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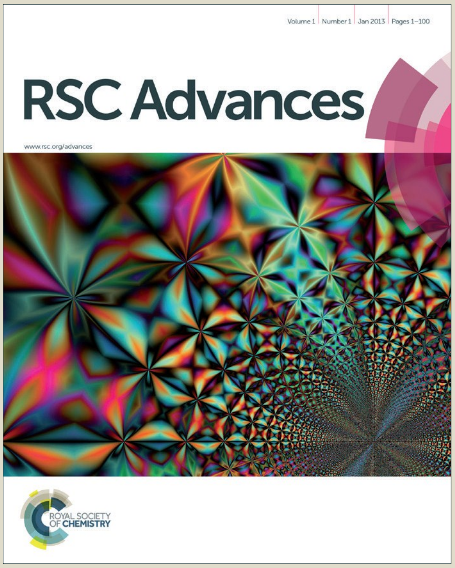

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Relationship between crosslinking structure and low dielectric constant of hydrophobic epoxies based on substituted biphenyl mesogenic units

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ABSTRACT

In this work, a series of low dielectric constant hydrophobic epoxies based on substituted biphenyl mesogenic were prepared and characterized. The liquid crystalline phase structure and the crosslink density of substituted biphenyl epoxies were determined by polarized optical microscopy, wide angle X-ray diffraction measurements and dynamic storage moduli data. Relationship between crosslinking structure and dielectric and water resistance properties was discussed in our paper. The samples showed lower dielectric constants down to 2.24, owing to the oriented structure and increased crosslink network density caused by the orientation of biphenyl mesogenic, indicating a new idea to prepare low dielectric constant epoxies by introducing the mesogenic units into epoxy resins. And the comprehensive contributions of oriented structure and increased crosslink network in epoxies cured by aromatic amines, less hydroxyl groups existing in epoxies cured with anhydride and the hydrophobic methyl substituents or larger tert-butyl substituents, could afford good water resistance properties with water absorptions during 48 h at 25℃ ranging from 0.31-0.36%, which indicated that the water resistance was apparently better than that of conventional epoxy systems.

KEYWORDS: epoxy; substituted biphenyl mesogenic; low dielectric constant; hydrophobicity

1.INTRODUCTION

For various modern high-speed electrical devices, the epoxy resin (EP) materials with low dielectric constant (D_k), good water resistance and dimensional stability are expected to play increasingly crucial roles in meeting the requirement of high integrated circuit density, elevated operating temperature and high reliability. Thus, novel EP and its composites with reduced D_k and dielectric loss (D_f) are paid attractive attention to the application in the next generation of high performance electrical devices. [1-3]

It can be observed that the majority of the researches on reducing dielectric constant of epoxy resin materials were conducted by incorporating fluorine atoms into polymers, introducing porosity or free volume, minimizing polarizability and synthesizing porous polymers. [4-10] A novel fluorinated epoxy resin was synthesized by Tao et al[11] using a four-step procedure and cured with hexahydro-4-methylphthalic anhydride (HMPA) and 4,40-diaminodiphenyl-methane (DDM); The cured fluorinated epoxy resins exhibited improved dielectric properties as compared with the commercial available epoxy resins with the dielectric constants lower than 3.3. Ching Hsuan Lin et al[3] used a novel curing agent of propargyl ether-containing phosphinated benzoxazine to reduce the dielectric constant of epoxy thermosets. Yalan Wu[12] reported that the dielectric constant and dielectric loss values decreased with the increasing addition of NH_2-POSS into original epoxy resin. Amendola, E[13] and S. S. Vaisakh[14] found the dielectric constant could be decreased with introduction of ceramic nano fillers. Jiao, Jian[2] added novel organic–inorganic particles (denoted POSS–MPS) into the epoxy resin and the POSS–MPS/EP nanocomposites containing 5 wt% of POSS–MPS showed a lower dielectric constant (D_k=3.66) and loss factor (D_f=0.017) in comparison to pristine EP with the value of 4.03 and 0.031. Yu, Wenqi[15] synthesized a graphene hybrid material functionalized with octa-aminophenyl polyhedral oligomeric silsesquioxanes (OapPOSS-g-GO) and reduced dielectric constant and dielectric loss by applying OapPOSS-g-GO into epoxy resin. However, conventional cross-linked epoxy polymers (or epoxy based SMPs) were highly water absorbing (about 1–4 wt%) and hydrophilic (water contact angle of 50–52 degrees) owing to the existence of large number of hydroxyl groups in the cross-linked networks.[16] The epoxies with more porosities might be even more hydrophilic.

