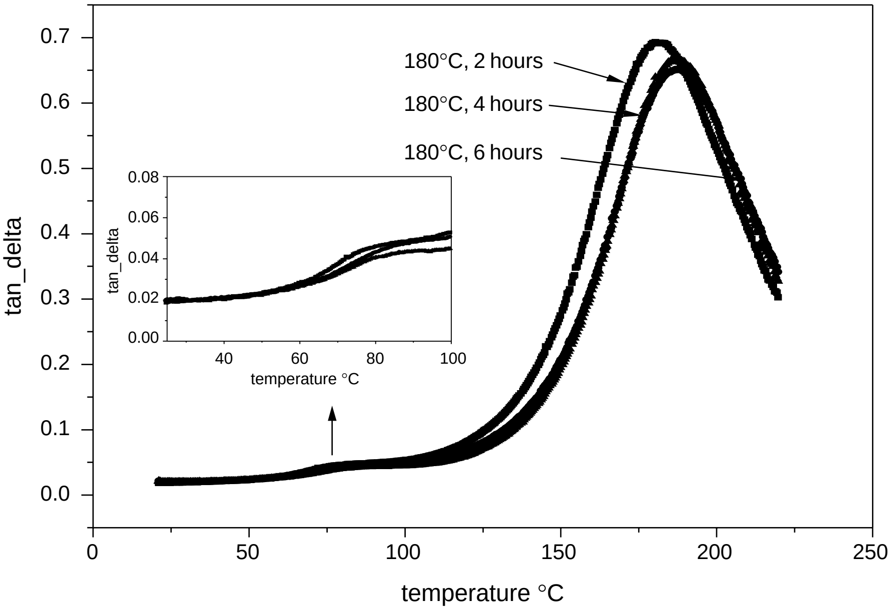


Fig. 6. Effect of thermal treatment at 180 °C with different time duration on T_g of ternary copolymer induced by BPO. T_g is 180.3, 187.7 and 188.1 °C, respectively. The sub-transition near 85 °C appears more clearly than the case of thermal treatment at 160 °C.

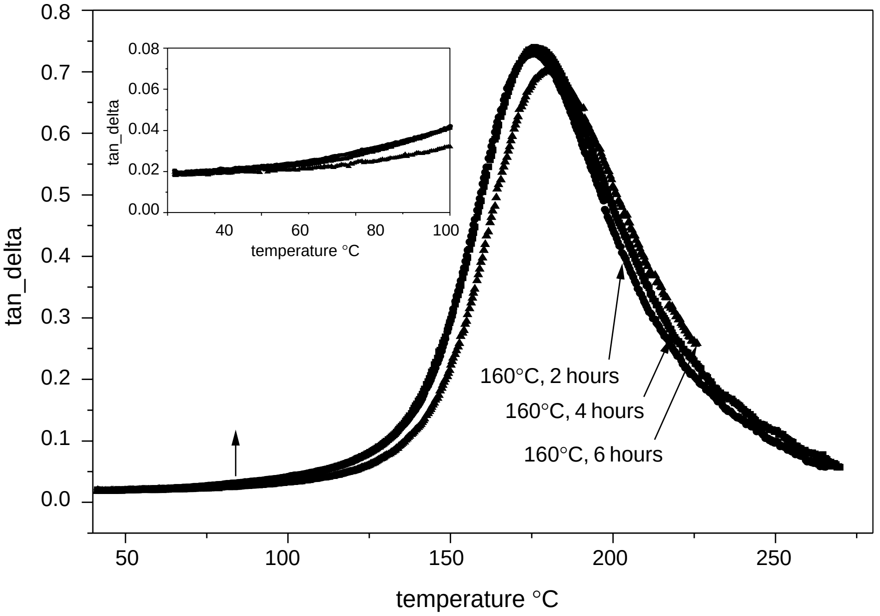


Fig. 7. Effect of thermal treatment at 160 °C with different time duration on T_g of ternary copolymer induced by gamma ray irradiation. T_g is 175.6, 176.1 and 179.7 °C, respectively. No sub-transition near 85 °C appears for all cases.

difference between DMAA and oligomer. Simultaneously, introduction of DVB brought about the increased crosslink degree of copolymer resin, which led to lower water uptake and higher glass transition temperature. Effect of water uptake on the mechanical properties of ternary copolymer resin was shown in entry d* in Table 1.