Liquid crystalline epoxides (LCEs) are superior to conventional amorphous epoxies in the performance of good water resistance properties, better mechanical properties, better dimensional stability, lower coefficients of thermal expansion, increased fracture toughness and noticeable high temperature properties.[17-24] It was reported that the oriented structure of LCEs could increase packing density of the segments, resulting in increased crosslink network density.[25, 26] The molecular motivation of liquid crystalline epoxies under electric field was hindered by the enhanced intermolecular interactions caused by oriented and increased cross-linked networks, resulting in ultra-low dielectric constant and low dielectric loss compared with current polymeric matrix without introducing pores or fluorine. In addition, the closely packed arrangement of mesogens could lead to dramatically reduced solvent absorptions. [21, 27] Therefore, it was attractive that biphenyl mesogenics were induced into cross linked epoxy systems, to gain low dielectric constant and good water resistance epoxy resins, which indicated that liquid crystalline epoxies could be novel epoxy resin (EP) materials applied in the next generation of high performance electrical devices. However, there were only few works that were focused on the low dielectric constant of hydrophobic liquid crystalline epoxies.

In our latest work, a novel epoxy monomer denoted as 3,5'-Di-t-butyl-5,3'-dimethyl biphenyl diglycidyl ether (t-BuMBPDGE) was synthesized and applied into situ composites with 3,3’,5,5’-tetramethyl-4,4’-biphenyl Diglycidyl ether (TMBPDGE), accompanied with curing agent aromatic amines. The epoxies showed good mechanical and water resistance properties and extraordinary shape memory properties. [28] In this paper, it was found that substituted biphenyl epoxies owned excellent dielectric properties with low dielectric constant and low dielectric loss. To further investigate the relationship between crosslinking structure and low dielectric constant of hydrophobic epoxies, epoxy resins cured with different curing agents and cured at different temperatures were prepared and characterized.

2. EXPERIMENTAL

2.1 Materials

3,3’,5,5’-tetramethyl-4,4’-biphenyl Diglycidyl ether [TMBPDGE, epoxide equivalent weight (EEW):198 g/mol, abbreviated as (1)] and 3,5'-Di-t-butyl-5,3'-dimethyl biphenyl diglycidyl ether [t-BuMBPDGE, (EEW):263 g/mol, abbreviated as (2)] were synthesized in our laboratory according to the program proposed by our group in early reports.[28] 4,4’-Diaminodiphenylmethane (DDM) and methyl hexahydrophthalic anhydride (MHHPA, See Scheme 1) were purchased from Aladdin and were used as curing agent. N-Benzyldimethylamine (BDMA, See Scheme 1) was purchased from Aladdin and was used as an accelerator when cured with MHHPA. All other reagents were of analytical grade and used as received.

2.2 Curing of substituted biphenyl epoxies

The stoichiometric amount of epoxy monomer [different weight ratios of (1) and (2)] (10 mmol) and DDM (5 mmol) or MHHPA (10 mmol) and 1 phr of accelerator BDMA were cured at 105 ℃ for 5 h, 160℃ for 4 h and 200℃ for 1 h. To investigate the relationship between crosslinking structure and low dielectric constant of hydrophobic epoxies, (1)/DDM and (1)/MHHPA were also cured directly at higher temperature 160℃ for 6 h, 200℃ for 1 h to guarantee completely branching and crosslinking, while the totally reaction of linear chain extension might not be afforded.

2.3 Physical measurements

The liquid crystalline phase structure of substituted biphenyl epoxies was examined by polarized light optical microscopy (POM) (Orthoglan, LEITZ, Germany) and wide angle X-ray diffraction measurements (WAXS) which were carried out with a Rigaku Diffractometer (D/MAX-1200), using monochromatic Cu Karadiation (40 kV, 30 mA) and secondary graphite monochromator, with the X-ray scatting intensities being detected by a scintillation counter incorporating a pulse-height analyzer.

The response of the samples to small-strain mechanical deformation was measured as a function of temperature (-120 to 200℃) using a NETZSCH DMA 242 dynamic mechanical analyzer in a tensile mode. The testing was carried out at a heating rate of 5℃/min in a N_2 atmosphere, frequencies of 1 Hz, a dynamic stress of 5 N, and a static stress of 0.5 N. The sample displacement was 30 μm. Storage moduli (E’), loss moduli (E”), and loss tangent (tan δ) were recorded.

The dielectric properties were measured by a dielectric analyzer (DEA 2970, TA Instruments), up to a frequency of 1 MHz at 25℃.

Water sorption as a function of immersion time was monitored by a gravimetric method. The sample sheets (20 mm*10 mm * 0.6 mm) were polished and dried under vacuum oven at 85℃ for a week. The specimens were periodically removed from water bath at 25℃, followed by wiping with tissue paper for removal of any water on the surface, and then weighed by a hundred thousandths microanalytical balance (AUW120D, Japan, 42/120g, 0.01/0.1mg) immediately. Three samples were used to repeat the test and averages were selected.

The contact angle test was carried out by contact angle meter (JC2000D1, Shanghai zhongchen digital technic apparatus co.,ltd).

3. RESULTS AND DISCUSSION

3.1. The liquid crystalline phase structure and crosslink density of substituted biphenyl epoxies

Figure 1 showed the polarized optical microscopic pictures after curing of (1)/MHHPA and (2)/MHHPA. Birefringence was observed from all of the POM pictures of (1)/MHHPA and (2)/MHHPA network. And density of bright droplet-like liquid crystalline domains of (2)/MHHPA was lower than that of (1)/MHHPA. While the liquid crystalline domains density of these epoxy/MHHPA systems was lower than that of epoxy/DDM systems. [28]

In order to further investigate the nematic structure of biphenyl epoxies affected by substituents and curing agent, wide angle X-ray diffraction patterns of (1)/DDM, (2)/DDM, (1)/(2)/DDM composite, (1)/MHHPA, (2)/MHHPA and (1)/(2)/MHHPA composite were analyzed, as shown in Table 1 and Figure 2. It could be seen from Table 1 that all the samples showed broad peaks around 23°. While (1)/MHHPA, (2)/MHHPA and (1)/(2)/MHHPA composite showed similar peaks with 2θ increased from 17.5° to 18.8° corresponding to d-spacing of 5.1 Å to 4.7 Å (See Figure 2).

The crosslink density defined as the number of moles of elastically effective network chains per cubic centimeter of sample was determined by the following equation[28, 29, 30, 31]

$$v_c = G'/RT = E'/3RT \qquad (1)$$

The calculated crosslink density v_c was shown in Table 1 and Table 2, from which it could be seen that the crosslink density of epoxy/DDM systems was higher than that of epoxy/MHHPA systems. And the crosslink density of both epoxy/DDM and epoxy/MHHPA systems decreased as the increasing of the content of (2). While crosslink density of (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature was lower than that of (1)/DDM and (1)/MHHPA systems which were cured at lower temperature.

There were four reactive sites in each molecular structure of DDM (See Scheme 2), while there were only two reactive sites in each MHHPA molecular structure (See Scheme 2), moreover, the steric hindrance of the tert-butyl substituents was larger than that of methyl substituents. So during linear chain extension stage, the packing density of mesogenic might be higher in the epoxy/DDM systems than that in epoxy/MHHPA systems. And the density of liquid crystalline domains decreased in the order in (1)/DDM, (2)/DDM , (1)/MHHPA and (2)/MHHPA networks with d-spacing increased from 3.9

Å to 5.1 Å, resulting in the highest v_c in (1)/DDM resin. However, the linear chain extension could not catch up with the branching and crosslinking and the uniaxially oriented structure could not be formed in epoxy systems which were cured directly at higher temperature, so that no birefringence was observed in (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature and the packing density of molecules ranked the lowest.

Uniaxial oriented nematic structure mode and the reaction process mechanism of (1)/DDM and (1)/MHHPA were shown schematically in Scheme 2. From which the orientation of substituted biphenyl mesogenic could be more easily analyzed and understood.