3.5. Effect of initiation approach on general properties of ternary copolymer resin

Ternary copolymer resin (entry e in Table 1) involving DMAA, oligomer and DVB was obtained by heating homogeneous solution in the presence of 0.3% BPO with temperature program as mentioned previously. Properties of BPO-induced ternary copolymer resin was compared with that induced by gamma ray irradiation, as shown by entry c and e in Table 1.

It can be seen that general properties of ternary copolymer resin induced by gamma ray irradiation are slightly better than that induced by BPO. When determining water uptake, it was interesting to observe that few white substance was extracted out into water. The collected white substance was analyzed with ^{1}H NMR, 2.90 ppm (s, 6H), 2.30 ppm (m, 1H), 1.43 ppm (m, 2H), which can be concluded as poly-DMAA.

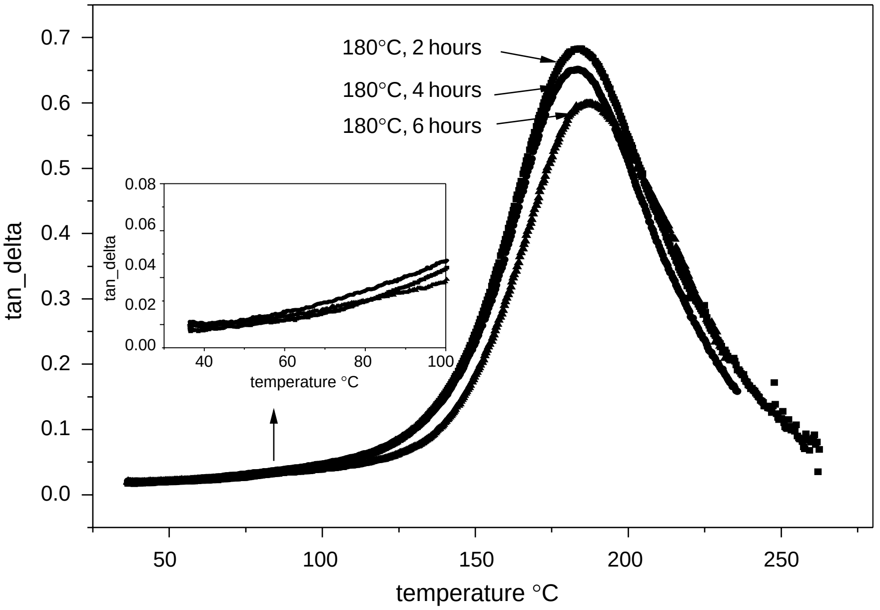


Fig. 8. Effect of thermal treatment at 180 °C with different time duration on T_g of ternary copolymer induced by gamma ray irradiation. T_g is 183.1, 184.2 and 187.5 °C, respectively. No sub-transition near 85 °C appears for all cases.