3.2 Dynamic mechanical analysis

The dynamic storage moduli (E’) of (1)/MHHPA, (2)/MHHPA and (1)/(2)/MHHPA composite were shown in Figure 3, from which it could be found that all the samples illustrated higher dynamic storage moduli over 2 GPa at room temperature, which indicated that these epoxies based on substituted biphenyl mesogenic exhibited high dimensional stability to external force. And this high dimensional stability was an attractive property for electric device materials. It could also be found that the E’ of epoxy/DDM systems were higher than that of epoxy/MHHPA systems, owing to higher crosslink density in epoxy/DDM systems. While the E’ increased with the content of (2) increasing in both epoxy/DDM and epoxy/MHHPA systems, in that the orientation of biphenyl mesogenic along the direction of stress was obstructed by the larger steric hindrance of the tert-butyl substituents in (2)/DDM and (2)/MHHPA resins.

The compared data of the dynamic storage moduli (E’) of (1)/DDM and (1)/MHHPA systems which were cured at lower temperature and directly at higher temperature was shown in Figure 4. It could be seen that the (E’) of both (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature was higher than that of (1)/DDM and (1)/MHHPA systems which were cured at lower temperature. Although the crosslink densities of (1)/DDM and (1)/MHHPA systems which were cured at lower temperature were higher than that of (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature, more physical entanglement might formed in the latter, the orientation of biphenyl mesogenic along the direction of stress might be obstructed by the physical entanglement, thus, the (E’) of both (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature was higher than that of (1)/DDM and (1)/MHHPA systems which were cured at lower temperature.

The loss tangent (tan δ) data of (1)/DDM, (2)/DDM, (1)/(2)/DDM composite, (1)/MHHPA, (2)/MHHPA, (1)/(2)/MHHPA composite and (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature were shown in Table 1, Figure 3 and Figure 4. The glass transition temperature of the samples decreased from 178℃ to 96℃ in the order in (1)/DDM, (1)/(2)/DDM composite, (2)/DDM, (1)/MHHPA, (1)/(2)/MHHPA composite, (2)/MHHPA. Two peaks could be seen in (2)/MHHPA resin. The glass transition temperature of (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature were lower than that of (1)/DDM and (1)/MHHPA systems which were cured at lower temperature.

As was well known, Tg in DMA referred to the temperature at which the network segments began to move. And the movement of network segments could be influenced by the chemical crosslinking, physical entanglement and the packing density of the segments. The interchain interactions were strongly dependent on the packing density of the segments which was affected by the orientation of substituted biphenyl mesogenics. Highly oriented substituted biphenyl mesogenics could enhance the interchain interactions, making the substituted biphenyl mesogens slip and rotate not easily. Therefore, the Tg of (1)/DDM resin ranked the highest with the lowest one in (2)/MHHPA resin. While two peaks could be found in the loss tangent (tan δ) data of (2)/MHHPA resin, which was because that the orientation of substituted biphenyl mesogenics was obstructed by the larger steric hindrance of the tert-butyl substituents in (2)/MHHPA resin. And the molecular structure of MHHPA itself, compared to the rigid molecular structure of aromatic amines DDM, could also decrease the liquid crystalline domains. Thus, a liquid crystalline phase and an isotropic phase existed in (2)/MHHPA resin (It could be seen in Figure 1a that the density of liquid crystalline domains was the lowest one with isotropic domains existing between the bright droplet-like domains of the liquid crystalline.). In the liquid crystalline phase, mainly oriented biphenyl mesogenics were obtained so that the crosslinks are mostly chemical in nature. Larger number of physical crosslinks was expected to be present in addition to the chemical crosslinks in the isotropic phase and extra constraints on the molecular motions were exerted in the isotropic state because of existence of physical crosslinks, which caused the shift of the Tg to higher temperatures.[17, 32, 33] Therefore, the peak at 112℃ is owing to the Tg of the liquid crystalline phase, while the peak at 126℃ is due to the Tg of the isotropic phase. However, the glass transition temperature of (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature (isotropic state) were lower than that of (1)/DDM and (1)/MHHPA systems which were cured at lower temperature (liquid crystalline phase), which might be the reason that the crosslink densities of the former were far less than that of the latter (See Table 1) and these totally isotropic states were essentially different from the isotropic domains existing between the domains of the liquid crystalline.

3.3. The dielectric properties analysis

The dielectric constant and dielectric loss of the samples were listed in Table 3. The dielectric constant of epoxy/DDM systems at 1 MHz increased from 2.24 to 2.52 and the dielectric loss at 1 MHz increased from 0.022 to 0.034 as the decrease of the content of (1). And the dielectric constant of epoxy/MHHPA systems at 1 MHz increased from 3.13 to 3.95 and the dielectric loss at 1 MHz increased from 0.024 to 0.035 as the increase of the content of (2). While dielectric constant and dielectric loss of (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature were higher than that of (1)/DDM and (1)/MHHPA systems which were cured at lower temperature.

Low dielectric constant and low dielectric loss epoxy resin materials were expected to play enormously crucial roles in the next generation of high performance electrical devices, which were increasingly attractive to researchers. In this paper, much lower dielectric constant epoxy resin materials, compared to the reported works[2, 3, 11, 12, 14, 15], were prepared by introducing biphenyl mesogenic. The molecule motion under external alternating electric field was hindered by the oriented structure and increased crosslink network density caused by the orientation of biphenyl mesogenic, resulting in lower dielectric constant and lower dielectric loss epoxy resins, which indicated a new way to reduce the dielectric constant of epoxy thermosets by importing mesogenic. As discussed above, larger substituents of tert-butyl and curing agent MHHPA could decrease crosslink density and the orientation of biphenyl mesogenics, thus, the dielectric constant and the dielectric loss decreased as the increase of the content of (2) with epoxy/MHHPA systems exhibiting higher dielectric constant and dielectric loss. The oriented structure and higher crosslink density could be obtained in (1)/DDM and (1)/MHHPA systems which were cured at lower temperature, therefore, the dielectric constant and dielectric loss of (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature were higher than that of (1)/DDM and (1)/MHHPA systems which were cured at lower temperature.

3.4. The water resistance properties of substituted biphenyl epoxies

The water resistance properties of substituted biphenyl epoxies were determined by contact angle test and water sorption test, as was shown in Table 1, Figure 5 and Table 4. It could be seen that the contact angles of both epoxy/DDM and epoxy/MHHPA systems increased with the content of (1) increasing while the water absorptions during 48 h and 2 weeks at 25℃ decreased as the increase of the content of (2). Epoxy/DDM systems illustrated slightly better water resistance properties than epoxy/MHHPA systems. And (1)/DDM and (1)/MHHPA systems which were cured at lower temperature exhibited better water resistance properties than (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature.

As was known, conventional cross-linked epoxy polymers (or epoxy based SMPs) were highly water absorbing (about 1–4 wt%) and hydrophilic (water contact angle of 50–52 degrees) owing to the existence of large number of hydroxyl groups in the cross-linked networks.[16] In our work, epoxies based on substituted biphenyl mesogenics with extremely better water resistance properties were prepared. The orientation of substituted biphenyl mesogenics could contribute to an increased crosslink network density, resulting in closely packed polymer chains. Therefore, (1)/DDM and (1)/MHHPA systems which were cured at lower temperature exhibited better water resistance properties than (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature. Although the crosslink network density could be decreased by the larger steric hindrance of tert-butyl substituents and the curing agent MHHPA, the hydrophobic tert-butyl group could play a positive role in the good water resistance properties, and less hydroxyl groups existed in epoxy/MHHPA systems than in epoxy/DDM systems (Scheme 2), thus, epoxy/DDM systems illustrated slightly better water resistance properties than epoxy/MHHPA systems with not very much obvious changes in epoxy/DDM and epoxy/MHHPA systems individually.

4. CONCLUSION

In this paper, it was found that substituted biphenyl epoxies owned excellent dielectric properties with low dielectric constant and low dielectric loss. The low dielectric constant down to 2.24 and good water resistance properties with water absorptions during 48 h at 25℃ ranging from 0.31-0.36% indicated a new idea to prepare low dielectric constant hydrophobic materials by introducing the mesogenic units into epoxy resins in the application of high performance electrical devices.

Higher dynamic storage moduli over 2 GPa at 25℃ could be seen in all the samples, indicating high dimensional stability in these epoxies. E' of epoxy/DDM systems were higher than that of epoxy/MHHPA systems, owing to higher crosslink density in epoxy/DDM systems. While the E' increased with the content of (2) increasing in both epoxy/DDM and epoxy/MHHPA systems, in that the orientation of biphenyl mesogenic along the direction of stress was obstructed by the larger steric hindrance of the tert-butyl substituents in (2)/DDM and (2)/MHHPA resins.