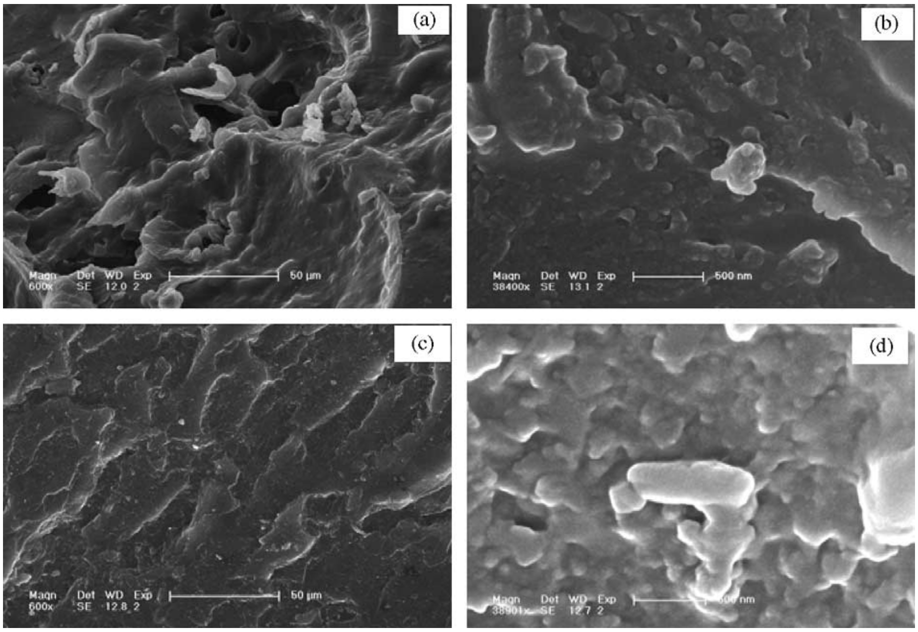


Fig. 9. SEM images of ternary copolymer resin. Image (a) and image (b) show fracture surface morphology of ternary copolymer resin induced by BPO. Image (c) and image (d) show fracture surface morphology of ternary copolymer resin induced by gamma ray irradiation.

In comparison, no substance was found into water for the case of ternary copolymer resin induced by gamma ray irradiation. This piece of finding implies that phase separation may occur in ternary copolymer resin when it is heated using BPO as radical initiator. DMTA results correspond to this assumption. Thermal treatment at 160 °C, 180 °C with different time duration were performed for ternary copolymer resin induced by gamma ray irradiation and that by BPO, respectively. DMTA traces (Figs. 5–8) show that T_g of ternary copolymer resin increases with increasing temperature and time duration of thermal treatment for both the case of gamma ray irradiation and the case of involving BPO as radical initiator. It is also observed that for the case of involving BPO as radical initiator, a sub-transition appears near 85 °C. Further, with increased temperature and time duration, the sub-transition goes more clearly. Whereas, for the case of gamma ray irradiation, there is not such a sub-transition. The existence of sub-transition confirmed that phase separation may occur during thermal initiation for the case of involving BPO as radical, initiator.

It can be suggested that during thermal initiation, unpolymerized DMAA molecules inside tend to move out to the surface of ternary copolymer resin. This movement arise from the thermal release of DMAA molecules, which leads to aggregation of poly-DMAA and phase separation in a degree, and it would be aggravated by further thermal treatment.

Morphological images derived from SEM photographs confirmed this thermal movement of DMAA molecules. Fig. 9 shows that fracture surface of ternary copolymer resin induced by BPO is rough with some pores which may be the result of thermal evaporation of unpolymerized DMAA molecules. In comparison, SEM images of ternary copolymer resin induced by gamma ray irradiation demonstrated that no pores exist on the fracture surface. The freedom from thermal initiation process offered by powerful gamma ray irradiation at room temperature explains well the absence of thermal release of bulk DMAA molecules. Because of no emission of volatile, copolymerization induced by gamma ray irradiation proceeds steadily and no phase separation occurs.

3.6. Isomeric effect of thioether dianhydride on general properties of final copolymer resin

Isomeric effect of thioether dianhydride on thermal property of thioetherimide oilgomer was evaluated by DSC. DSC traces

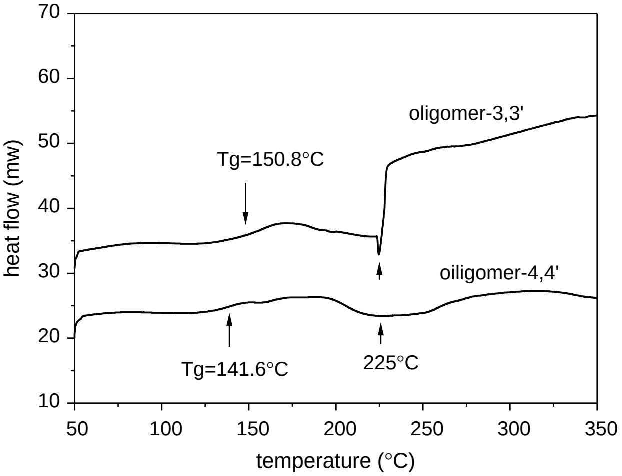


Fig. 10. DSC traces of thioether imide oliogmers composed of 100% 3,3′-TDPA and 4,4′-TDPA, respectively.