Highly oriented substituted biphenyl mesogenics could enhance the interchain interactions, making the substituted biphenyl mesogens slip and rotate not easily. Therefore, the Tg of (1)/DDM resin ranked the highest with the lowest one in (2)/MHHPA resin.

Larger substituents of tert-butyl and curing agent MHHPA could decrease crosslink density and the orientation of biphenyl mesogenics, thus, the dielectric constant and the dielectric loss decreased as the increase of the content of (2) with epoxy/MHHPA systems exhibiting higher dielectric constant and dielectric loss.

The comprehensive contributions of oriented structure and increased crosslink network in epoxies cured by aromatic amines, less hydroxyl groups existing in epoxies cured with methyl hexahydrophthalic anhydride and the hydrophobic methyl substituents or larger tert-butyl substituents, could afford good water resistance properties with contact angles ranging from 89 to 98 degrees and water absorptions during 48h at 25℃ ranging from 0.31-0.36%, which indicated that the water resistance was apparently better than that of conventional epoxy systems.

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Figure captions

Scheme 1 Chemical structures of MHHPA and BDMA

Scheme 2 Uniaxial oriented nematic structure mode and reaction mechanism of (1)/DDM resin and (1)/MHHPA resin

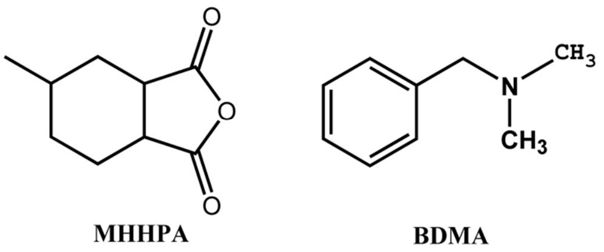
Fig 1 Polarized optical microscopic pictures of (1)/MHHPA and (2)/MHHPA after curing at room temperature

Fig 2 Wide angle X-ray diffraction measurements of (1)/MHHPA, (2)/MHHPA and (1)/(2)/MHHPA composite

Fig 3 Dynamic storage moduli (E’) and loss tangent (tan δ) of (1)/MHHPA, (2)/MHHPA and (1)/(2)/MHHPA composite

Fig 4 Compared data of the dynamic storage moduli (E’) of (1)/DDM and (1)/MHHPA systems which were cured at lower temperature and directly at higher temperature

Fig 5 Contact angles of (1)/MHHPA, (2)/MHHPA, (1)/(2)/MHHPA composite and (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature



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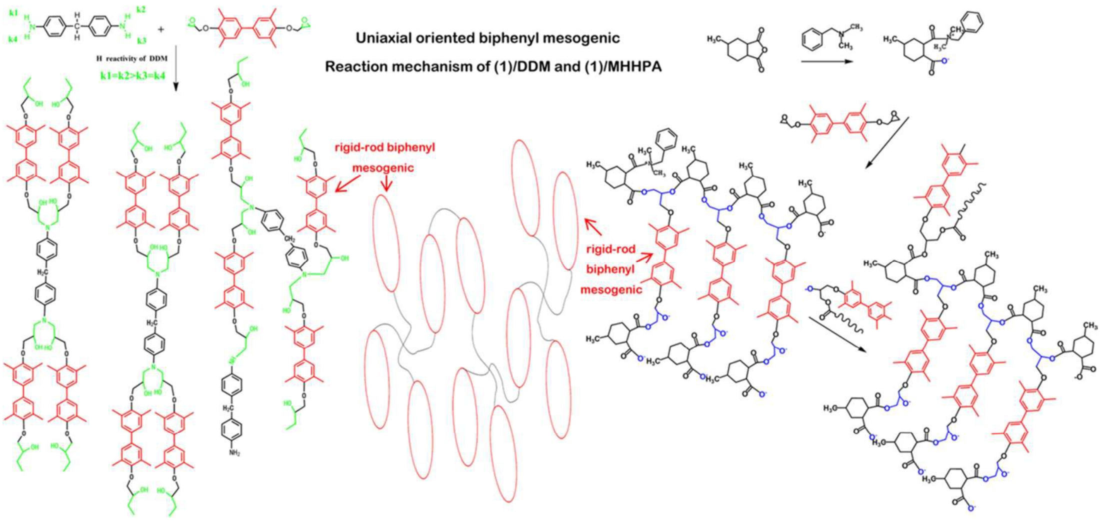

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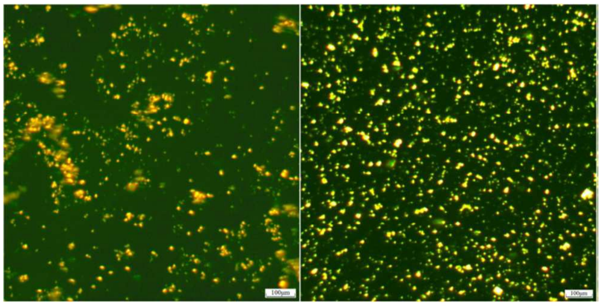

a. (2)/MHHPA b. (1)/MHHPA

Fig 1 Polarized optical microscopic pictures of (1)/MHHPA and (2)/MHHPA after curing at room temperature

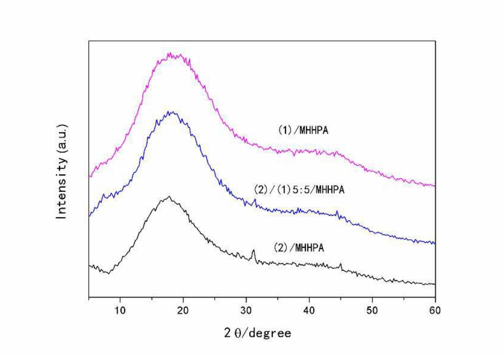

Fig 2 Wide angle X-ray diffraction measurements of (1)/MHHPA, (2)/MHHPA and (1)/(2)/MHHPA composite

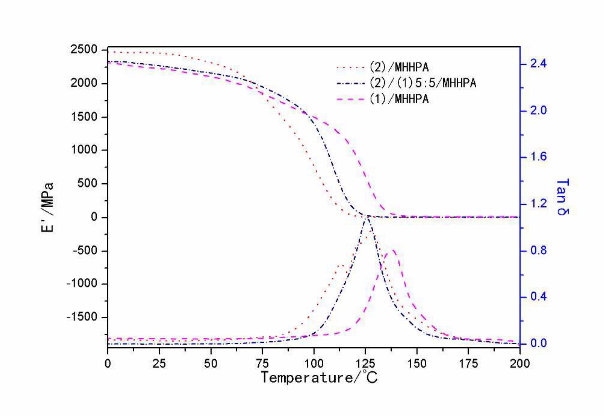

Fig 3 Dynamic storage moduli (E') and loss tangent (tan δ) of (1)/MHHPA, (2)/MHHPA and (1)/(2)/MHHPA composite

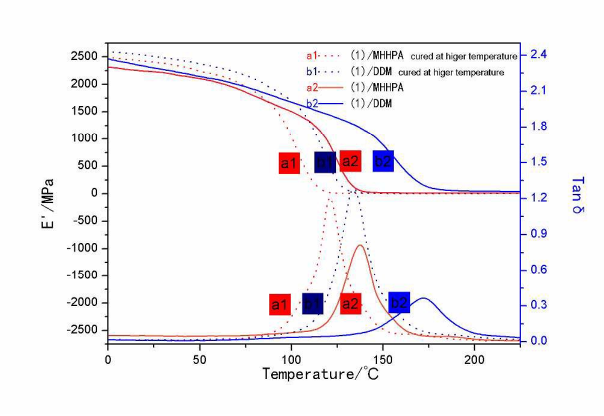

Fig 4 Compared data of the dynamic storage moduli (E') of (1)/DDM and (1)/MHHPA systems which were cured at lower temperature and directly at higher temperature