Table 2
Effect of monomer molar fraction of 3,3′-TDPA and 4,4′-TDPA on general property of ternary copolymer resin involving maleimide-terminated thioetherimide oligomer, DMAA and DVB

Entry	Molar fraction of 3,3′-TDPA	Molar fraction of 4,4′-TDPA	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (kJ/m^2)	Water uptake (wt%)	$T_{5\%}$ (°C)	T_g (°C)
f	100%	–	93.5	3.13	6.35	6.7	297	189
g	66.7%	33.3%	98.5	3.31	7.54	7.2	286	184
c	50%	50%	103.4	3.51	8.88	8.8	278	177
h	33.3%	66.7%	112.3	3.62	9.10	9.3	274	172
i	–	100%	116.5	3.69	9.51	9.6	270	163

of oligomers composed of 100% 3,3′-TDPA and 100% 4,4′-TDPA, designated as oligomer-3,3′ and oligomer-4,4′, respectively, were shown in Fig. 10. It is revealed that oligomer-3,3′ possesses higher T_g than oligomer-4,4′ does. DSC traces also show that both oligomers with terminal maleimide polymerize at about 225 °C.

Isomeric effect of thioether dianhydride on general properties of final ternary copolymer resin was investigated by varying molar ratio of 3,3′-TDPA and 4,4′-TDPA during the preparation of oligomer. It can be seen from Table 2 that with the increase of molar ratio of 3,3′-TDPA to 4,4′-TDPA (indicated by increase of molar fraction of 3,3′-TDPA in Table 2), thermal properties (T_g and $T_{5\%}$) of final copolymer resin demonstrates an corresponding increase. This may be due to the increased rigidity in copolymer resin network corresponding to the increase of molar fraction of 3,3′-TDPA, for the fact that ortho-linking of 3,3′-TDPA moiety in oligomer chain backbone contributes to constrained molecular rotation as a result of steric hindrance. In contrast, meta-linking of 4,4′-TDPA moiety in oligomer chain backbone provides relatively flexible structure for copolymer resin network.

On the other hand, with increasing molar ratio of 4,4′-TDPA to 3,3′-TDPA (indicated by increase of molar fraction of 4,4′-TDPA in Table 2), mechanical properties of final copolymer resin exhibit corresponding enhancement, especially impact strength. This may be attributed to the fact that oligomer derived from 4,4′-TDPA is structurally more linear that that from 3,3′-TDPA, and so 4,4′-TDPA moiety endows final copolymer resin with more flexural strength and impact strength than 3,3′-TDPA moiety does.

4. Conclusion

A novel cure of polyimide with improved processability was successfully attained in this paper. Maleimide-terminated thioetherimide oligomer derived from isomeric dianhydride 3,3′-TDPA and 4,4′-TDPA exhibits good solubility in reactive solvent NVP and DMAA. Binary and ternary homogenous system are capable of copolymerization by way of gamma ray irradiation initiation and thermal initiation utilizing BPO as radical initiator. The thus-obtained copolymer resins demonstrate fairly good mechanical properties and the glass transition temperature reaches as high as 187.5 °C after thermal treatment.

Compared with binary copolymer resin involving NVP and thioetherimide oligomer induced by gamma ray irradiation, binary copolymer resin involving DMAA and thioetherimide oligomer has higher glass transition temperature, lower water uptake but poorer mechanical properties. After incorporating DVB, copolymer resin involving DMAA and thioetherimide oligomer induced by gamma ray irradiation obtains improved mechanical properties. It is found that ternary copolymer resin based on DMAA induced by gamma ray irradiation maintains its mechanical properties as high as up to above 60% after soaking in water for one week.

In contrast with the case of gamma ray irradiation, thermal initiation using BPO as radical initiator need to be improved. Copolymer resin initiated by BPO shows poorer mechanical properties and phase separation in a degree. Thermal movement of DMAA molecules accounts for undesired efficiency of thermal initiation, which can be evidenced by small pores existing in the bulk of copolymer resin, as seen from SEM images.

With the increase of 3,3′-TDPA moiety in oligomer, thermal properties, T_g and $T_{5\%}$ of copolymer resin exhibit corresponding increase. In contrast, increased 4,4′-TDPA moiety in oligomer leads to improved mechanical properties of final copolymer resin.

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