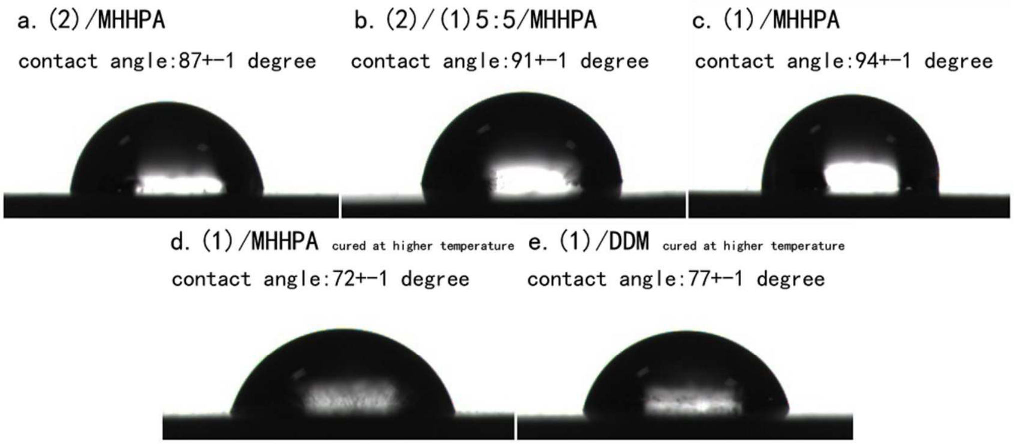

Fig 5 Contact angles of (1)/MHHPA, (2)/MHHPA, (1)/(2)/MHHPA composite and (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature

Table 1 Overview results of (2)/DDM resin, (1)/DDM resin and (1)/(2) /DDM composite published in Rsc Adv, 2015, 5, 67247 - 67257

Samples	**Storage moduli (E')(MPa)20℃**	**T_g by DMA/(℃)**	**Crosslink density ν_c (mol/cm^3)**	**XRD/2θ/º**	**XRD/d/Å**	**Contact angles /degree**
(1)/DDM	2007	178	$3.07*10^{-3}$	22.5	3.95	98
(2)/(1)5:5/DDM	3145	169	$2.42*10^{-3}$	21.8	4.08	96
(2)/DDM	3215	160	$1.75*10^{-3}$	21.8	4.08	92

Table 2 DMA results and crosslink density of (1)/MHHPA, (2)/MHHPA, (1)/(2)/MHHPA composite and (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature

Samples	**Storage moduli (E')(MPa)20℃**	**(E_R')(MPa) (T_g+50℃)**	**T_g(℃)**	**ν_c (mol/cm^3)**
(1)/MHHPA	2238	11.83544	137	$1.04*10^{-3}$
(2)/(1)5:5/MHHPA	2286	5.54834	126	$0.49*10^{-3}$
(2)/MHHPA	2461	2.31652/2.1697	112/126	$0.21/0.19*10^{-3}$
(1)/DDM cured at higer temperature	2528	4.99284	133.9	$0.43*10^{-3}$
(1)/MHHPA cured at higer temperature	2420	3.005	121.6	$0.27*10^{-3}$

Table 3 deelectric properties of (1)/DDM resin, (2)/DDM resin, (1)/(2)/DDM composite, (1)/MHHPA, (2)/MHHPA, (1)/(2)/MHHPA composite and (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature

Samples	Dielectric constant D_k/1 MHz	Dielectric loss D_f/1 MHz
(1)/DDM	2.24	0.022
(2)/(1)5:5/DDM	2.49	0.028
(2)/DDM	2.52	0.034
(1)/MHHPA	3.13	0.025
(2)/(1)5:5/MHHPA	3.57	0.027
(2)/MHHPA	3.95	0.035
(1)/DDM cured at higer temperature	3.05	0.029
(1)/MHHPA cured at higer temperature	3.16	0.036

Table 4 Water absorbance of (1)/DDM resin, (2)/DDM resin, (1)/(2)/DDM composite, (1)/MHHPA, (2)/MHHPA, (1)/(2)/MHHPA composite and (1)/DDM and (1)/MHHPA systems which were cured directly at higher temperature

Samples	Water absorbence/% 48h	Water absorbence/% 2 weeks
(1)/DDM	0..35	1.01
(2)/(1)5:5/DDM	0.33	0.88
(2)/DDM	0.31	0.84
(1)/MHHPA	0.36	0.94
(2)/(1)5:5/MHHPA	0.34	0.88
(2)/MHHPA	0.33	0.83
(1)/DDM cured at higer temperature	0.68	1.63
(1)/MHHPA cured at higer temperature	0.51	1.32